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Manganese Ore Potential Related to Hydrosulfuric Pollution of Bottom Waters (with the Black Sea as an Example)

R. I. Nedumov

Geological Institute (GIN), Russian Academy of Sciences, Pyzhevskii per. 7, Moscow, 119017 Russia
e-mail: nedumov@ginras.ru

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Abstract—Conditions and scales of the accumulation of dissolved manganese in waters of marine basins with hydrosulfuric contamination are considered. It is shown that the Kalamit ferromanganese nodule field, most probably, originated due to the delivery of manganese from the hydrosulfuric zone of the Black Sea. Precisely this source converts the normal diagenetic process of material redistribution into the ore process. It is demonstrated that the formation of ferromanganese nodules in the Black Sea represents an embryonic manganese ore process. Its full-scale development seems to have taken place in the Early Oligocene Maikop basin owing to the spatiotemporal coincidence of a series of favorable conditions.

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The phenomenon of hydrosulfuric contamination of bottom waters in recent marine basins is quite widespread. This is recorded in the Black Sea, where hydrosulfuric regime dominates in the almost 2-km-thick water column and oxic environment is only retained in the upper (approximately 200-m-thick) layer. Anoxic conditions are also recorded in the Baltic Sea (Gotland, Barnholm, and Landsort depressions), Caribbean Sea (Cariaco Trough), Gulf of Mexico (Orca Trough), several Norwegian and Swedish fiords, and some lakes on continental blocks.

Hydrosulfuric contamination of the Black Sea has been most comprehensively investigated by N.I. Andrusov, A.D. Arkhangel'skii, N.M. Strakhov, S.B. Bruevich, B.A. Skopintsev, I.I. Volkov, A.Yu. Mitropol'skii, E.F. Shnyukov, and many others. Results of the study of hydrosulfuric contamination in the Black Sea are summarized in (Kholodov, 2002).

The hydrosulfuric contamination can be provoked by different reasons. However, its origination requires the following essential conditions: complete or partial isolation of the basin or its part, weak hydrodynamic activity or its absence, and intensive input of organic matter, the oxidation and mineralization of which lead to the reduction of sulfates in marine water and hydrogen sulfide generation. If the basin is contaminated with hydrogen sulfides, sedimentary strata accumulated therein will be characterized by specific lithological, paleoecological, and mineral–geochemical features.

As is well known, manganese is accumulated in dissolved form in anoxic conditions (particularly, in H_2S-rich waters). In normal marine water, the content of dissolved manganese is approximately 10 μg/l (Roy, 1986). In the Baltic Sea, the Mn content is as much as 1480 μg/l in hydrosulfuric waters of the Gotland Depression (Shishkina *et al.*, 1981) and up to 31800 μg/l in mud waters (Blazhchishin and Emel'yanov, 1975).

In the Black Sea, the concentration of dissolved Mn in the oxic zone does not exceed 20–25 μg/l (Mokievskaya, 1961). The maximal Mn content (500 μg/l) is recorded in the upper part of the hydrosulfuric zone and is commonly 200–250 μg/l. In mud waters, the content of dissolved Mn reaches 1760 μg/l (Sevast'yanov and Volkov, 1967a).

If we know the volume of H_2S-containing waters in the Black Sea and the concentration of dissolved Mn in them, it is easy to calculate its absolute mass. Based on the data of Mokievskaya (1961), Skopintsev and Popova (1963) performed such calculation and found that more than 100 Mt of Mn accumulated during 7–8 ka of hydrosulfuric contamination in the Black Sea water. It is quite evident that destruction of the hydrosulfuric zone and restoration of oxic conditions in the basin will result in the precipitation of dissolved Mn. The extrapolation of recent conditions in the Black Sea on tens and hundreds of thousand years yields billions and tens of billion tons of Mn that can rapidly settle during changes of hydrosulfuric medium into oxic one.

Naturally, many researchers noted the property of basins with H_2S-contaminated bottom waters to accumulate significant masses of dissolved Mn in the course of relatively short periods. Sapozhnikov (1967, 1984) proposed the mechanism of the formation of manganese deposits due to accumulations of dissolved Mn. In particular, he considered hydrosulfuric waters of the Maikop Basin as the source of Mn for Oligocene deposits of the Black Sea–Caspian region.

Until the mid1960s, all these deposits were thought to be classic sedimentary formations. However, G.S. Dzotsenidze interpreted them as effusive-sedimentary formations in papers devoted to Chiatura deposits. Ideas of Dzotsenidze were subjected to justified criticism by Strakhov *et al.* (1968). However, the idea of the endogenic source of Mn is still living due to the following reason. The factual material collected to date permits neither to admit nor to reject the input of endogenic material into sedimentation basin, whereas the classical sedimentary-diagenetic interpretation contains some assumptions. That is why even works of proponents of the sedimentary genesis of Oligocene manganese deposits often contain the reservation about the possible participation of some endogenic sources in the manganese ore process (Sapozhnikov, 1984; Kholodov, 2002).

The normal sedimentary mechanism of the formation of Oligocene manganese ores was developed in detail by Strakhov (1968). He believed that Mn of South Ukrainian ores was derived from Precambrian crystalline rocks that make up a narrow peninsula between the Black Sea part of the Oligocene basin and the Dnieper–Donetsk part (Fig. 1). The Mn content in them is 0.13–0.21%, which is 1.5–2 times higher than the clarke level.

The presence of favorable climatic and tectonic conditions in the drainage area in the Early Oligocene promoted the long-term existence of alkaline weathering crust that provided the leaching and removal of Mn from crystalline rocks and its separation from Fe remained on the spot. Waters strongly enriched in the dissolved Mn^{2+} flowed down from the drainage area into the marine basin and mixed with marine water. After oxidation, they formed amorphous particles of hydrated manganese dioxide, which precipitated on the seafloor and formed ore sediment. The subsequent diagenetic reworking of this sediment produced manganese deposits and occurrences.

This scheme suggests that manganese was delivered to the basin from a limited area of land (more likely, a peninsula) with an area of 12000–15000 km^2 (Fig. 1). A simple calculation demonstrates that the formation of South Ukrainian deposits due to the evacuation of Mn from this land area is unlikely. If we accept Mn resources in these deposits equal to 1 Gt and the average Mn concentration in eroded crystalline rocks equal to 0.2%, the accumulation of Mn resources mentioned above would require the washout of 500 Gt of rocks, which would be equal to 200 km^3 of rocks at the grade of 2.5 t/m^3. The thickness of the eroded layer of source rocks in the peninsula would be 13–16 m.

It is known that erosion rate on the plain is ~0.01 mm/yr or 1 m/100 ka (Sokolov, 1952). Hence, the release of Mn quantity needed for the formation of South Ukrainian deposits will take no less than 1.5 Ma. If we assume that not all Mn delivered from the provenance was concentrated in deposits and a significant portion of Mn was scattered, the time needed for the formation of deposits increases to 2–3 Ma, which is rather problematic. Strakhov assumed that the Mn concentration in river runoff was extremely high (5–10 mg/l). However, the existence of such high concentrations in river runoff has not been proven. The necessity of such high concentrations of dissolved Mn is caused by the fact that the evacuation of Mn to the basin would be too long in the case of lower concentrations. The maximum river discharge in the Russian Plain is 10 l/s/1 km^2 (Sokolov, 1952). If we adopt this value for the peninsula as the source of Mn, the discharge rate is 150×10^3 l/s. Assuming the Mn content as 170 μg/l (such concentration of the dissolved Mn was found in waters of the Rioni River washing out the Chiatura deposit), the transport of 1 Gt of Mn will take 1.2 Ma (only 40 ka at the Mn concentration of 5 mg/l).

It has been established that hydrosulfuric conditions repeatedly arose in marine basins during the Earth's evolution. The Oligocene–Early Miocene Maikop Basin is a characteristic example of the existence of hydrosulfuric contamination over a long period. Ideas about anoxic conditions in the Maikop Sea have long been developed (Arkhangel'skii, 1927) and were repeatedly substantiated (Nevesskaya *et al.*, 1984; *Neftematerinskie...*, 1966; Stolyarov, 1993; Popov *et al.*, 1993; Kholodov, 2002; Nedumov, 1996, and others). In these works, the presence of hydrosulfuric contamination of bottom waters was suggested based on some lithological and paleoecological features of sediments (first of all, the appearance of the so called "fish facies").

In addition to the qualitative lithological and paleoecological criteria of hydrosulfuric contamination of bottom waters, we also proposed a quantitative geochemical criterion, namely stagnation index ($K_{Mo/Mn}$) that represents the ratio of concentrations of Mo and Mn in sediments (Kholodov and Nedumov, 1991).

The choice of these particular elements is related to their opposite behavior in the hydrosulfuric medium. Under conditions of hydrosulfuric contamination, Mn is actively delivered to sediment. Intense settling of Mn is caused by several reasons, among which its coprecipitation with sulfides is the principal one (Korolev, 1958). In oxic medium, on the contrary, Mo accumulates in the dissolved form. Under hydrosulfuric conditions, Mn accumulates in water column in the dissolved form. When the gas regime becomes oxic, Mn virtually completely passes to sediment as oxides and hydroxides. Analysis of the abundant factual material related to concentrations of Mo and Mn in sediments of recent and ancient marine basins revealed that the stagnation index equal to 0.00*n* units testifies to oxic conditions of sedimentation (Kholodov and Nedumov, 1991). Increase of the index to 0.0*n*–0.*n* units suggests anoxic sedimentation conditions.

In order to obtain a general idea of changes in gas regime of bottom waters in the Maikop Basin, we described and sampled several Maikop sections in the western, central and eastern areas of the Ciscaucasia region, Azerbaijan, and Turkmenistan. This allowed us to reconstruct sedimentary conditions in different parts of the vast Maikop paleosea.

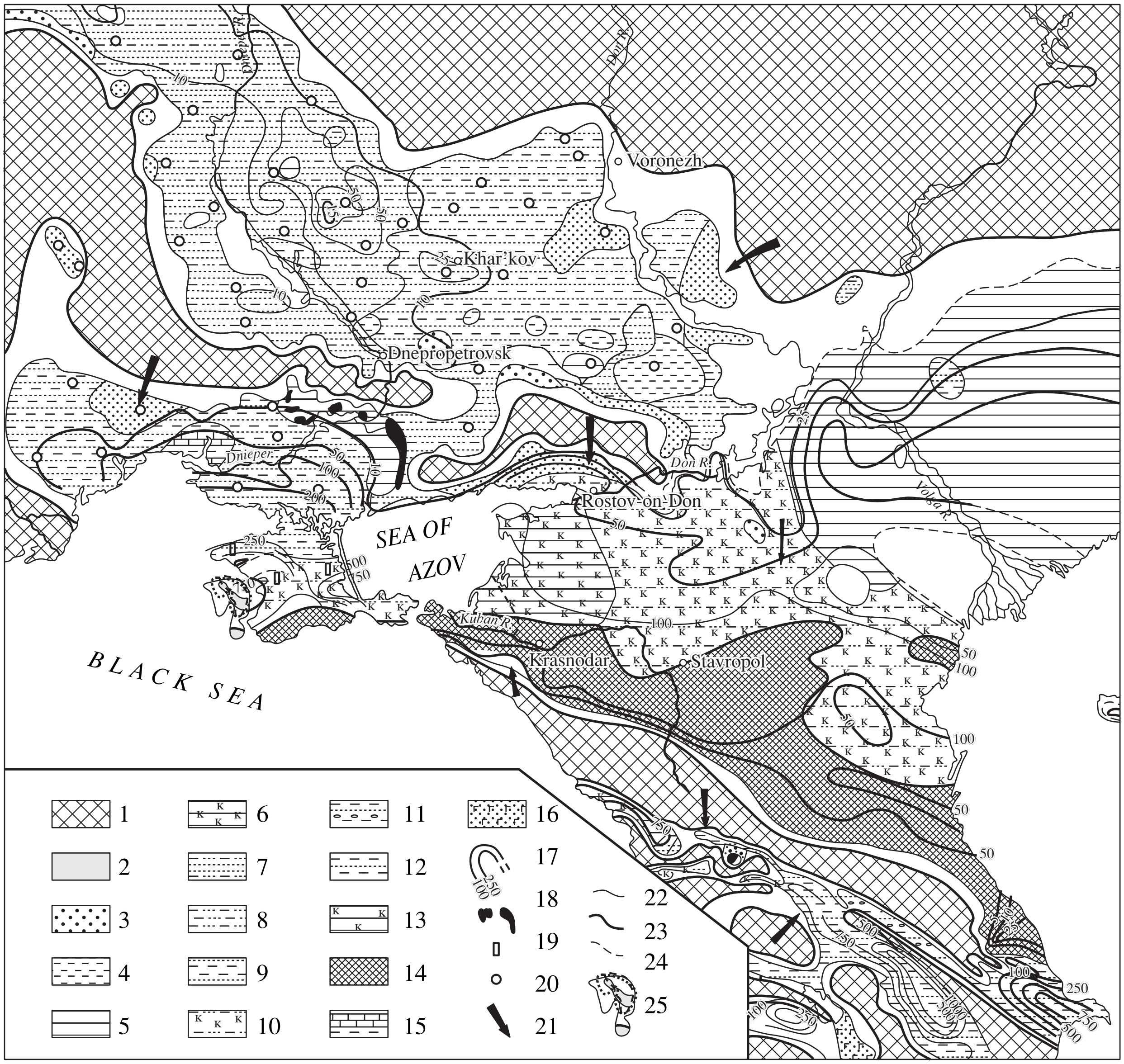

Fig. 1. Paleogeography of the Early Oligocene epoch based on (Strakhov *et al.*, 1968) and supplemented with contours of the Kalamit nodule field. (1) Erosion areas; (2) medium- to fine-grained sands and sandstones; (3) coarse-grained sands and sandstones; (4) silty clays; (5) clays; (6) carbonate clays; (7) alternation of sands (dominant) and silts; (8) clayey sands and sandy clays; (9) alternation of sands and silts; (10) silty carbonate clays; (11) alternation of sands, silts, and gravel-pebble interlayers; (12) alternation of silty clays and sands; (13) alternation of noncarbonate and carbonate clays; (14) marls and carbonate-rich clays; (15) clays with interlayers of limestones; (16) tuffs and tuffogenic rocks of basic composition; (17) isopachs; (18) manganese deposits and occurrences; (19) siderite and ankerite nodules; (20) glauconite; (21) principal direction of clastic material transport; (22) boundaries of lithological complexes; (23) boundaries of eroded areas; (24) boundaries of pinchout or washout of lithological complexes; (25) contours of the Kalamit nodule field.

The use of calculations of the stagnation index in combination with the analysis of paleogeographic situation in the region and the estimation of intensity of postsedimentary transformations made it possible to confirm the conclusion that hydrosulfuric conditions dominated during the Oligocene in the Maikop Basin. They began to change into the oxic environment only from the initial Miocene. Additionally, it was established that hydrosulfuric conditions were unstable, and the degree of hydrosulfuric contamination was sufficiently variable. Hence, large masses of Mn were repeatedly transferred from solution to sediments (Nedumov, 1998). However, manganese deposits only formed at two stratigraphic levels (the Early and Late Oligocene).

At the same time, the Mn content in Oligocene sediments, which overlie and underlie the ore bed near the South Ukrainian group of deposits, sharply exceeds the clarke level. Similar relationships are recorded at the Chiatura, Mangyshlak, and Labinsk deposits, which are also situated in coastal zones of the Maikop Sea. These data enabled Strakhov to assume an embryonic manganese ore process, which was sufficiently extended in time and space and only episodically culminated in the formation of deposits (Strakhov *et al.*, 1968).

According to Sapozhnikov (1984), hydrosulfuric waters with an appreciable amount of dissolved Mn were delivered to the coastal well-aerated zone of sea from the central deep-water parts of the basin owing to currents and transgressions of the sea. At the same time, oxidation and reduction of the partial pressure of CO_2 promoted the precipitation of Mn in the form of oxyhydroxides and carbonates. The subsequent fate of the newly formed suspension could be different (scattering or concentration depending on specific conditions).

The concept of genetic links of both manganese and uranium–rare metal deposits with the dynamics of hydrosulfuric contamination of bottom waters in the Maikop Basin was also developed in the subsequent period (Kochenov and Stolyarov, 1996; Stolyarov, 1993; Stolyarov and Kochenov, 1995; Kholodov, 1984, 2002; Nedumov, 1996, 1998). Khovanskii and Mitropol'skii (1989) proposed the model of manganese ore formation from Mn dissolved in waters of stagnant basin.

The sedimentary-basinal hypothesis, which is popular among the Uralian researchers in recent years, represents an advanced version of Sapozhnikov's concept that was designed to explain the genesis of Middle Carboniferous–Lower Permian manganese carbonate ores of the Paikhoi–southern Novaya Zemlya province (Koroteev *et al.*, 1997). The main point of this version is two-stage Mn concentration during sedimentogenesis. When terrigenous material fills the H_2S-contaminated deep-water troughs, Mn-bearing minerals are dissolved and Mn^{2+} ions are transferred to the solution. Very high Mn concentrations in waters of these troughs result in the formation of a specific intermediate manganese collector. At the second stage, manganese rises in the upwelling zone and precipitates in coastal parts of the basin saturated with oxygen.

The main objection to the concept of Sapozhnikov—manganese in hydrosulfuric waters served as the source for Oligocene ores—is as follows. In recent H_2S-contaminated seas, ore concentrations of Mn are not observed. Hence, Mn from hydrosulfuric zone cannot serve as the source of sedimentary manganese ores (Kalinenko, 1990). Therefore, only the detailed analysis of ore-generating potential of recent basins can elucidate processes of ore genesis in the past.

Hydrosulfuric contamination appeared in the Black Sea 7–8 ka ago. The mechanism of its formation was suggested by N.M. Strakhov. At present, the hydrosulfuric boundary is located at a depth of approximately 200 m; i.e., the hydrosulfuric contamination embraces almost 500000 km^3 (Kholodov, 2002).

Figure 2 shows that ore concentrations of Mn are found as ferromanganese nodules (FMN) in the Kalamit Gulf, near the Romanian and Bulgarian coasts, at the Rioni River mouth, in the Kerch Strait, and near the Turkish coasts (Shnyukov and Ziborov, 2004). All nodule findings are situated near the boundary of oxic and hydrosulfuric zones of the sea at a depth of 40–200 m.

The Kalamit field, the largest and best studied site of ferromanganese nodules (Fig. 3), was investigated and sampled in the 1970s–1980s during expeditions of the R/V *Geokhimik.* The sampling was executed by heavy gravity corers that made it possible to take samples from the upper 3 m of sediments. The FMN field has an area of 2700 km^2 (Shnyukov and Ziborov, 2004). The nodules are mainly situated in the upper 2-m-thick layer of sediments. The nodules are irregularly distributed and concentrated at the Djemetinian, Upper Djemetinian, and Recent levels of the Holocene (*Geologiya…*, 1983).

The FMN field in Recent sediments is the largest one (Fig. 3). In the Kalamit Gulf, the nodules are encountered at depths of up to 200 m. In most cases, they are distributed at a depth of 70–140 m. The maximum quantity of nodules is concentrated on the seafloor and in the uppermost 20 cm of sediment. According to Shnyukov *et al.* (see *Kalamitskoe…*, 1973), the content of nodules on sediment surface is 25–1300 g/m^2 (as much as 2.5 kg/m^2, according to estimates of Sevast'yanov and Volkov). According to Shnyukov *et al.* (*Kalamitskoe…*, 1973), the total mass of FMN in the upper layer of sediments is 2.8 Mt. Naturally, this figure is rather rough, because the sampling network is rare and the FMN distribution is irregular.

In the interval of 60–100 cm bsf, we have recorded the second level of high FMN content. The thickness is 10–20 cm (sometimes, more). The FMN cluster is situated just above a bed of gray mud enriched in remnants of partly broken and partly well-preserved fauna allowing to date this bed as the Djemetinian (upper Drevnechernomorian sediments). The absolute age of this bed varies from 900 to 1200 yr. The FMN area at this level is 1550 km^2 and the approximate mass is 0.5 Mt.

The oldest FMN level is located immediately below the fauna-containing bed (sometimes, including this bed) at a depth of up to 1.5 m bsf. Its thickness reaches 30–50 cm, the distribution area is 980 km^2, and the reserves are 1.8 Mt.

Centers of FMN crystallization are commonly represented by shell valves (more rarely, fucoids filled with mud). Generally, the size of nodules does not exceed 1.5 cm. The thickness of coating is 4 mm or less.

Average Fe and Mn concentrations in nodules of the Kalamit field are 25 and 7.7%, respectively (Shnyukov and Ziborov, 2004). The nodules are characterized by zoning owing to variations in Mn and Fe concentrations (Fig. 4). According to (*Kalamitskoe…*, 1973), one can distinguish six zones from 0.3 to 0.7 mm wide, in which the average Fe content changes from 1–2 to 25% and

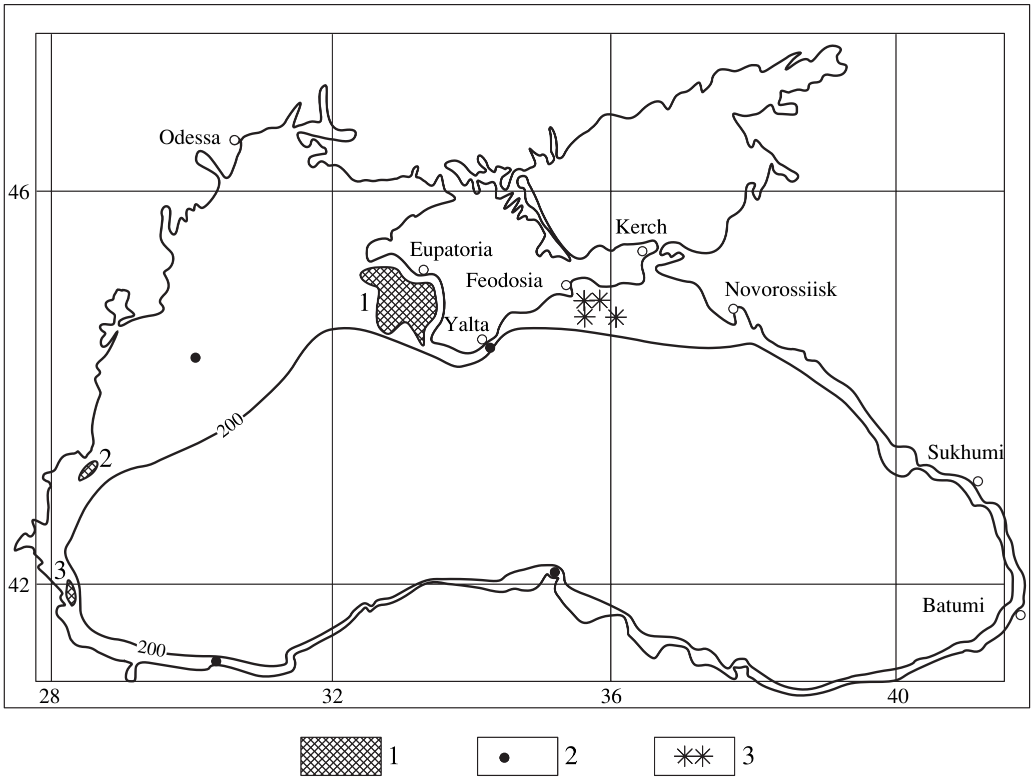

Fig. 2. Distribution of ferromanganese nodules in the Black Sea (Shnyukov and Ziborov, 2004). (1) Nodule fields; (2) single findings of nodules; (3) surface ferrugination of sediments.

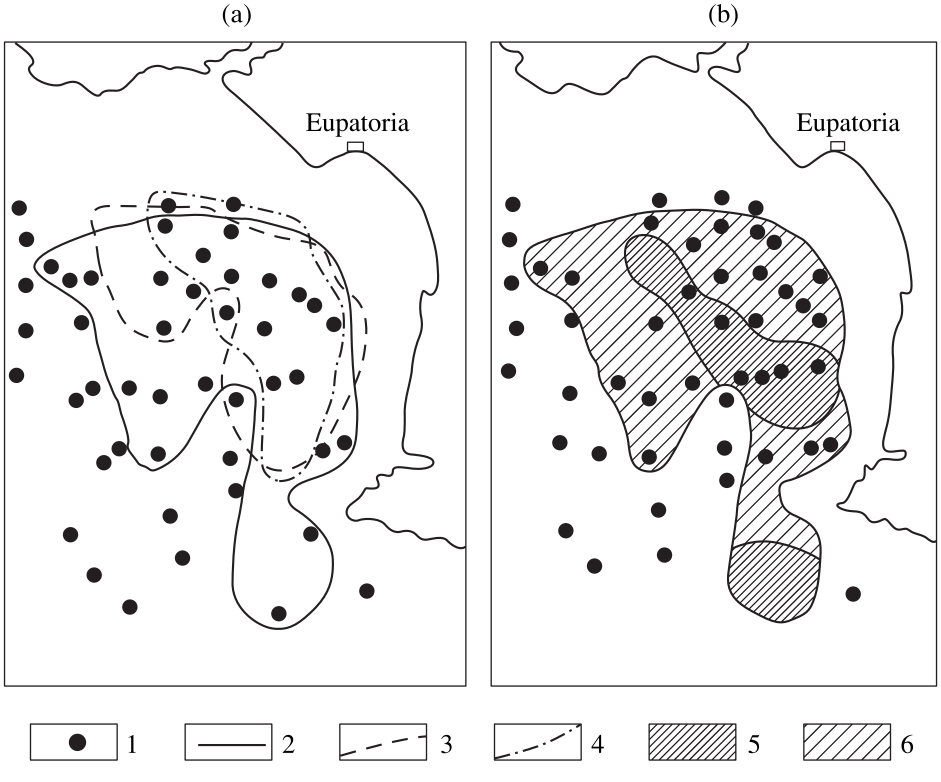

Fig. 3. The Kalamit ferromanganese nodule field (*Geologiya…*, 1983). (a) contours of different-age nodule fields; (b) content of nodules in the surface layer. (1) Sampling stations; (2–4) contours of nodule fields: (2) surface, (3) Upper Djemetinian, (4) Djemetinian; (5–6) nodule concentration in the surface layer: (5) high, (6) low.

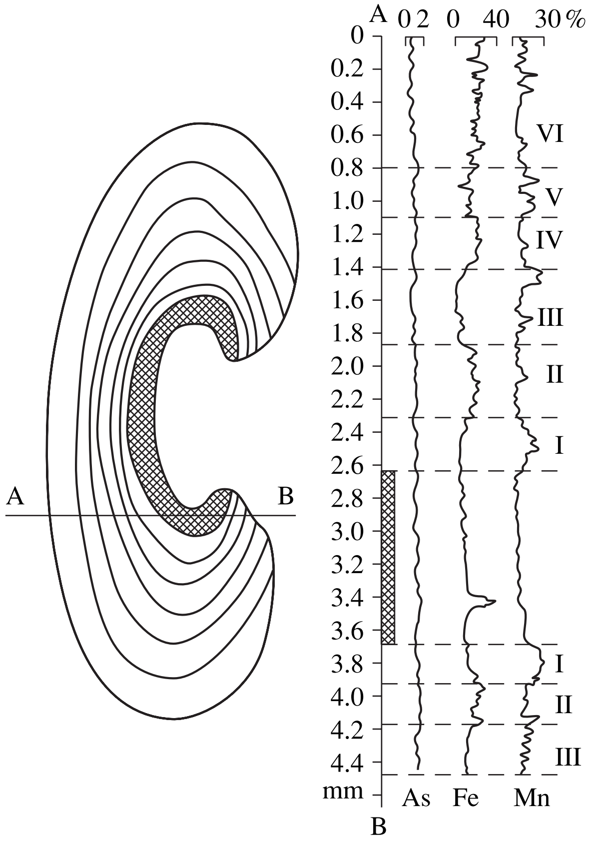

Fig. 4. Zonal distribution of Fe, Mn, and As in nodule along overgrowth zones (I–VI) around the shell of *Modiola phaseolina* (hatched) along section A–B. The Kalamit nodule field.

the average Mn content changes from 1–2 to 20% (the scatter of single determinations is 0–35% for Fe and 1–40% for Mn). Correlation between Fe and Mn contents is inverse, i.e., zones enriched in Fe and depleted in Mn alternate with zones enriched in Mn and depleted in Fe. It is interesting that the variability of single determinations of Fe and Mn is very high. Differences of contents in adjacent points of determination frequently exceed 10%, and the bar chart generally looks like a palisade. Moreover, Fe and Mn contents are inversely proportional even in single determinations. The inverse correlation between Fe and Mn concentrations is also typical of nodules as a whole (Fig. 5).

The majority of investigators recognize that the formation of ferromanganese accumulations in the Black Sea (first of all, in the Kalamit Gulf) is governed by processes at the oxidative–reductive geochemical barrier (Kholodov, 2002; Sevast'yanov and Volkov, 1967b; Khovanskii and Mitropol'skii, 1988; Shnyukov and Ziborov, 2004). According to Sevast'yanov and Volkov (1967a, 1967b), nodules are formed as result of the two-stage diagenetic concentration of Fe, Mn, and a number of minor elements. The first stage is marked by the redistribution of elements between reduced and oxidized zones of bottom sediments. Owing to the concentration gradient, dissolved Fe^{2+} and Mn^{2+} migrate from the reduced zone of sediments to the oxidized zone, where they are oxidized and transformed into colloidal oxyhydroxides and accumulated. In the subsurface oxidized layer of sediments, the second stage of diagenetic concentration—the directed migration of colloidal particles of Fe and Mn and their crystallization on shells lying on sediment surface results in the formation of ferromanganese nodules. According to this mechanism, when the nodules are buried in sediments and transferred to the reduced layer, they are dissolved, and the released matter is again involved in the process of diagenetic redistribution and migration.

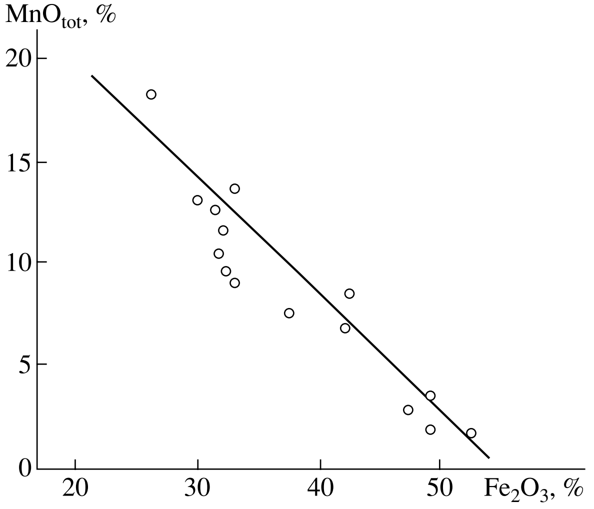

Fig. 5. Relationship between contents of Mn and Fe in nodules (Sevast'yanov and Volkov, 1976b).

The existence of diagenetic mechanism described by I.I. Volkov and V.F. Sevast'yanov is beyond question. However, some available data contradict the idea that all ore matter of nodules is delivered from sediments.

First, this is the zoning of nodules. Indeed, from the standpoint of more or less regular input of material from below, it is difficult to explain the alternation of drastically Fe- or Mn-rich layers in nodules. At the same time, such a zoning is quite explainable, if we assume a periodic increase in the delivery of Fe or Mn to the upper oxidized layer from the lateral zone.

Second, sediments of the Kalamit Gulf contain three horizons of nodules that are quite comparable in absolute masses of Fe and Mn. During the more or less stable diagenetic process described by I.I. Volkov and V.F. Sevast'yanov, the nodules should concentrate on sediment surface and dissolved in depth. If we assume that the nodules did not have time to be completely dissolved during the subsidence and burial in sediments, they should be sufficiently evenly distributed within the sedimentary sequence and their absolute mass should be significantly lesser than the mass of surface nodules. This contradiction is also eliminated if the delivery of

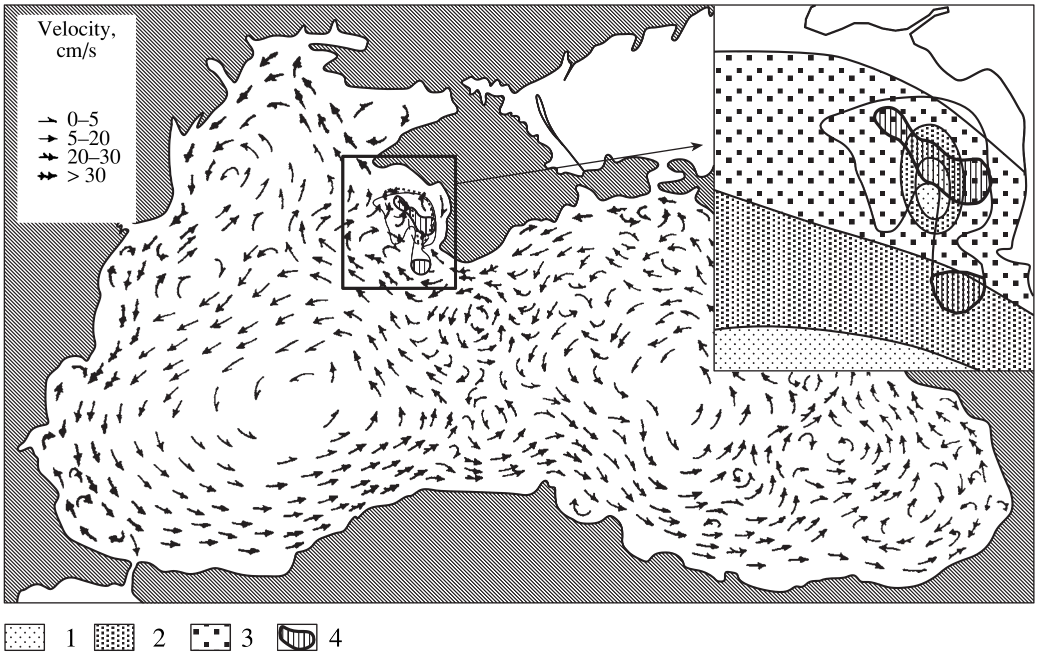

Fig. 6. Scheme of currents in the Black Sea modified after (Shimkus and Trimonis, 1974). (1–3) Concentration of particulates in surface water of the Black Sea in September 1966 (mg/l): (1) 0.5, (2) 1–1.5, (3) 1.5–2; (4) zones with high nodule concentration in surface layer of the Kalamit field.

ore material to the nodule formation zone is periodically enhanced. Consequently, the intensity of nodule formation is periodically intensified and nodule-rich interlayers are formed in sediments. However, it should be noted that the appearance and disappearance of nodules could be related to changes in sedimentation rate. High sedimentation rate would hamper high Fe and Mn concentrations that are sufficient for the formation of nodules, and the second stage of diagenetic concentration would be suppressed.

In addition, conditions for the functioning of this mechanism of nodule formation exist along the entire Black Sea shelf above the level of hydrosulfuric contamination, whereas the nodule formation is only recorded in a few sites.

Shnyukov and Ziborov (2004) also noted this contradiction and tried to link nodule formation in the Kalamit field with the delivery of Fe and Mn from continental rocks of the Pliocene Tavr Formation that are enriched in these elements. They indicated three possible ways of matter input from land in the Kalamit field: river discharge, coastal abrasion, and submarine discharge of groundwaters. As for the river discharge, the authors themselves recognize the insignificance of Fe and Mn delivery by recent Crimean rivers. Coastal abrasion is sufficiently developed on shores of the Kalamit Gulf. However, as far back as 1958, Zenkovich (1958) showed that abraded material transported along the coast to north starts to accumulate only slightly south of Eupatoria. In addition, analysis of the map of FMN distribution in the Kalamit field presented in (Shnyukov and Ziborov, 2004) clearly shows that the southern maximum of nodule distribution situated south of the Khersones Cape latitude could not originate from the Crimean material, because a northerly marine current is active in this area (Fig. 6). It is hard to believe that Fe and Mn were transported against the current to form the southern maximum of the Kalamit field.

The submarine discharge of groundwaters in the Kalamit field has not been proved, although this process could be possible. In general, the Crimean provenance of Fe and Mn could hardly make a sufficient contribution to the nodule formation, although its influence cannot be completely neglected.

Mn and Fe dissolved in hydrosulfuric waters could serve as an additional source of ore material. Khovanskii and Mitropol'skii (1989) proposed a model of FMN formation in the Black Sea based on the hypothesis of D.G. Sapozhnikov. All FMNs revealed in the study area and even slightly enhanced Mn concentrations in sediments are situated in the oxic marine zone near its contact with the hydrosulfuric zone. The concentration gradient of dissolved Mn between the hydrosulfuric and oxic waters drives this element upward. At the contact with oxic waters, Mn is oxidized and accumulated in suspension. The Mn content reaches 58 μg/l, which is hundreds of times higher than its concentration in the oxic waters (Brewer and Spenser, 1974). The particulates precipitate and again enter the reductive environment, where Mn is once more transferred into solution. Consequently, a layer with enhanced content

Table 1. Absolute masses of sediment and concentrations of Fe and Mn in the oxidized layer and upper 60 cm of reduced sedimentary layer

	Absolute mass	Average concentration, %		Maximum concentration, %	
		Fe	Mn	Fe	Mn
Oxidized sediment	7×10^7 t	4.87	0.37	7.6	1.05
Reduced sediment (60 cm)	21×10^8 t	3.5	0.04	4.8	0.07
Fe–Mn nodules	2.8×10^6 t	25	7.7	36	17.7

of suspended Mn is formed near the lower boundary of oxic waters, while a layer with increased content of dissolved Mn arises near the upper boundary of hydrosulfuric waters. At a depth of 150–190 m, the water layer enriched in suspended Mn meets bottom sediments along the whole shelf perimeter. In areas with deep currents directed toward the shore, the suspension is transported to the oxic zone on the shelf, where the particulates settle down and participate in the diagenetic mechanism proposed by I.I. Volkov and V.F. Sevast'yanov.

A question arises as to whether or not the additional source of Fe and Mn is essential for the formation of nodules. To elucidate this issue, let us try to define which part of Fe and Mn disseminated in sediments is mobilized in diagenesis and transported to the oxidized layer.

If the area of the nodule field is 2700 km^2, the thickness of the oxidized layer is 2 cm, and the density of sediments is 1.3 t/m^3, then the absolute mass of the oxidized layer in the nodule field is 7×10^7 t. The absolute mass of the upper 60-cm layer of sediments is 2.7×10^9 m^2 $\times$ 0.6 m $\times$ 1.3 t/m^3 = 2.1×10^9 t. Average contents of Fe and Mn in the oxidized layer and upper 60 cm of sediments based on the data of Sevast'yanov and Volkov (1967a) are presented in Table 1. Results of sampling of the upper part of the 60-cm-thick layer of reduced sediments were used for the calculations. The choice of this particular thickness is dictated by two reasons. First, chemical elements are redistributed between the oxidized and reduced muds only in the upper 30 cm of sediments (Sevast'yanov and Volkov, 1967a). Hence, estimates of the portion of transported material obtained from calculations for the 60-cm-thick layer of sediment will be certainly lower than the real ones. Second, the interval of 60 cm is the depth of appearance of the second nodule layer, the existence of which testifies to the cessation of Fe and Mn diffusion into the overlying layers.

The quantity of Fe and Mn transported to the oxidized layer from the reduced one is equal to the difference in contents of these elements in the oxidized and reduced layers and the absolute mass of these elements in the nodules (Table 2).

Knowing the absolute mass of sediment, from which Fe and Mn have emigrated, and absolute masses of transferred components, one can calculate these masses in sediments prior to the transportation of elements. We found that concentration of Fe and Mn in the upper 60-cm layer of sediment decreased by 0.08 and 0.02%, respectively, as result of the diagenetic redistribution and diffusion into the oxidized layer (Table 3).

Thus, calculations based on average values show that the 60-cm-thick layer loses 0.08% of Fe (i.e., not more than 2–3% of the initial content) and 0.02% of Mn (i.e., more than 30% of the initial concentration). According to (Sevast'yanov and Volkov, 1967a; Demina and Zavadskaya, 1987), the content of mobile forms of Fe in the upper 60 cm of sediments is normally 20–50% (sometimes, more). The content of mobile forms of Mn is still higher (30–60 vol %). Consequently, the internal reserves of sediments are enough for the formation of nodules in the Kalamit field, and searching for an additional source of ore matter seems to be unnecessary. Volumes of the redistributed matter are mainly controlled by the intensity of diagenetic transformations and sedimentation rate.

Thus, if diagenetic processes are intense, mobile forms of Fe and Mn, which are present in sediments, are enough for the formation of nodules and high concentration of these elements in the oxidized layer. This is obvious for Fe. However, the internal reserves are not so enough for Mn. Since the sample volume is not too

Table 2. Input of Fe and Mn to the oxidized layer

	Delivered Fe, %	Absolute mass of delivered Fe, 10^5 t	Delivered Mn, %	Absolute mass of delivered Mn, 10^5 t
Oxidized layer (average values)	4.87 – 3.5 = 1.37	9.6	0.37 – 0.04 = 0.33	2.3
Nodules (average values)	25	7	7.7	2.15
Total		16.6		4.45
Oxidized layer (maximum values)	7.6 – 4.8 = 2.8	19.6	1.05 – 0.07 = 0.98	6.9
Nodules (maximum values)	36	10	17.7	4.9
Total		29.6		11.8

Table 3. Absolute masses and amounts of Fe and Mn delivered to the oxidized layer

	Sediment (upper 60 cm)	Average values of Fe and Mn delivered to the oxidized layer		Maximum values of Fe and Mn delivered to the oxidized layer	
		Fe	Mn	Fe	Mn
Absolute mass, t	21×10^8	16.6×10^5	4.45×10^5	29.6×10^5	11.8×10^5
Concentration, %	100	0.08	0.02	0.14	0.056

big and the calculated values of average contents can strongly differ from the real ones, let us try to estimate the quantity of diagenetically transported ore matter on the basis of maximal quantities of Fe and Mn rather than average ones. It should be noted that contents of ore components in other Black Sea nodule fields significantly differ from those in the Kalamit field. For instance, the minimal Mn concentration in nodules on the Turkish shelf (22.3%) is higher than the maximal contents (17.7%) in the Kalamit field (Shnyukov and Ziborov, 2004).

Analogous calculations presented in Table 3 show that the portion of the evacuated Fe did not essentially increase (0.14%) and continues to remain much less than the content of mobile Fe in sediments. The situation for Mn is dramatically different. The value obtained (0.056%) exceeds not only the value of mobile constituent, but also the bulk Mn content in sediments. In other words, additional input of Fe into the oxidized layer was probably absent or minimal during the formation of nodules, while Mn was presumably delivered and its role was significant.

Thus, results of the calculations unambiguously testify to the contribution of ore components from the hydrosulfuric zone. In this case, masses of the Mn input appreciably surpass masses of the Fe input.

The zoning of nodules (Fig. 4) also indicates that a part of manganese was delivered from the hydrosulfuric zone of the sea rather than the sedimentary sequence. The inverse correlation between Fe and Mn contents and their extremely strong variability may be explained by their irregular delivery into the nodule formation zone. It is evident that this irregularity is caused by the periodic intensification and attenuation of the delivery of ore components (first of all, Mn) from the hydrosulfuric zone. It is very possible that the sharp variations in Fe and Mn contents correspond to seasonal changes in the activity of currents. The number of inflections in plots of Fe and Mn contents based on microprobe data (Fig. 4) is approximately 100. If we assume that the inflections reflect seasonal changes, it turns out that the nodules formed in ~50 yr. Based on the assumption of average sedimentation rate of 2 cm/100 yr over the last 8 ka, Sevast'yanov and Volkov (1967b) found that the duration of nodule formation is approximately 100 yr. Even if the average sedimentation rate mentioned above is correct, we should bear in mind that its specific values could significantly change in time. According to E.F. Shnyukov, absolute age of the reference shell interlayer located at a depth of 80–100 cm bsf is 920–1200 yr. Hence, the average sedimentation rate of this unit should be 7–10 cm/100 yr. Thus, the sedimentation rate was significantly variable, and nodules were developed at a minimal sedimentation rate.

Inhomogeneous distribution of nodules in the Kalamit section and their zoning are consistent with the irregular delivery of hydrosulfuric waters into the oxic zone, presumably, due to oscillations of the level of hydrosulfuric contamination that are recorded both in recent seas (e.g., the hydrosulfuric contamination periodically disappears completely in depressions of the Baltic Sea) and in ancient basins (Nedumov, 1998). Causes of changes in this level are not clear so far. However, it is evident that sea transgressions should be followed by increase in the delivery of hydrosulfuric waters into the oxic zone and transport of manganese precipitates by currents to the coastal zone.

In the Black Sea, the origination of hydrosulfuric contamination is related to the Drevnechernomorian transgression, when the invasion of salt waters through Bosporus approximately 7–8 ka ago formed a halocline and gave rise to hydrosulfuric contamination of deep waters. According to (Fedorov, 1978), the Novochernomorian transgression recorded in the subsequent history of the Black Sea gave way to the Fanagorian regression approximately 3.5 ka ago; the youngest Holocene transgressive phase (Nimphean) was recorded at the end of the first millennium of our era; and the new transgression that began after the short-period low-amplitude Korsun regression persists today (Fig. 7). It is easy to see that the second and third layers of nodules in the Kalamit field, which are situated near the gray mud interlayer with coquina dated at ~1 ka, probably, reflect two phases of the Nimphean transgression. The recent nodule formation is possibly related to a new phase of transgression.

Based on these suppositions, the Kalamit field can incorporate one more level of ferromanganese nodules that corresponds to the Novochernomorian transgression assumed by P.V. Fedorov. It should be emphasized that the input of Mn alone from hydrosulfuric waters is not sufficient for nodule formation. The spatiotemporal coincidence of several factors favorable for manganese ore process is essential for the formation of nodules.

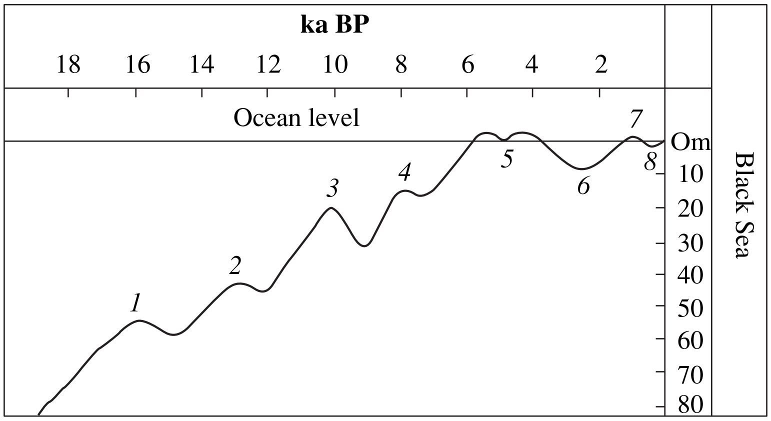

Fig. 7. Schematic curves of fluctuations of the Black Sea level in the Late Pleistocene–Holocene (Fedorov, 1978). (*1–3*) Phases of the Neoeuxinian transgression; (*4*) Drevnechernomorian transgression; (*5*) Novochernomorian transgression; (*6*) Fanagorian regression; (*7*) Nimphean phase; (*8*) Korsun regression.

Precisely such conditions were created in the Kalamit field in the Holocene.

First, the Kalamit field is located near the oxic–hydrosulfuric boundary zone of the sea characterized by oxidation of Mn and transition of the dissolved Mn into suspension.

Second, this area incorporates a current that can transport Mn suspension into the Kalamit field. A simple calculation makes it possible to demonstrate the ability of this current. According to Sailing Directions of the Black Sea, the current near the Sarychi-Aiya point flows with a velocity of up to 3 knots or 5.5 km/hr. The content of dissolved Mn in the upper part of the hydrosulfuric zone is 500 μg/l and decreases to 200–350 μg/l in lower water layers. If we imagine a current flowing along a front of 5 km with the thickness of transported water mass equal to 1 m, velocity of 60 m/min (approximately 2 knots), and Mn content of 250 μg/l, then we find that the current can transport 75 kg of Mn per minute. Knowing the absolute mass of the nodule-hosted Mn in the surface layer (215 kt), we obtain that this current can delivery the mass of Mn needed for the formation of nodules in the Kalamit field over just 5.5 yr.

Third, terrigenous sedimentation was subdued and, consequently, concentration of ore components was fostered in the Kalamit field due to its specific hydrodynamic features. Sedimentation rates were not measured in the Kalamit field. Nevertheless, there are indirect data testifying to an inverse correlation between sedimentation rate and nodule formation intensity. The map of suspension content in surface waters of the Black Sea is presented in (Shimkus and Trimonis, 1974). If we superpose data from this map over contours of the Kalamit field (Fig. 6, inset), we can see that zones of the maximal nodule concentration exactly coincide with zones of the minimal suspension content, and, correspondingly, zones of the minimal sedimentation rate.

Fourth, the Black Sea was subjected to at least three transgressions that evacuated significant masses of hydrosulfuric waters into the oxic zone during the last 5 ka. The nodule field near the western shore of the Crimea was formed precisely due to the combined action of these factors.

Thus, manganese accumulated in the hydrosulfuric zone of the sea and evacuated from deeps to the shelf during transgressions can be considered one of the main (although not single) sources of ore substance for the formation of ferromanganese nodules in the Black Sea. Precisely due to the additional delivery of manganese from the hydrosulfuric zone of the sea, the normal sedimentary diagenetic process of the matter redistribution is transformed into the ore-forming process. Therefore, the Kalamit nodule field can be considered an embryonic analogue of Oligocene manganese deposits in the southern Ukraine. Even shapes and sizes of the Kalamit nodule field and manganese deposits in the southern Ukraine are highly similar (Fig. 1). This suggests the activity of a current directed from the open sea toward the shore.

Hypothesis of the hydrosulfuric contamination of bottom waters as an accumulator of Mn is also attractive from the point of view of the reconciliation of ideas of sedimentary and hydrothermal-sedimentary sources of ore matter.

Drawing the conclusions about the significant role of hydrosulfuric contamination in the formation of manganese deposits, one should take into account that the presence of hydrosulfuric contamination by itself does not necessarily lead to high Mn concentrations in the course of sedimentation. The formation of high and ore-grade concentrations requires the existence of certain favorable conditions that can be subdivided into several groups corresponding to stages of release, transport, and high concentrations of Mn.

The first group of favorable conditions, which provide the active release of Mn within the drainage area, is as follows:

(1) A significant part of the drainage area should be composed of rocks with high concentrations of Mn.

(2) Climatic conditions in the provenance should provide the maximum extraction of Mn, i.e., a wide development of alkaline weathering crusts.

(3) The tectonic regime should promote a continuous involvement of new portions of rocks in the process of their reworking in alkaline crusts. In this case, the bulk mass of Mn migrates in the most mobile and reactive dissolved form. Moreover, at this stage, Mn is separated from Fe, the bulk mass of which remains in weathering crusts.

The second group of conditions, which provide the transport and accumulation of dissolved Mn in waters of the hydrosulfuric zone, is as follows:

(1) The catchment area should include a well-developed river network that can deliver the released Mn to marine basin.

(2) The volume of anoxic waters should be sufficient: the larger the volume of anoxic waters, the larger mass of dissolved Mn can be accumulated in the basin.

(3) The anoxic grade of waters must be high enough: in waters with free hydrogen sulfide, more Mn is accumulated than in waters with a certain quantity of oxygen.

The third group of conditions, which promote the extraction of Mn from hydrosulfuric waters and its concentration, is as follows:

(1) The precipitation of significant masses of Mn requires the injection of large volumes of hydrosulfuric waters into the oxic coastal zone by means of currents or during transgressions of the sea.

(2) The area should include sedimentary traps (various depressions and seafloor deeps).

(3) The area should also be characterized by low rates of terrigenous sedimentation when the settling Mn is not diluted by terrigenous material. It should be noted that decrease in sedimentation rate is possibly one of the crucial conditions, because the lower rate of terrigenous sedimentation favors a more complete diagenetic redistribution of ore components from the reduced layer to the oxidized layer and, correspondingly, the formation of ore concentrations.

(4) The sediments should be supplied with a sufficient quantity of organic matter that fosters the diagenetic redistribution of Mn.

Since the probability of the spatiotemporal coincidence of all favorable conditions is very low, the ore-generating potential of H_2S-contaminated basins is rarely realized. In the overwhelming majority of cases, the process does not go beyond the embryonic stage of the formation of deposits.

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