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Sources of Manganese Deposited As Oceanic Fe–Mn Ore

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Abstract—The current concepts of two competing sources of manganese deposited as oceanic Fe–Mn ore are reviewed and assessed critically. A new solution of this problem proposed in this paper is a further development of fundamental works by N.M. Strakhov in the light of new facts and with allowance for geological, geochemical, and geohistorical data. It has been concluded that terrigenous material removed from land serves as a main source of manganese fixed in oceanic Fe–Mn ore. The history of sedimentation and nodule formation in the World Ocean lasted for more than two billion years. Manganese has been supplied to recent bottom sediments from both present-day and older sources. The closed geochemical cycle of Mn circulation in the ocean is intimately related to its circulation in the hydrosphere. Seawater is oversaturated with Mn and serves as its immediate source for ore deposition and elevated concentrations in bottom sediments affected by hydrothermal solutions or other manifestations of endogenic activity. Seawater is a repository for Mn, where this element is retained during global cataclysms, which have repeatedly occurred in geological history.

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INTRODUCTION

The problem of the source of the enormous accumulations of Fe–Mn oxide ore at the oceanic bottom is far from being completely solved and has acquired particular importance in regard to the forthcoming development of oceanic mineral resources.

This paper examines alternative (hydrothermal and terrigenous) sources supplying metals to the ocean. After the decease of N.M. Strakhov, the author of classic works that provided evidence for the leading role of terrigenous Mn influx to the ocean (95%), the discussion on these topics in the Russian literature stopped and the standpoint that gives preference to the hydrothermal source became monopolistic.

Lisitsyn (2005) wrote, in his recent publication on the geology of the World Ocean in the third millennium: “The enormous contribution of endogenic matter that is supplied to the present-day oceanic bottom at mid-ocean ridges … became the sensation of the century.” Judging from Lisitsyn’s works, this statement applies to manganese as well. Yu.A. Bogdanov also states, in the preface to the book written by Gurvich (1998), that “the main part of Mn … contained in seawater is hydrothermal in origin.” In regard to such an opinion, it is necessary to return to the problem of Mn sources for oceanic Fe–Mn ore. The concept developed in this paper is based on my own studies and a critical survey of the literature.

Fe–Mn ORE FORMATION IN SPREADING ZONES OF THE ATLANTIC OCEAN

Long-term studies of Fe–Mn ore formation in different geodynamic settings of the Mid-Atlantic Ridge (rift and fracture zones, their junction zones, etc.) have led to the conclusion that endogenic processes are not crucial for supply of Mn to oceanic Fe–Mn sediments. The Fe–Mn accumulation in the spreading ridge is characterized by the prevalence of Fe over Mn, and the Mn content gradually increases toward the flanks of the ridge (Table 1).

These relationships may indicate a possible ore-forming role of the spreading ridge in the Fe supply to sulfide ore and demonstrate an obvious deficiency of Mn in this process (Bazilevskaya and Skolotnev, 2001).

For the entire extent of both the northern (0°–16° N) and some southern segments of the Mid-Atlantic Ridge (MAR) examined, constituting together more than 2500 km, substantially Mn crusts within the rift zone were found only in two localities. Their compositional and structural features, as well as sedimentation conditions, show that the crusts were brought from outside, probably as a result of indirect tectonomagmatic reactivation (Bazilevskaya, 2004).

The elevated Mn contents are documented in crusts formed on slopes of active volcanic seamounts, e.g., in the junction zone of the Chain Fracture Zone with the adjacent rift segment in the south and in the eastern Bouvet area. Thereby, closer to the summit, i.e, to the center of volcanic activity, the crusts are enriched in Fe, whereas, at deeper levels, the crusts are substantially manganese (Fig. 1). Such a distribution of crust compositions testifies to the existence of a geochemical barrier

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in seawater at the boundary between the reducing conditions of submarine volcanism and hydrothermal activity and the highly oxidizing seawater environment.

OCEANIC ORE-FORMING MEDIUM

Of great significance for metallogeny is the fact that all the ore-forming processes at the oceanic bottom function in the medium of seawater, which is a moderate electrolyte. Geochemical barriers arise in seawater in all transitional zones, whether mechanical (water–bottom), physical (pressure, temperature, etc.), or physicochemical (Eh, pH, concentration of elements, salt concentration, etc.) (Perel'man, 1968; Emel'yanov, 1998). The main barrier is the boundary between the electrolyte (seawater) and the solid substrate (bottom), which is marked by the formation of a double electric layer and by a change in the water structure. The water at this interface differs from the bulk mass of seawater, and ion exchange proceeds here coherently with changes of physicochemical parameters in boundary zones. Seawater, which contains salts of weak acids, is a buffer solution, where anions of salts of these acids, accreting protons (H^+), control the acidity of the system and smooth variations in the pH value. Most common ion equilibria in seawater are reached rapidly; their rates are determined by the intensity of mixing (Horn, 1972).

It is incorrect to identify processes in seawater with those occurring on land. This can be exemplified by the widely known succession of hydrothermal ore deposition (*Hydrothermal…*, 1992), which shows that deposition of hydroxide (MnO_2) sediments completes the hydrothermal ore formation at the oceanic bottom. This is interpreted as evidence for the hydrothermal supply of Mn to the ocean. It would be true if this process proceeded on land. However, deposition of Mn hydroxides in the ocean occurs beyond the geochemical barrier in the highly oxidizing environment of present-day seawater, which serves as a Mn source. The gradient in physicochemical parameters between the reduced fluid and the oxidized seawater favors accelerated deposition of Mn and Fe hydroxides.

The Mn contents in seawater strongly depend on the redox conditions and vary from <0.01 μg/l in the pelagic oceanic zone to hundreds or thousands of micrograms per liter in basins with a reduced medium (Baturin, 1986). The ocean is saturated with Fe–Mn hydroxides that accumulated on the bottom during the whole geological history of the ocean and are characterized by high migration mobility under changeable environmental conditions. Seawater is oversaturated with Mn hydroxide, the concentration of which is many times higher as compared with its solubility product (see below). The conditions in the present-day ocean can change only in one direction, namely, toward the depletion in oxygen that accompanies any manifestations of endogenic activity (spreading, subduction, volcanism, etc.) and promotes the reduction and dissolution of Mn hydroxides. Mn is intimately related to the hydrosphere and is characterized by a closed cycle in the ocean (Bazilevskaya, 1997, 2003), where its sole species is the hydroxide, free of chemical bonds with other elements (Bazilevskaya, 1976).

Table 1. Average Mn/Fe ratio in ore crusts from rift zones, fracture zones, and seamounts of the Atlantic Ocean

Structural features	Number of samples	Mn/Fe
Rift segments	49	0.32
Fracture zones	96	0.60
Seamounts beyond the MAR*	77	0.91

* After Skornyakova and Murdmaa (1995).

In the course of geological evolution, Mn cannot be removed from the ocean. Moreover, Mn always is deposited in highly oxidized environments and, therefore, concentrates as nodules or crusts at the bottom surface. This mode of occurrence does not rule out the burial of Mn-bearing deposits in oxidized sediments. However, under reducing conditions, these deposits cannot be retained and are dissolved. These properties of Mn hydroxide substantially differ it from Fe, which is able to form insoluble sulfides under reducing conditions or to enter into clay and other minerals and thus to withdraw from oceanic Fe–Mn ore formation. The separation of Mn and Fe in the ocean results in the increase in the Mn/Fe ratio from 0.017 at the mean level of the crust to 1.44 in ferromanganese nodules (*Metallogenic…*, 1998).

As concerns the hydrothermal activity, the elevated Mn concentrations in seawater arise irrespective of the Mn content in initial hydrothermal fluids. The increase in Mn contents in seawater is stimulated by changes in physicochemical parameters related to decreasing oxygen concentrations and a sharply increasing Mn solubility product. This process proceeds in various oceanic settings and occurs in seawater oversaturated with Mn that serves as its source. Let us consider some examples.

The Mn concentrations in seawater commonly rise in zones of an oxygen minimum, which underlies sur-

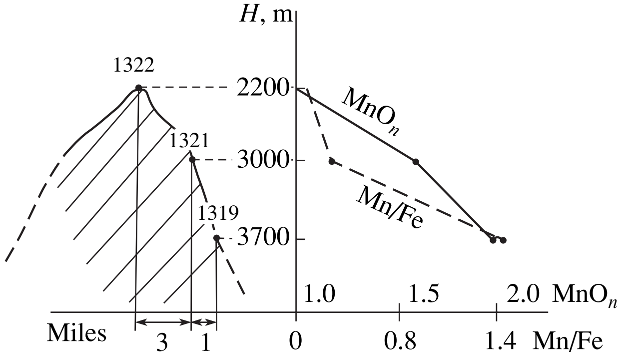

Fig. 1. Mn/Fe ratio and n in MnO_n in samples versus their morphostructural position on the volcanic Chain Seamount.

Fig. 2. The initial phase of nodule formation on shark teeth in the Clarion–Clipperton province of the Pacific.

face water layers with abundant biota. This is caused by intense breakdown of the organic matter of dead organisms, which consumes oxygen. As a result, the redox potential of seawater drops.

Ocean and sea basins with a reducing environment are always characterized by elevated Mn contents. The most striking example is H_2S-contaminated zones in the Black Sea and in bays of the Baltic Sea, where Mn contents in the reduced water layers are tens of thousands of times higher than in oxidized seawater (Baturin, 1986). It should be emphasized particularly that no hydrothermal activity is detected in these areas.

A similar situation is widespread at the oceanic bottom, where acid and reduced hydrothermal fluids discharge into highly oxidized bottom seawater to make up the main geochemical barrier. In addition, the areas around hydrothermal vents are frequently populated by abundant benthic organisms. After the death of these organisms, their organic remains break down with subsequent development of reducing conditions favorable for extraction of Mn from seawater. This process results in local formation of Fe–Mn crusts on rocks free of living mollusks. Such a situation has been described in the Logachev hydrothermal field, where the crew of a *Mir* manned submersible observed a thick carpet of mollusks around the active Irina-2 hydrothermal mound (Bogdanov et al., 2004). Although a fragment of the Mn crust that was taken nearby was referred to a hydrothermal Mn source, in my opinion, this is a typical hydrogenic deposit. The rich biotic communities near hydrothermal vents are living in normally oxidized seawater beyond the zone of acid and reduced fluids; otherwise, biota cannot exist. The elevated temperature of seawater and decomposition of organic remains produce local reducing environments favorable for formation of Fe–Mn crusts.

The initial stage of nodule formation in the Clarion–Clipperton Fracture Zone of the Pacific demonstrates the implication of organic remains for Mn deposition (Fig. 2). The cores of these nodules are frequently composed of shark teeth. The overgrowth of Fe–Mn hydroxides begins from the tooth base, where decomposition of soft tissues is still in progress. This is a geochemical microbarrier typical of the ocean.

Manganese hydroxides are active oxidizing catalysts. Readily giving back their oxygen, they become reduced up to complete dissolution. Their specific chemical property is the ability to form sorption bonds within a wide range of MnO/MnO_2 values. I have observed hydroxide crusts with oxidation degree ranging from $MnO_{1.3}$ to $MnO_{1.98}$. This property likely allows Mn to exist as a solid phase in a wide redox range of seawater.

As was mentioned, this element is readily mobilized in Mn-oversaturated seawater to increase its contents sharply and synchronously with activation of hydrothermal fluid discharge in the course of mixing of hydrothermal fluid with seawater. The high oxidation degree and buffer properties of the bulk seawater result in relatively rapid regeneration of Mn sediments beyond the geochemical barrier zone. The areas directly affected by hydrothermal solutions are barren of Mn sediments, although the hydrothermal plumes (tongues) above large hydrothermal vents, which are spread by currents, are commonly characterized by elevated Mn concentrations. This is explained by the fact that, for some period after fluid discharge, the hydrothermal plumes remain relatively reduced and Mn concentrations therein increase.

The most distinct geochemical barrier is formed near the vents of hydrothermal chimneys that serve as conduits for thermal metalliferous solutions. The water samples taken from these vents by submersibles show high Mn contents, which are interpreted as evidence for endogenic supply of Mn to the oceanic bottom. Nevertheless, it should be noted, first, that the discharged solution is not a primary fluid and experiences notable transformation in the course of its transportation. The precipitated sulfides plug up some vents and force solutions to break through in other places, sometimes located tens to hundreds of meters away from the previous vents, with Fe–Mn hydroxides deposited around and inevitably dissolved in the reduced fluid. The different Mn contents in discharged solutions, which may vary by an order of magnitude in different vents (Butuzova, 1998), support this suggestion. Second, the geochemical barrier under these conditions is very sharp because of both the high temperature gradient and the physicochemical parameters of the solution. Thus, these areas are favorable for significant concentrations of Mn supplied from seawater.

ARGUMENTS FOR AN ENDOGENIC Mn SOURCE

The concept of hydrothermal leaching of metals from basalts in the world system of oceanic rifts, 60000 km long, is among the most popular hypotheses. It is assumed that circulation of seawater within spreading ridges of this system is accompanied by leaching of basalts, from where metals are removed to the bottom surface. The hydrothermal solutions discharge in the same zones, where seawater penetrates deep downward into the oceanic basaltic crust along fissures, faults, and other conduits. According to Gurvich (1998), the bulk volume of oceanic water passes through the high-temperature hydrothermal circulation system in spreading ridges every 1 million years. In my opinion, this is hardly possible because the oceanic bottom of over 360×10^6 km^2 is largely covered by sediments. Deep-sea drilling data indicate that sediments become progressively more compact downward because of decreasing porosity and dehydration. Thus, the major part of the oceanic bottom is screened from free penetration of seawater into basalts. As concerns the rift zones, where seawater penetrates into basalts to discharge subsequently in the form of hydrothermal solutions, this process can hardly result in leaching of basalts in amounts sufficient for sulfide ore formation.

Furthermore, the mid-ocean ridges do not "breathe" by hydrotherms over their entire extent. Active vents occasionally are clustered but generally are sporadic, and it is not simple to discover them. The volume of basalts subject to the so-called hydrothermal leaching in spreading zones is negligible if this process takes place at all. Leached and Mn-depleted basalts are as yet unknown. Moreover, all the available data show that the Mn contents in hydrothermally altered basalts either remain unchanged or increase (Butuzova, 1998).

Nevertheless, the significant contribution of seawater to hydrothermal solutions is an undoubted fact. The question arises of how it appears therein. In this regard, very interesting and extremely important data were obtained during ODP Leg 158 in the TAG area of hydrothermal mounds at 26° N of the MAR (Humphruz et al., 1995). In this area, 17 holes were drilled at a distance of 10–15 m from one another. All the recovered core sections are largely composed of breccia. Newly formed hydrothermal deposits composed of pyrite and chalcopyrite are observed only in the upper several meters of the mound section and ore breccia cemented by anhydrite was penetrated beneath. This was unexpected because anhydrite ($CaCO_3$) is soluble in seawater. However, its solubility sharply decreases with increasing temperature. Humphruz et al. (1995) suggested that precipitation of anhydrite at a depth of 3650 m requires seawater heating to >150°C. This implies that a large volume of cold seawater penetrated into the mound to be heated to a high temperature and form compact anhydrite deposits in discharge areas of hot hydrothermal fluids. Seawater enters the hydrothermal systems along mound margins and is heated within ascending flows under black smokers by mixing with high-temperature hydrothermal fluids. A significant quantity of seawater passes through the hydrothermal system during its life in such a way. During long-term inactive periods alternating with active phases, the temperature inside the mound falls and anhydrite dissolves to increase the porosity of the substrate and destroy the breccia.

Thus, the drilling results have shown that seawater enters hydrothermal systems from outside, bypassing the basaltic crust.

Butuzova (1998), thoroughly examining experimental works on basalt leaching, stated that "…there is no definite geological, petrological, geochemical, or experimental evidence for the crucial role of oceanic rocks' leaching in the formation of metalliferous hydrothermal solutions and related ore occurrences, and the problem of contribution of the crustal component to the total balance of metals and specific geochemical features of this component remains unsolved." Butuzova comes to a conclusion on the important role of a deep fluid phase in hydrothermal ore formation, i.e., confirms the classical hypothesis developed by V.I. Vernadsky, A.G. Betekhtin, D.S. Korzhinsky, and others.

Such a seemingly obvious argument in favor of endogenic Mn supply as the hydrothermal mounds covered by Fe–Mn crusts in the Galapagos spreading center (Bolger et al., 1978; Gordeev et al., 1979) also cannot be omitted. If it were not for several deep-sea holes drilled by *Glomar Challenger* during Legs 54 and 70 (Hekinian et al., 1978; Williams et al., 1979; Bazilevskaya, 1980, 1984), it would be difficult to contest this fact. Particularly important information was obtained during Leg 70, when the hydraulic coring technique was first used instead of rotary drilling, which destroys the upper 10–15 m of sediments. The drilling showed that the center of hydrothermal activity is located beneath a 33-m-thick unit of pelagic sediments containing up to 1% of Mn. Holes located 300 m apart recovered both uniform pelagic sediments and members where these sediments alternate with reduced green clay, a product of reworking of these sediments by hydrothermal solutions. The Mn content in the green clay that occupies the upper part of a sedimentary sequence is as low as 0.1%. In addition, fragments of buried Fe–Mn nodules are hosted in the sediments. Thus, pelagic sediments, as well as nodules, from which reduced acid hydrothermal solutions remove Mn to the bottom surface and redeposit it at the geochemical barrier in the form of crusts, serve as a source of Mn in the Fe–Mn capping covering mounds. Some manganese is removed into seawater with formation of Mn-enriched plumes. The model developed by Gordeev et al. (1979) that depicts the distribution of "hydrothermal" Mn in seawater may be supplemented by the lower part that shows the Mn source in this area (Fig. 3). It should be noted that two holes penetrated fresh basalts unaltered by hydrothermal fluids (Hekinian et al., 1978). Of interest are variable Mn contents in seawater along the vertical section of the above model, which demonstrates a second peak confined to the oxygen minimum.

The metalliferous sediments in the East Pacific Rise (EPR), which were discovered during the first expedi-

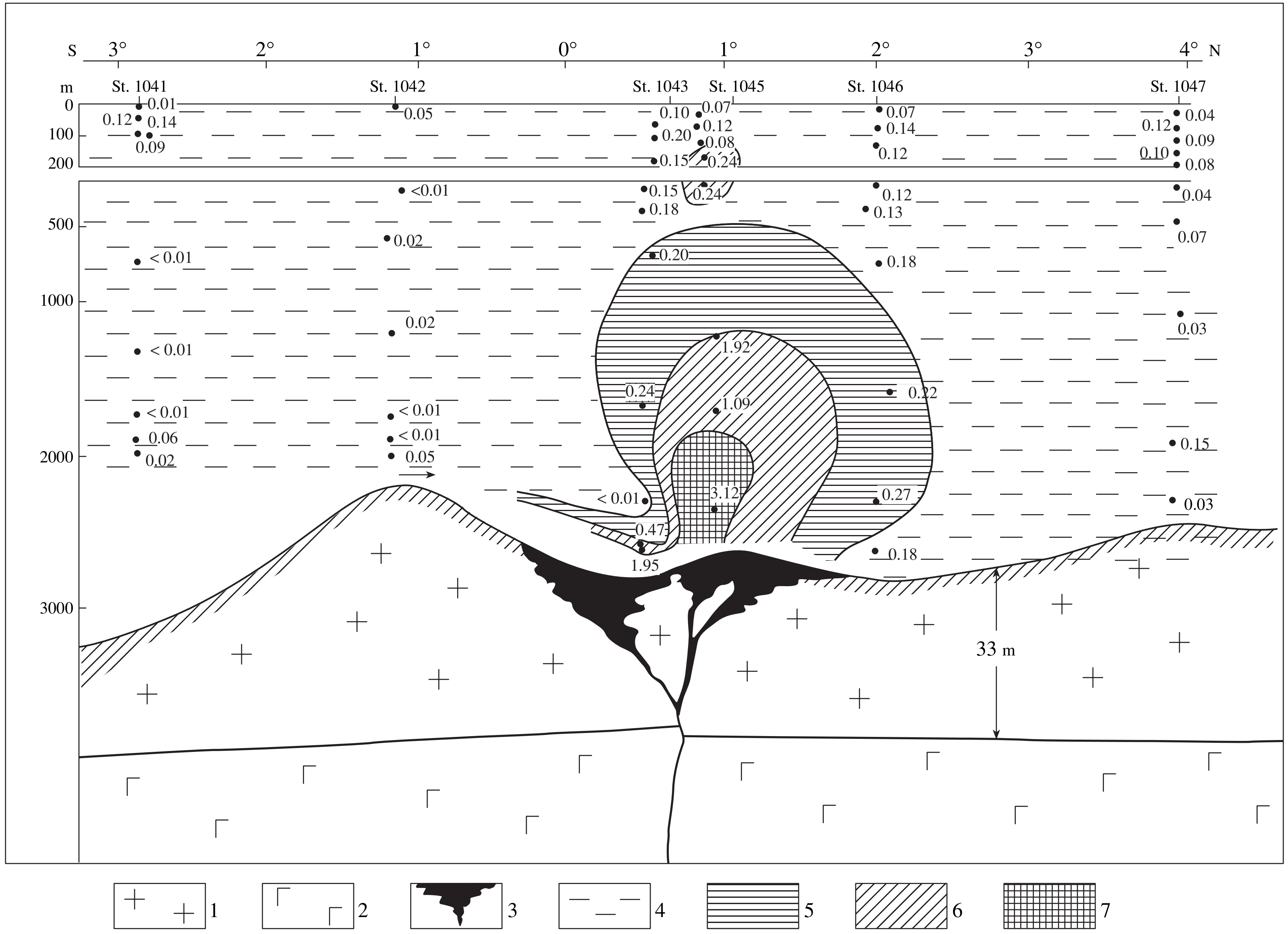

Fig. 3. Formation of Mn plume in the Galapagos spreading center: a conceptual scheme, modified after Gordeev et al. (1979). (1) Pelagic sediments; (2) basaltic basement; (3) hydrothermally altered sediments (green clay); (4–7) distribution of suspended Mn in seawater (μg/l): (4) <0.5, (5) 0.2–0.5, (6) 0.5–2.0, (7) >2.0. The arrow indicates the direction of the bottom current.

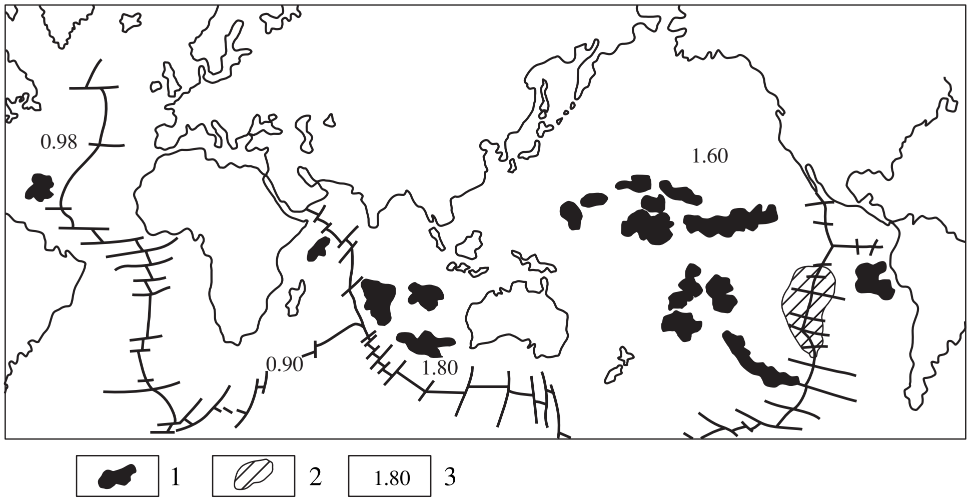

Fig. 4. Ore fields with Fe–Mn nodules and crusts in the World Ocean, simplified after Andreev et al. (1995). (1) Ore fields; (2) metalliferous sediments of the East Pacific Rise; (3) Mn/Fe values for different segments of the ocean.

tion of *Challenger* in 1873–1876 and interpreted as volcanic in origin, are considered undoubted evidence for the endogenic supply of Mn to the ocean. The metalliferous character of these sediments is revealed by recalculating metal contents to the abiogenic, carbonate- and silica-free matter. Inasmuch as these sediments are localized at the rise summit above the carbonate compensation depth, the percentage of the carbonate component commonly exceeds 70%. The Mn content may be five to six times higher (after recalculation) than in surrounding pelagic sediments. Nevertheless, Fe–Mn nodules that fix 25% of sedimentary Mn on average (*Metallogenic*…, 1998) occur at the surface of pelagic sediments. It should be noted that the nodules absorb metals from sediments in the process of diagenesis; i.e., they are sedimentary in origin (Arrhenius, 1963; Volkov and Shterenberg, 1981; Bazilevskaya, 1985). Thus, correct calculations of the general Mn balance in the ocean should take into account the sum of Mn contents in sediments and nodules, which averages 26% for ore fields adjacent to the EPR. In this case, it appears that the areas of metalliferous sediments, where nodules are practically missing, are substantially (fivefold) depleted in Mn as compared with surrounding areas and, hence, there is no reason to search for an additional hydrothermal Mn source. The metalliferous sediments in the EPR are located between ore fields rich in Fe–Mn nodules: the Peruvian in the east and the Penrhyn, South Pacific, and Menard in the west (Fig. 4).

Thus, no convincing evidence in favor of an endogenic source of Mn may be furnished.

Recently, the problem of oceanic metallogeny has been divided into two lines of research: deposition of sulfides and oxide Fe–Mn ore. Thereby, the two subjects of investigation become as if competitive. As a matter of fact, these two processes are incomparable in both scale and metallogenic nature. The Fe–Mn ore formation is unique because it proceeds only in seawater under oxidizing conditions and, thus, is widespread in the ocean. Metals accumulate in Fe–Mn sediments slowly in terms of geological time and under favorable environmental conditions.

The sulfide ore formation in the ocean is localized in limited areas, mostly in the rift zone of mid-ocean ridges. This process may develop both on land and in the ocean. In the ocean, it occurs in an aggressive to sulfide deposition medium during short geologic periods and does not disturb the equilibrium in seawater.

Precisely such is the relationship between the vigorous Fe–Mn ore deposition throughout the World Ocean and local manifestations of hydrothermal metalliferous activity against this background.

TERRIGENOUS SUPPLY OF MANGANESE

Vernadsky (1954) pointed out that igneous rocks contain negligible quantities of Mn as an isomorphic admixture and never as minerals of its own. At the same time, in vadose (biospheric) minerals, Mn occurs as the most stable MnO_2 phase. “This process proceeded during all the past geological epochs to result in concentration of Mn in the hydrosphere and the zone of weathering and in formation of pure Mn compounds unknown in such quantities and such speciation in deeper crustal layers.” In fact, this statement clearly defines the mechanism of Mn concentration in water basins, its speciation, and the duration of this process (“during all the past geological epochs”).

How did such enormous quantities of Mn fixed in ores accumulate at the oceanic bottom? What is the role of a terrigenous source in this process?

Answers to these questions are central in fundamental works by Strakhov (1960–1962, 1976, to name only a few), subjected until now to unfounded criticism by Lisitsyn (2005), who has developed a new scientific concept called "lithology and geochemistry of lithospheric plates." Lisitsyn writes: "Contrary to the opinion widespread among lithologists, the diagenetic transformation of sediments at the oceanic bottom is to a significant extent controlled by the tectonics of lithospheric plates." It should be noted that diagenesis is a geochemical process and has nothing to do with plate tectonics; these processes and subjects of research are quite different.

Let us dwell on some points discussed by Lisitsyn et al. (1985) in an attempt to disprove Strakhov's doctrine. The authors write: "Beyond the river–sea barrier, the main form (…90%…) of all elements in seawater is the dissolved species…. To prove this, long-term studies of oceanic water and suspended matter have been required. This discovery is of paramount importance for understanding Mn geochemistry."

First, this conclusion may be drawn without long-term efforts by dividing the total external discharge of 43000 km^3/yr (Alekin and Brazhnikova, 1964) by the volume of oceanic water (1370×10^6 km^3). It turns out that the annual supply of river water is 0.00003 of the bulk oceanic water volume. Correspondingly, the Mn content in oceanic water can change by the same value. Taking into account that the annual Mn influx into the ocean from rivers is estimated at 20.8×10^6 t (Lisitsyn et al., 1985), the annual growth of the Mn concentration in seawater should be 1.5×10^{-6} µg/l, i.e., negligible and not responsible for the Mn speciation in the ocean.

Second, only that part of Mn that passes through a membrane filter with a mesh size of 0.45–0.70 µm is considered as the "dissolved" species. The size of elementary particles of Fe hydroxides is measured in tens of angstroms (Van der Gissen, 1966) (1 µm = 10000 Å). The particles of Mn hydroxides likely have similar dimensions. Therefore, the filtration results may be accounted for only by the ability of Mn to aggregate in seawater (Kranck, 1973). By the way, these results may change depending on the filtration method applied; i.e., they are conditional.

Available thermodynamic calculations show that Mn in seawater occurs as the oxidized quadrivalent species (Murray and Brewer, 1977). Under such conditions, the solubility product of MnO_2 is extremely low and amounts to $K_{sp} = 10^{-56}$ (Charlot and Bezier, 1957). Therefore, all analytically determinable Mn in oxidized seawater is represented by suspended hydroxide particles <0.45 µm in size.

Filtration is mechanical separation of particles by their sizes rather than chemical dissolution; i.e., this is precisely the process that was characterized by Strakhov with a "special clearness" (as is mentioned in the reviewed work), namely, "…in the ocean, the geochemical process is primarily (90–93%) physical, or, still more exactly, mechanical, i.e., the process of mechanical scattering and fractionation of solid phases…." Nevertheless, the authors add further that Strakhov's concept "…includes significant errors" (Lisitsyn et al., 1985) and conclude finally: "Thus, in the ocean, the dissolved Mn species, which constitutes approximately 93% of its bulk content, becomes dominant in contrast to the suspended species in rivers. Already this fact demonstrates to what extent the views on Mn geochemistry are erroneous if they admit the crucial role of mechanical fractionation of river-transported suspensions because such suspensions contain less than 1/10 of the bulk Mn in seawater!"

As concerns the balance calculations cited in the reviewed work, they were critically considered by Volkov (1993). The list of remarks could be continued, but I would like to emphasize the main purpose of the reviewed work: to show the necessity of an additional, hydrothermal source of the Mn supplied to the ocean. In this regard, the authors contend that 90% of land-derived Mn is buried in zones of avalanche sedimentation. However, these zones are characterized by generation of hydrocarbons, and this is incompatibly with Mn accumulation. Actually, we deal here with diagenetic Mn mobilization, as was discussed in detail by Strakhov.

According to the above calculations, the annual Mn gain in oceanic water provided by stream transportation could be as high as 1.5×10^{-6} µg/l. Nevertheless, this seemingly very low value is quite consistent with rates of nodule and crust growth, which amount to a few millimeters per million years. The calculated annual increase in Mn content is also equal to millionths of a microgram. Although these calculations are approximate, nevertheless, they help us to understand that the terrigenous supply of Mn corresponds to the Mn accumulation rate characteristic of oceanic ore.

HISTORICAL ASPECTS OF OCEANIC ORE FORMATION

The objective assessment of the duration of oceanic ore formation is an important aspect of the problem. Adherents of the endogenic concept define the period just as "geologic" without specifying details and state further that "this" time is insufficient for accumulating the actual quantity of manganese in the ocean at the expense of terrigenous supply (Lisitsyn et al., 1985). The age of the modern ocean (170 Ma) or the Phanerozoic (500 Ma), which is mentioned in some publications, probably is assumed here. If this is the case, then this period is indeed insufficient.

The history of oceanic ore formation was considered thoroughly elsewhere (Bazilevskaya, 1997; Bazilevskaya and Pushcharovsky, 1999). Here, I would like to note briefly the following. According to the current ideas, the oceanic sedimentation and, correspondingly, the Fe–Mn ore formation developed over the past 2 Ga. Already 2 Ga ago, the total volume of seawater and its composition were close to the parameters of the present-day ocean (Galimov, 1988; Garrels and

Table 2. Areas of ore fields and provinces in the oceans taken into account, hypothetical Mn resources, and Mn/Fe ratio values calculated after (*Metallogenic* …, 1998)

Ocean	Atlantic Ocean	Indian Ocean		Pacific Ocean
		western part	eastern part	
Area, 10^3 km^2	207	226	756	7671
Mn/Fe	0.76	0.8	1.9	1.6
Mn resources, 10^6 t	–	206	2070	12014

Mackenzie, 1971). The oldest bedded sediments in Greenland with attributes typical of rocks deposited from aqueous solutions are dated back to 3850 Ma (Nutman et al., 1997). More and more evidence for the existence of an ancient ocean that existed on the Earth is furnished in recent publications.

This is primarily confirmed by giant chemogenic–sedimentary Mn deposits in South Africa, Brazil, and India formed in the Early Proterozoic within the shelf zone of an ancient supercontinent and revealing a specific zoning from carbonate to oxide ore (Schissel and Aro, 1992). This fact testifies to the existence of an oxygen atmosphere at that time.

The geological history of the Earth bears signs of both evolutionary (slow) and catastrophic events. During the past 170 Ma, the Earth developed in line with the evolutionary scenario, accompanied by the divergence of continental blocks and the gradual formation of the present-day appearance of our planet. If spreading in the Pacific proceeds uniformly with an average rate of 10 cm/yr (half-rate), the newly formed basaltic crust would move away from the spreading axis by 6500 km over 65 Ma. Correspondingly, the sedimentary sequence with the Fe–Mn nodules resting upon it would "ride off" by a similar distance. It is known that the continental margins are surrounded by a zone of high-rate accumulation of terrigenous sediments. The reducing environment within these sequences is incompatible with retention of oxidized deposits therein. Under such conditions, Mn dissolves and migrates into seawater, where it is regenerated and deposited under favorable conditions in abyssal basins. In contrast to Fe, Mn cannot be consumed along with subducted plates; its cycle in the ocean is closed.

The catastrophic scenario always results, irrespective of its causes, in the activation of endogenic tectonomagmatic processes with an increase in temperature and a decrease in oxygen content in seawater and, hence, in dissolution of oceanic Fe–Mn sediments. The altered seawater becomes a repository for Mn, where it is retained in the dissolved state up to normalizing of environmental conditions and afterwards regenerated as hydroxide species. The buffer properties of seawater promote a relatively rapid recovery of its composition. Similar events are reflected in the geological record. For instance, evidence for the fall of a giant asteroid dated back to 251.4 Ma, when 70% of vertebrate organisms on land and 90% of marine organisms became extinct, has been found in rocks of China, Japan, and Hungary ("Noble…," 2002). The epicenter of the catastrophe was probably located in the ocean and it was accompanied by giant volcanic eruptions. It should be noted that the initiation of the breakup of the ancient continent of Gondwana is dated back to precisely that time.

Thus, the problem of the sources that supply Mn into the ocean cannot be solved without answering many related questions. At the same time, making use of the principle of actualism, the Mn phenomenon allows us move forward in the understanding of intricate natural enigmas and their geohistorical consequences.

For example, the World Ocean is characterized by pronounced asymmetry in accumulation of Mn ore. As follows from the map (Fig. 4), most of the highly productive fields with high-grade Mn and base-metal ores are located in the Pacific and the eastern Indian oceans. With regard to Mn accumulation, the Indian Ocean is divided by the Mid-Indian Ridge into eastern and western segments, substantially different from each other in Mn deposits. The total areas of the largest ore fields and provinces (larger than 10^4 km^2) in different oceans, average Mn/Fe ratios in ore, and forecasting estimates of Mn reserves in ore fields are summarized in Table 2. Calculations are based on the data from (*Metallogenic*…, 1998).

It should be noted that hypothetical resources for the Atlantic Ocean have not been calculated because only one, the North American, ore field, with low-grade ore, is known in this basin. Other provinces (Brazil, Dampier, and Cape) are smaller and still insufficiently studied, although local occurrences of high-grade nodules cannot be ruled out.

As follows from Table 2, the Mn accumulation in oceanic Fe–Mn nodules and crusts points to a pronounced global asymmetry in ore distribution between the eastern and western hemispheres. In the Indian–Pacific segment, these deposits occupy an area 20 times larger in comparison with that in the Indian–Atlantic segment. Moreover, the ores in the Indian–Pacific segment are twice as rich in Mn; i.e., the Mn resources are 40 times greater.

The proposed concept explains these discrepancies by the different geological history of the oceans. The Atlantic Ocean and the western part of the Indian

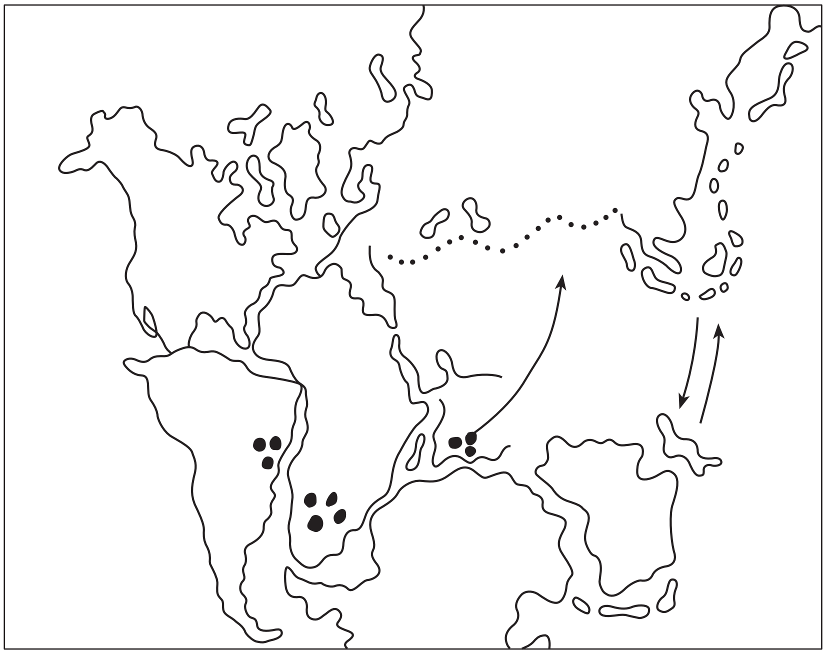

Fig. 5. Paleoreconstruction of continental blocks in the course of the Gondwana breakup 200 Ma. Dots are Paleoproterozoic Mn ore occurrences; arrows indicate the directions of continental block motion, simplified after Jankins (1993/1994).

Ocean are young basins opened after the Gondwana breakup (250 Ma) followed by the continental drift (Fig. 5). Correspondingly, the Fe–Mn ore deposition is also young there.

The western segment of the ancient Pacific Ocean was cut off from its main domain by the north-northeastern drift of Australia to form the present-day eastern part of the Indian Ocean, which inherited ancient Mn accumulations.

Hence, the multifold excess of the Mn grade in oceanic ore of the Eastern Hemisphere is explained by its much older age as compared with the Western Hemisphere. These relationships confirm the older age of the Pacific Ocean and, probably, its primary origin (Pushcharovsky, 1997).

The geochemical properties of Mn allow us to suggest that the gain of this element in oceans was a primordial phenomenon on the Earth. Manganese does not bear chronological marks; therefore, it is not feasible to detect ancient portions of Mn contained in present-day Fe–Mn ore. It is also impossible to specify the sources that supplied Mn to the oceanic bottom because Mn is contained in seawater as free hydroxides. This problem can be settled only by comprehensive analysis of many factors, most of which are interdisciplinary with respect to different sciences and different branches of geology.

In conclusion, it should be emphasized that insights into the problem of sources that supply metals to oceanic Fe–Mn nodules and crusts promote progress in the general theory of oceanic ore formation.

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REFERENCES

1. O. A. Alekin and L. V. Brazhnikova, *External Drainage of Dissolved Substances from the USSR Territory* (Nauka, Moscow, 1964) [in Russian].
2. S. I. Andreev, L. I. Anikeeva, A. N. Vishnevskii, et al., “Mineral Resources of the World Ocean, Their Potential and Outlook for Development,” in *Geology and Mineral Resources of the World Ocean* (VNIIOkeanologiya, St. Petersburg, 1995), pp. 141–157 [in Russian].
3. G. Arrhenius, “Pelagic Sediments,” in *The Sea* (Interscience, New York, 1963), Vol. 3, pp. 655–727.
4. G. N. Baturin, *Geochemistry of Oceanic Ferromanganese Nodules* (Nauka, Moscow, 1986) [in Russian].
5. E. S. Bazilevskaya, *Chemical and Mineralogical Study of Manganese Ores* (Nauka, Moscow, 1976) [in Russian].
6. E. S. Bazilevskaya, “Sources of Manganese in the Ocean,” Priroda, No. 3, 25–29 (1980).
7. E. S. Bazilevskaya, “Ocean Floor Metallogeny from Deep-Sea Drilling Data,” in *Ocean Floor Geology from Deep-Sea Drilling Data* (Nauka, Moscow, 1984), pp. 85–91 [in Russian].

8. E. S. Bazilevskaya, "Contribution of Diagenesis to Ferromanganese Nodule Formation in the Clarion–Clipperton Ore Province," Tikhookean. Geol. **4** (6), 60–70 (1985).
9. E. S. Bazilevskaya, "Asymmetry of Oceanic Ore Formation in Terms of Tectonics," in *Tectonic and Geodynamic Phenomena* (Nauka, Moscow, 1997), pp. 70–84 [in Russian].
10. E. S. Bazilevskaya, "Phenomenon of Manganese on the Earth," Priroda, No. 5, 35–42 (2003).
11. E. S. Bazilevskaya, "New Data on the Fe–Mn Deposition in the Markov Depression (Sierra Leone, Central Atlantic)," Dokl. Akad. Nauk **397** (6), 791–796 (2004) [Dokl. Earth Sci. **397A** (6), 788 (2004)].
12. E. S. Bazilevskaya and Yu. M. Pushcharovsky, "Oceanic Manganese Accumulation in the Light of Historical Tectonics," Ross. Zh. Nauk Zemle **1** (3), 1–20 (1999).
13. E. S. Bazilevskaya and S. G. Skolotnev, "Tectonic Settings and Fe–Mn Ore Formation in the Central and South Atlantic," Geol. Rudn. Mestorozhd. **43** (4), 308–323 (2001) [Geol. Ore Deposits **43** (4), 274–287 (2001)].
14. Yu. A. Bogdanov, E. G. Gurvich, O. Yu. Bogdanova, et al., "Low-Temperature Deposits in the Logachev Hydrothermal Field (Mid-Atlantic Ridge)," Geol. Rudn. Mestorozhd. **46** (4), 313–331 (2004) [Geol. Ore Deposits **46** (4), (2004)].
15. G. W. Bolger, P. R. Betzier, and V. V. Gordeev, "Hydrothermally-Derived Manganese Suspended over the Galapagos Spreading Centre," Deep-Sea Res. **25** (8), 721–733 (1978).
16. G. Yu. Butuzova, *Hydrothermal-Sedimentary Ore Formation in the Red Sea Rift Zone* (GEOS, Moscow, 1998) [in Russian].
17. G. Charlot and D. Bezier, *Quantitative Inorganic Analysis* (Wiley, New York, 1957).
18. E. M. Emel'yanov, *Barrier Zones in the Ocean: Sedimentation, Ore Deposition, and Geoecology* (Yantarnyi Skaz, Kaliningrad, 1998) [in Russian].
19. E. M. Galimov, "Origin and Evolution of the Ocean As Deduced from the $^{18}O/^{16}O$ Variation in the Earth's Sedimentary Shell through Geological Time," Dokl. Akad. Nauk SSSR **299** (4), 966–981 (1988).
20. R. Garrels and F. Mackenzie, *Evolution of Sedimentary Rocks* (Norton, New York, 1971; Mir, Moscow, 1974).
21. V. V. Gordeev, L. L. Demina, and A. M. Konkin, "Hydrothermal Iron and Manganese in Abyssal Waters of the Pacific Ocean (Galapagos Active Zone, Hess Deep)," in *Metalliferous Sediments of the Pacific Ocean* (Nauka, Moscow, 1979), pp. 224–236 [in Russian].
22. E. G. Gurvich, *Metalliferous Sediments of the World Ocean* (Nauchnyi Mir, Moscow, 1998) [in Russian].
23. R. Hekinian, B. R. Rosendahl, D. S. Cronan, et al., "Hydrothermal Deposits and Associated Basement Rocks from the Galapagos Spreading Centre," Oceanological Acta **1** (4), 473–482 (1978).
24. R. Horn, *Marine Chemistry (Water Structure and Hydrosphere Chemistry)* (Mir, Moscow, 1972).
25. S. E. Humphruz, P. M. Herzig, D. J. Miller, et al., "The Internal Structure of an Active Sea-Floor Massive Sulphide Deposit," Nature **377** (6551), 713–717 (1995).
26. *Hydrothermal Sulphide Ores and Metalliferous Sediments in the Ocean* (Nedra, St. Petersburg, 1992) [in Russian].
27. H. C. Jankins, "Early History of the Oceans," Oceanus **36** (4), 49–50 (1993/1994).
28. K. Kranck, "Flocculation of Suspended Sediment in the Sea," Nature **246**, 348–350 (1973).
29. A. P. Lisitsyn, "Geology of the World Ocean in the Third Millennium—New Approaches, Achievements, and Outlooks," in *New Ideas in Oceanology* (Nauka, Moscow, 2005), Vol. 2, pp. 7–66 [in Russian].
30. A. P. Lisitsyn, V. V. Gordeev, L. L. Demina, and V. N. Lukashin, "Manganese Geochemistry in the Ocean," Izv. Akad. Nauk SSSR, Ser. Geol., No. 3, 3–29 (1985).
31. *Metallogenic Map of the World Ocean. Explanatory Notes*, Ed. by S. I. Andreev (VNIIOkeangeologiya, St. Petersburg, 1998) [in Russian].
32. J. W. Murray and P. G. Brewer, "Mechanisms of Removal of Manganese, Iron and Other Trace Metals from Sea Water," in *Marine Manganese Deposits* (Elsevier, Amsterdam, 1977), pp. 291–325.
33. "Noble Gases Testify to an Ancient Catastrophe," Priroda, No. 5, 85 (2002).
34. A. P. Nutman, S. J. Mojzsis, and C. R. L. Friend, "Recognition of 3850 Ma Water-Lain Sediments in West Greenland and Their Significance for the Early Archean Earth," Geochim. Cosmochim. Acta **61** (12), 2475–2484 (1997).
35. A. I. Perel'man, *Geochemistry of Epigenetic Processes* (Nedra, Moscow, 1968) [in Russian].
36. Yu. M. Pushcharovsky, "Major Tectonic Asymmetry of the Earth: Pacific and Indo–Atlantic Segments and Their Relations," in *Tectonic and Geodynamic Phenomena* (Nauka, Moscow, 1997), pp. 8–24 [in Russian].
37. D. Schissel and Ph. Aro, "The Major Early Proterozoic Sedimentary Iron and Manganese Deposits and Their Tectonic Setting," Econ. Geol. **97** (5), 1367–1374 (1992).
38. N. S. Skornyakova and I. O. Murdmaa, "Ferromanganese Nodules and Crusts in the Atlantic Ocean," Litol. Polezn. Iskop. **30** (4), 339–361 (1995).
39. N. M. Strakhov, *Theoretical Principles of Lithogenesis* (Acad. Sci. USSR, Moscow, 1960–1962), Vols. 1–3 [in Russian].
40. N. M. Strakhov, *Geochemistry of Modern Oceanic Lithogenesis* (Nauka, Moscow, 1976) [in Russian].
41. A. A. Van der Gissen, "The Structure of Iron (III) Oxide-Hydrate Gels," J. Inorg. Nucl. Chem. **28**, 2155–2159 (1966).
42. V. I. Vernadsky, *Selected Works* (Nauka, Moscow, 1954), Vol. 1 [in Russian].
43. I. I. Volkov, "Sources of Metals for Modern Ferromanganese Ore Deposition in Oceanic Pelagic Zones," Litol. Polezn. Iskop. **28** (3), 17–40 (1993).
44. I. I. Volkov and L. E. Shterenberg, "Main Types of Ferromanganese Ores in Modern Water Basins," Litol. Polezn. Iskop. **16** (5), 4–26 (1981).
45. D. L. Williams, K. Green, T. H. Van Andel, et al., "The Hydrothermal Mounds of the Galapagos Rift Observation with DSRV Alvin and Detailed Heat Flow Studies," J. Geophys. Res. **84** (1313), 7467–7482 (1979).