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The Role of Dissimilatory Fe(III)-Reducing Bacteria in Transformation of Iron Minerals

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Abstract—The possible role of bacteria in the formation and transformation of iron minerals is considered on the basis of the Recent biogeochemical cycle of iron. Dissimilatory Fe(III)-reducing bacteria are the main agents in the reductive part of the cycle. These bacteria are capable of reducing iron oxides and hydroxides to magnetite and siderite. A high degree of crystallinity of the iron oxides is the most important factor preventing bacterial transformation of minerals. The main component that links the oxidative and reductive parts of the cycle is ferrihydrite (a weakly crystalline mineral). Because of its large surface area, it is the optimal acceptor for bacterial iron reduction.

Key words: Dissimilatory Fe(III)-reducing bacteria, ferrihydrite, magnetite, siderite.

INTRODUCTION

Interpretations of the events of the Early Proterozoic should be supported by microbiological data, because bacteria were the main (if not the only) active agents in the Proterozoic biosphere. Such a study usually compares the products of metabolism of recent microorganisms with Precambrian minerals and rocks in the framework of a uniform approach (in this case, uniform bacterial paleoecology, which allows reconstruction of processes that took place in the past). Carrying out a purely paleontological study is an independent method that reveals the presence of fossil microorganisms preserved in various ways in ancient rocks. The presence of iron bacteria (participating in the iron cycle) in the Proterozoic (2 Ga ago) was first established by Barghoorn and Tyler (1965) in the iron formations of Lake Superior. The accumulation of thick sedimentary series of iron rocks that occurred in the Proterozoic and ceased in the Phanerozoic was one of the most important events in the geological history of the Earth. The cessation of this accumulation in the Phanerozoic restricts the use of the comparative method. The reconstruction of the possible role of microorganisms in the Proterozoic environment, which was different from the Recent, can be based on microbiological data. The possible participation of microorganisms in the iron cycle, either by direct precipitation of Fe(III) oxides by iron bacteria or indirect production of O_2 by cyanobacteria with subsequent chemogenic precipitation, has been suggested for some time (Claud, 1980). However, the formation of magnetite, which is the major ore mineral of iron-rich quartzites, remains an unresolved problem. At present, microbiologists have progressed considerably in their understanding of the processes of the formation of magnetite by microorganisms. Because hydrothermal processes are at present considered to be the most likely source of iron in Precambrian beds, magnetite-forming thermophilic microorganisms are particularly important in this respect.

THE BACTERIAL CYCLE OF IRON

Of all the metals involved in biological processes, iron stands out because of the diversity of the physiological and biochemical functions performed by organisms using it. Supposedly, the extremely wide usage of iron by organisms is not due only to its chemical characteristics, but also largely to its wide distribution and availability on Earth (Ehrenreich and Widdel, 1994).

The bacterial cycle of iron is connected to the cycles of C, O, P, and S through minerals that are produced by the metabolism of microorganisms (Fig. 1). A general scheme of the bacterial processes involved in the cycle of iron at neutral pH is shown in Fig. 2, where the stable forms of iron minerals formed both in reactions with bacteria and abiogenically are shown in frames. In natural systems in a neutral and weakly alkaline environment, such as marine sediments and redox zones of chemocline in stratified basins, the iron cycle is combined with the sulfur cycle through the formation of stable sulfides. It is also known that siderite ($FeCO_3$) and vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) are products of bacterial reduction of iron oxides (Fredrikson *et al.*, 1998). The reductive and oxidative parts of the bacterial iron cycle are closely related (Fig. 2). To understand the influence

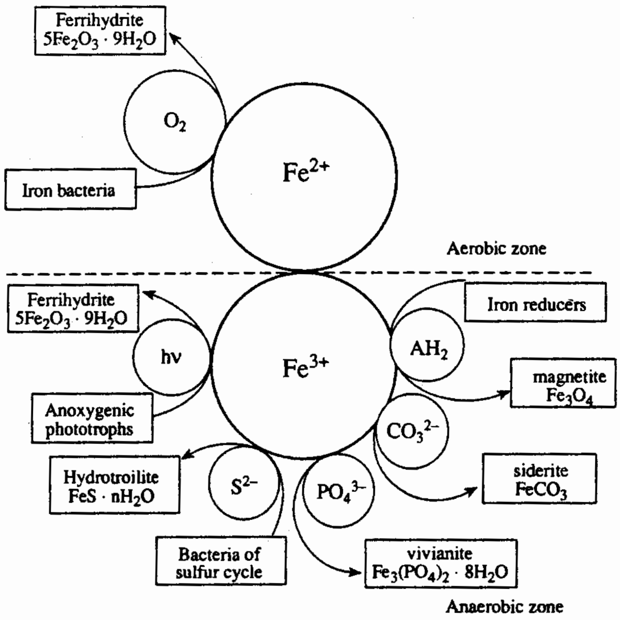

Fig. 1. Relationships of the bacterial cycle with the C, O, P, and S cycles.

of biogeochemical factors on the transformation of iron compounds in the reducing environment, it is necessary to take into account the processes occurring in the oxidizing zone.

BACTERIAL OXIDATION OF IRON

Bacterial oxidation of iron has been known since the mid-19th century, and the formation of sedimentary ores of ferric iron was one of the first problems studied by geological microbiology (see Zavarzin, 1972). The sedimentary environment of thin-layered deposits of iron and manganese in lake sediments was described in detail by Perfil'ev and Gabe (1964). The physiology and ecology of iron bacteria are poorly studied compared to other prokaryotic organisms. This is because the majority of neutrophilic iron-oxidizing bacteria cannot be presently cultivated in the laboratory, and their classification is still based on morphological criteria (Kholodnyi, 1953). These are mostly microaerophils, which develop at very low concentrations of O_2, although some species also grow at atmospheric concentrations of oxygen. Neutrophilic iron bacteria accumulate iron hydroxides produced by two reactions: (1) sorption of colloid iron hydroxides on acidic mucopolysaccharides (Dubinina, 1977) and (2) oxidation of iron by a non-specific peroxide mechanism (Balashova, 1990). Iron deposition of this type has been documented in the sediments of Lake Superior with a characteristic representative of the genus *Eoastrion*. Well-studied acidophilic iron bacteria (e.g., *Leptospirillum ferrooxidans* and *Acidithiobacillus ferrooxidans*) and thermophilic bacteria (e.g., *Acidianus* and *Ferroplasma*) develop in an environment of stable Fe^{2+}

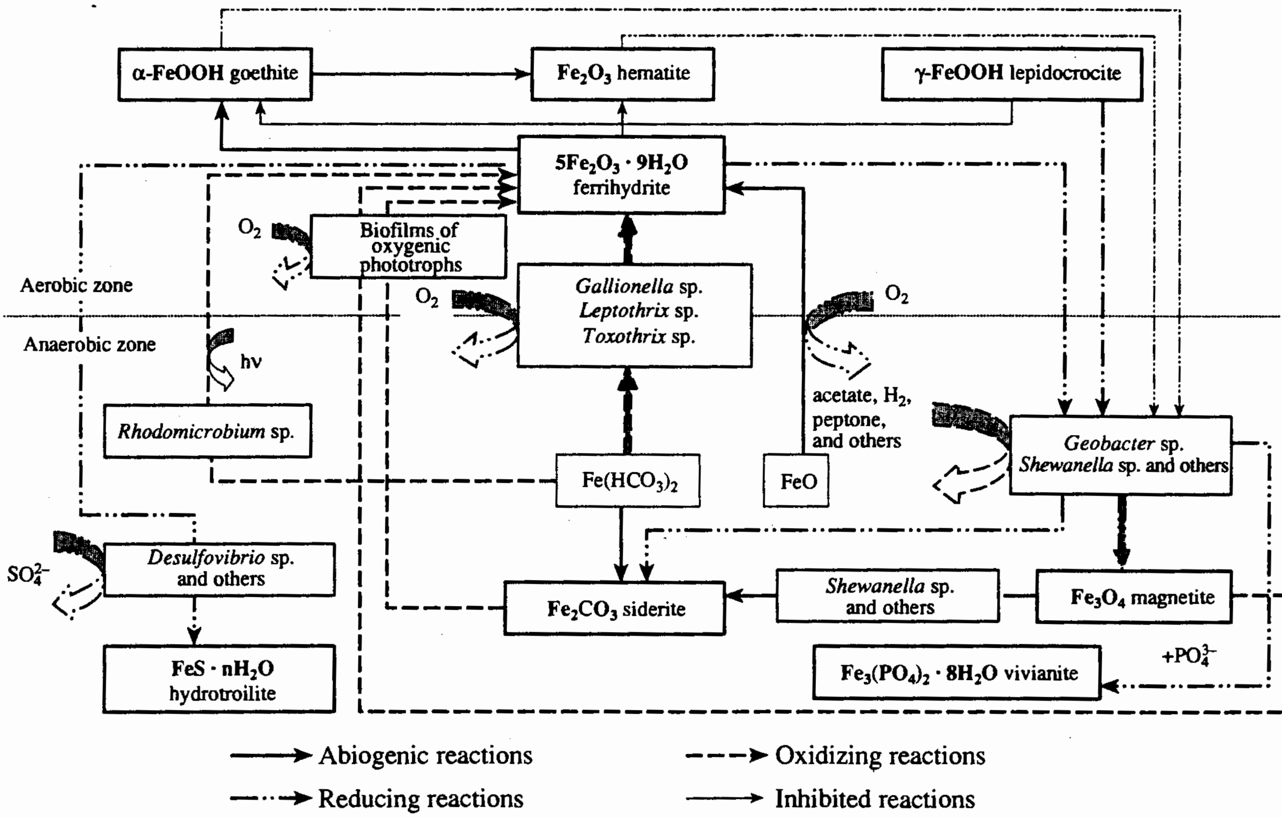

Fig. 2. Scheme of biogeochemical iron cycle at neutral pH.

mainly by the leaching of sulfides (Karavaiko *et al.*, 1972) with subsequent precipitation of limonite in areas of mixing of acidic and neutral waters. The biogenic oxidation of iron is almost entirely included in the field of stability of hematite in the Eh–pH coordinates (Fig. 3). In their geochemical activity, microorganisms do not contradict the laws of thermodynamics. They mainly affect the kinetics of the process (Zavarzin, 1972) and develop in the area of stability of the product of the oxidative-reductive reaction they perform. Of all the groups of iron-oxidizing microorganisms, only acidophilic bacteria play an active role in the leaching of rocks. The metabolism of other groups of iron-oxidizing bacteria leads to the deposition of iron hydroxides, thus supporting the position of these bacteria in the diagram (Fig. 3).

Although iron bacteria were known as early as the mid-19th century, detailed study of the minerals they produce has been made only relatively recently. Chukhrov *et al.* (1973) studied sediments formed by *Leptothrix ochracea* in the flooded plain of the Yakhroma River and described a new weakly crystalline mineral—ferrihydrite. The crystalline structure of ferrihydrite had been discovered earlier by Towe and Bradley (1967). However, Chukhrov was the first to conduct a detailed study of its properties and structure and described it as a new mineral. The ability of ferrihydrite to transform into hematite or goethite is its most important feature. Chukhrov considered this mineral to be the key form of iron in its transformation in the zone of hypergenesis (*Supergene*..., [1975]). In nature, the formation of ferrihydrite can occur abiogenically in the presence of organic matter, phosphates, or silicates. However, ferrihydrite most often has a biogenic origin (Vodyanitskii and Dobrovol'skii, 1998). The activity of iron bacteria excludes the formation of goethite, lepidocrocite, or delta oxides because the process of oxidation occurs too quickly, which enables only the appearance of the water oxide of iron with the least developed structure (ferrihydrite). The ability of ferrihydrite to transform into hematite leads to rapid solidification of the sediments of iron bacteria, with a loss of the characteristic bacterial structures. Therefore, even recently formed bacterial sediments very quickly lose the features that indicate their microbial origin. Their genesis is, accordingly, difficult to identify.

Formation of ferrihydrite has been recently shown to occur in anaerobic conditions due to oxidation of ferrous iron by anoxygenic phototrophs (Widdel *et al.*, 1993; Ehrenreich and Widdel, 1994) and nitrate reducers (Straub *et al.*, 1996). This discovery suggests the existence of a closed anaerobic cycle of iron, which may have been very important in the Precambrian, given that reducing environments were dominant on Earth at that time.

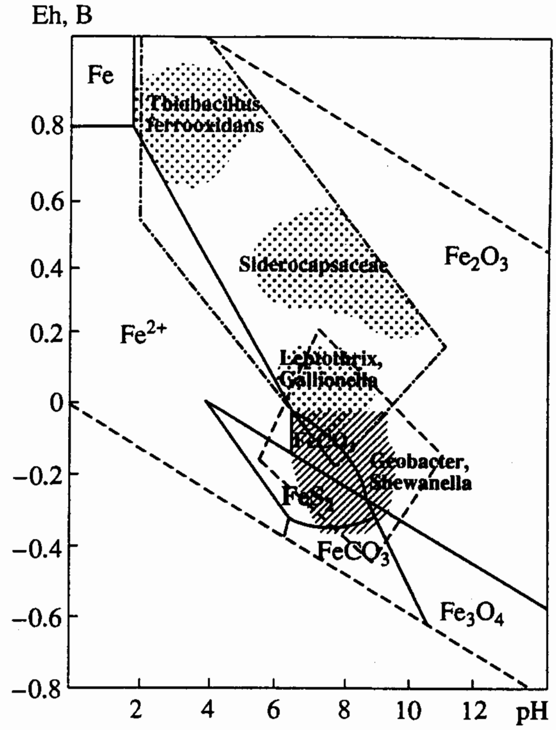

Fig. 3. Areas of stability of iron compounds in the area of development of major groups of iron-oxidizing and iron-reducing bacteria in Eh–pH coordinates.

BACTERIAL REDUCTION OF IRON

The reduction of iron by bacteria began to attract the attention of scientists much later than the process of biotic oxidation. The ability of microorganisms (mainly bacteria and, to a lesser degree, fungi) to reduce certain metals was established quite early.

The possibility of bacterial reduction of ferric iron in organic-rich conditions (sugars and peptides) was shown as early as 1927 by Halvorson and Starki (see Gabe *et al.*, 1964). Reduction of metals is often necessary to remove the toxic products of metabolism, e.g., hydrogen or hydrogen sulfide. The formation of poorly soluble sulfides by bacteria in the sulfur cycle is a typical example of such reactions.

Up to the end of the 1970s, the problem of the anaerobic cycle of iron had been addressed by soil microbiology and was concerned primarily with reduction of iron in soil and mud by heterotrophic organisms (Duda and Kalakutskii, 1961).

Blakemore (1975) discovered magnetotactic bacteria, which could be orientated in the same direction. It was convincingly shown that these bacteria are oriented in accordance with the Earth's magnetic field. This discovery induced further studies of this group of organisms by not only microbiologists, but also physicists, geologists, chemists, and engineers (Spring and Schleifer, 1995). The presence of magnetite crystals (Fe_3O_4) or greigite (Fe_3S_4) arranged in chains and enclosed in membranes (Frankel and Blakemore, 1980), which were named magnetosomes, produced an unusual spatial orientation for these microorganisms. The morphology of the crystals proved to be very diverse (from cubical and octahedral to variously shaped hexagonal prisms).

Magnetotactic bacteria have been discovered in marine sediments, soils, and stratified basins and have never been found in the oxygen-saturated, acidic, or thermal habitats (Spring and Schleifer, 1995). These are microaerophilic bacteria requiring a very low level of oxygen (and some bacteria are known to survive in completely anaerobic environments). Supposedly, these organisms need magnetosomes for correct spatial orientation in the narrow zone of the appropriate physicochemical environment (Bazylinsky and Moskowitz, 1998). Their narrow ecological specialization and the possibility of identifying magnetite and greigite of magnetotactic origin due to the high specificity of magnetosomes allow reconstructions of physical, chemical, paleoclimatic, and paleomagnetic conditions for various sedimentary environments.

Magnetotactic bacteria do not use iron in catabolic (exergonic) reactions. However, they affect the primary magnetism of sediments by intracellular formation of magnetite and greigite. Blakemore *et al.* (1985) and Frankel (1986) have suggested that magnetotactic bacteria could play a significant part in the accumulation of magnetite in Precambrian banded iron formations (BIFs). This hypothesis is problematic in various ways. First, despite the recognized role of magnetotactic bacteria in the primary magnetism of sediments, the amount of magnetotactic magnetite accumulated in the deposits is tiny. Second, magnetotactic bacteria are gradient organisms occupying a narrow ecological niche with specific physicochemical conditions that hardly agree with the scale of deposition of BIFs. Finally, the magnetotactic bacteria that are known at present have a relatively narrow phylogenetic affinity. Supposedly, they evolved from several ancestors, which may have included phototrophic, sulfate-reducing, or chemolithotrophic bacteria (Spring and Schleifer, 1995). At the same time, the most ancient representatives of the Bacteria and Archea domains are thermophilic prokaryotes, while no magnetotactic bacteria have been found in thermal environments.

The problem of whether microorganisms can receive energy through iron reduction remained unsolved for a long time. Balashova and Zavarzin (1980) showed the possibility of catabolic reduction of iron by lithotrophs using molecular hydrogen as electron donor. Soon after, a physiological group of dissimilatory iron reducers was discovered. Lovley and Phillips (1986) showed the ability of microorganisms to reduce iron accompanied by oxidation of acetate, butyrate, propionate, ethanol, and methanol, which are the typical metabolic products of heterotrophic microorganisms, i.e., they proved the possibility of complete oxidation of organic matter to carbon dioxide during iron reduction. The credit for the discovery of magnetite-forming pathways in the biogenic cycle of iron goes to Lovley. In the anaerobic community, hydrogen and acetate are major products of primary anaerobes. The complete decomposition of organic matter depends on the removal of these products by secondary anaerobes using external electron acceptors. While hydrogen is used by many secondary anaerobes, acetate is available to fewer of them, and accumulation of acetate is quite possible. Lovley's studies showed that iron reduction is an energetically favorable reaction for acetate oxidation. *Shewanella putrefaciens* is the first bacterium for which the ability of dissimilatory manganese- and iron reduction was shown (Myers and Nealson, 1988). Lovley *et al.* (1993) isolated and described strains of a new microorganism, *Geobacter metallireducens*, capable of catabolic reduction of iron oxides. At present, more than 20 species capable of this are known. Most of them are Proteobacteria (Slobodkin *et al.*, 1999).

The majority of currently known iron reducers are neutrophils with optimum growth at pH = 6.5–7.5. They include strict anaerobes and microaerophils (Slobodkin *et al.*, 1999). It is essential that the range of stability of magnetite (the final reduced product in Eh–pH coordinates) occur at high pH and low Eh values (see Fig. 3), i.e., iron reducers develop in the range of stability of the products of oxidizing-reducing reactions. Apart from iron, most iron reducers are able to reduce manganese, and many iron bacteria are capable of oxidizing it. The geochemistries of iron and manganese in the sedimentary process are closely connected. The isolation of these two elements occurs in the environment of a dominating sulfur cycle: iron is bound in sulfides, while manganese does not form insoluble sulfides.

To understand the biogeochemical function of iron reducers, it is important to show which iron oxides and hydroxides are most intensely involved in processes of anaerobic iron reduction. The most widespread minerals in the zone of hypergenesis include hematite (Fe_2O_3), goethite (α-FeOOH), akagenite (β-FeOOH), lepidocrocite (γ-FeOOH), ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$), maghemite (γ-Fe_2O_3), and magnetite (Fe_3O_4). Of these, hematite and goethite are the most thermodynamically stable in aerobic conditions and, therefore, the most widespread in soils and sediments as final products of transformations. It is currently known that goethite can precipitate directly from solution, whereas hematite requires the presence of ferrihydrite as a predecessor. In fact, hematite is formed by the dehydration of ferrihydrite. Lepidocrocite is less widespread in nature than goethite, but its formation is possible by the oxidation of ferrous iron. Thus, the presence of this mineral in soil indicates oxygen deficiency. The presence of carbonates in the medium precludes the formation of lepidocrocite. In this case, the oxidation of the ferrous iron leads to the formation of goethite. The formation of ferrihydrite, as mentioned above, occurs by rapid oxidation or in the presence of compounds prohibiting crystallization processes (organic matter, phosphate, or silica). Apart from spontaneous transformation into hematite, slow transformation by dehydration of ferrihydrite into goethite is possible. This transformation can be considerably accelerated in the presence of organic reducing compounds, e.g., cysteine. In fact, ferrihydrite is a protoxide of iron, which is why it is so widespread. The formation of maghemite is possible either by the oxidation of magnetite or, more likely, by transformation of other oxides, e.g., goethite. In this process, the presence of organic matter is a necessary condition. Hence, maghemite is most widespread in tropical soils (Schwertmann and Cornell, 1991; Vodyanitskii and Dobrovol'skii, 1998).

Ottow (1969) showed that the rate of bacterial iron reduction by organotrophs decreases with the growth of crystallinity of the mineral phase in the line $Fe(OH)_3$ > lepidocrocite > goethite > hematite. These results were completely supported for dissimilatory iron reducers (Lovley, 1987). The large rate of reduction of the least ordered iron minerals is explained by their greater solubility, developed surface, and thermodynamic instability. Arnold *et al.* (1988) have shown that complexing agents, such as chelates or citrates of Fe (III), considerably increase the rate of iron reduction. Another factor that affects the ability of iron reducers to reduce various oxides and hydroxides of iron is the availability of electron donors (Lovley and Phillips, 1986).

Despite the fact that iron reducers, in contrast to sulfate reducers and methanogens, have to reduce iron from poorly soluble oxides and hydroxides, they successfully compete for organic substrates. The level of the partial pressure of hydrogen in the sediment sufficient to develop iron reducers is 3×10^{-7} atm, whereas, for sulfate reducers and methanogens, this value should be at least 2×10^{-6} and 8×10^{-6} atm, respectively. The minimum concentration of acetate required for the development of iron-reducers, sulfate-reducers, and methanogens is 0.5, 2, and 5 mM, respectively (Lovley, 1987), i.e., iron reducers are capable of iron reduction under conditions where sulfido- and methanogenesis would be completely inhibited even if the necessary electron acceptors were present (Lovley and Phillips, 1986). Iron reduction is one of the most beneficial exchange processes for anaerobic microorganisms. Supposedly, it is the availability of iron in various forms rather than the competition with other anaerobic groups for substrates that has constituted a major factor regulating iron reduction in Recent sediments. At the same time, oxidation of iron leading to the formation of the most beneficial electron acceptor (ferrihydrite) is performed by iron bacteria in environments of minimal available oxygen and neutral pH. Hence, ferryhidrite is the key compound through which the connection between the aerobic and anaerobic parts of the bacterial cycle of iron is performed (see Fig. 2).

The most typical reduced iron compounds occurring in the zone of hypergenesis are various iron sulfides, siderite, magnetite, and vivianite. The formation of sulfides is possible through indirect biogenic reduction during the metabolic activity of microorganisms of the sulfur cycle. The rest of the above minerals are formed through the metabolism of iron reducers. Formation of magnetite as a final reduction phase was discovered for the first time by Lovley (1987). Magnetite formed by iron reducers through the reduction of amorphous iron hydroxide had oval or rounded crystals from 10 to 50 nm in diameter, with 90% corresponding to the superparamagnetic (<30 nm) state and the remaining 10% to the monodomain (>30 nm) state (Lovley, 1990). Despite the large amount of monodomain magnetite, the microorganisms were able to produce far more of it than the magnetotactic bacteria. It was shown that *G. metallireducens* produces 5000 times more magnetite than the equivalent biomass of magnetotactic bacteria (Lovley, 1990). This cast doubts on the genesis of monodomain magnetite that occurs in freshwater and marine sediments and in soils and has previously been identified as magnetotactic. In most sediments, magnetite of a typical size occurs in the anaerobic zone, i.e., under conditions that are unfavorable for the ecology of magnetotactic bacteria, which require oxygen for their metabolism. The sediments of Lake Geneva were found to contain superparamagnetic magnetite typical of dissimilatory iron reducers (Gibbs-Eggar *et al.*, 1999). Mössbauer studies of biogenic magnetite formed by thermophilic iron reducers showed that it largely represents thinly dispersed, incompletely formed magnetite. Further aging of the sediment was accompanied by processes of biogenic recrystallization of magnetite leading to the regulation of its structure and increased size of its crystals (Zavarzina, 2001; Chistyakova *et al.*, 2001). Thus, it is very difficult to recognize the biogenic origin of magnetite in ancient sedimentary beds and metamorphic rocks morphologically.

Magnetite is unstable in oxygenated conditions and can transform into hematite or maghemite, although this process is relatively slow. The pseudomorphs of hematite after magnetite (so-called martite structures) are typical of the zone of hypergenesis. The possibility of biogenic oxidation of magnetite into hematite was shown by Brown *et al.* (1997). A community of microorganisms transformed 11% of iron from magnetite into hematite in three weeks. Because two-thirds of iron atoms in magnetite are in a three-valence state, another possible process occurring in Recent sediments and leading to the loss of biogenic material is its further reduction by iron reducers. The possibility of microbial reduction of magnetite was first demonstrated by the example of *S. putrefaciens* (Kostka and Nelson, 1995). Magnetite in direct contact with a bacterium was rapidly reduced. The formation of mineral phases in the process of magnetite reduction was determined by physicochemical conditions, i.e., the concentration of bicarbonate and the presence of phosphorus or organic compounds (Dong *et al.*, 2000). Thus, both the reduction of magnetite by iron reducers resulting in the formation of siderite or vivianite, depending on the conditions, and relatively rapid bacterial oxidation of magnetite to hematite are possible in natural sediments. When the medium for *G. metallireducens* contained the increased concentration of bicarbonate, siderite was formed in addition to magnetite (Lovley, 1990). A number of subsequent studies have shown the decisive influence of physicochemical conditions on the rate and degree of reduction of various oxides and hydroxides of iron and accompanying mineral phases (Roden and Edmonds, 1997; Fredrikson *et al.*, 1998).

CONCLUSIONS

The biogenic cycle of iron performed by microorganisms of various physiological and phylogenetic groups has been described microbiologically. This cycle is most clearly defined in the conditions of nearly neutral pH and normal temperatures that dominate on the Earth's surface. Iron bacteria, which use iron in catabolic reactions and release weakly crystalline ferrihydrite, are the main agents in the oxidative part of the cycle. Dissimilatory iron reducers, which reduce various oxides and hydroxides of iron to magnetite, siderite, vivianite, or oxides of iron, depending on the physicochemical conditions, are the main agents in the reductive part of the cycle. Ferrihydrite is not only the key compound of the biogenic cycle, because it is the most readily available acceptor for bacterial reduction, it also plays the main part in the formation of the most important iron oxides in the zone of hypergenesis—hematite and goethite. In the course of iron reduction, which is one of the most energetically favorable processes, bacteria are able to carry out complete destruction of organic matter, including acetate, the major compound accumulating in the majority of anaerobic microbial processes. Despite the fact that iron reducers have to reduce poorly soluble minerals of iron, they successfully compete for substrate with two major groups of secondary anaerobes (methanogens and sulfate reducers) because of their high affinity to the substrates. Formation of magnetite as a major reduced product of iron reduction depends on many factors, including the concentration of bicarbonates, humic acids, phosphorous, and the pH of solution. The presence of monodomain biogenic magnetite in soil and sediment strongly affects their total and remaining magnetism. At present, many studies are appearing that point out the decisive role of dissimilatory iron reducers rather than magnetotactic bacteria in the formation of this mineral in the zone of hypergenesis. It is noteworthy that, at present, the anaerobic cycle of iron and processes of iron reduction are among the topics that are most intensely studied by microbiologists and geochemists. There are, however, many problems requiring more detailed examination, including the biochemistry of iron reduction, the kinetics of the formations of major reduced minerals, and the participation of bacteria in the formation of iron ore. Our studies have shown that one of the key problems is the stabilization of primary products of bacterial reduction in the process of postbiogenic crystallization in diagenesis.

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Formation of Magnetite and Siderite by Thermophilic Fe(III)-reducing Bacteria

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Abstract—Possible participation of thermophilic Fe(III)-reducing microorganisms in the formation of Precambrian banded iron formations has been studied using the actualistic approach. The laboratory experiments suggest that the formation of biogenic magnetite or siderite depends on the physical and chemical parameters of the medium. Magnetite is formed under low partial CO_2 pressure, excess of amorphous iron hydroxide, and absence of organic colloids. Siderite is formed under high CO_2 partial pressure, limited iron hydroxide, and in the presence of such organic gels as agar, sheaths of iron bacteria, or organic reducing compounds.

Key words: thermophilic Fe(III)-reducing bacteria, banded iron formations, magnetite.

INTRODUCTION

The growing interest in the hypothesis of the possible role of microorganisms in the formation of iron ores results from increased knowledge of the biogenic iron cycle and a better understanding of Precambrian bacterial paleontology. Banded iron formations are the only sedimentary iron ores that are often considered to be formed with the participation of iron reducing microorganisms.

PRECAMBRIAN BANDED IRON FORMATIONS AND DISSIMILATORY IRON REDUCERS FACILITATING THEIR ACCUMULATION

It is widely accepted that the two major stages of accumulation of sedimentary iron ores (Precambrian and Phanerozoic) were related to changes in the atmosphere and hydrosphere and drastic alterations in sedimentary conditions. This resulted in the disappearance of banded iron formations and the start of accumulation of lacustrine–marshy and oolitic ores at the beginning of the Phanerozoic (Strakhov, 1962). The formation of Precambrian iron ore formations was far more extensive than the accumulation of Phanerozoic ores. Banded iron formations are known in all continents and occur in all basic metamorphic complexes of all ancient shields. In the Phanerozoic, when the atmosphere and hydrosphere changed to their modern state, the accumulation of these formations ceased, suggesting that the Precambrian sedimentary environment was fundamentally different. Banded iron formations (iron quartzites) first appeared in the Archean, reached their maximum expansion in the Proterozoic, and, then, disappeared. This pattern and the characteristic thin bedding and rhythmical parageneses with sharp differences in the values of oxygen equilibrium fugacity of oxygen have no equivalents in metamorphic rocks.

Despite many publications on banded iron formations and discussion of various possible means of their accumulation, their genesis is still unresolved. To date, the sources of iron and silica, their means of transportation, forms of migration, reasons and condition of mineral precipitation, composition of primary sediments, character of diagenetic changes, and the true contribution of metamorphic processes to their accumulation are insufficiently studied.

Iron quartzites are thinly bedded rocks of sedimentary origin containing over 15% iron. All they have similar mineral composition represented by quartz (SiO_2), magnetite (Fe_3O_4), hematite (Fe_2O_3), siderite ($FeCO_3$), members of the dolomite–ankerite series ($CaMg(CO_3)_2CaFe(CO_3)_2$), calcite ($CaCO_3$), grunerite ($(Fe^{2+},Mg)_6Si_4O_{10}(OH)_8$), stilpnomelane ($K_{0.6}(Mg,Fe^{2+},Fe^{3+})_6Si_8Al(O,OH)_{27} \cdot 4H_2O$), ribekite ($Na_2Fe_3^{2+}Fe_2^{3+}(Si_8O_{22})(OH)_2$), pyrite ($FeS_2$), and pyrrhotite ($Fe_{1-x}S$) (Trendall and Morris, 1983). Iron quartzites are characterized by thin bedding formed by the interbedding siliceous and ore layers not exceeding 1–2 mm in thickness. These rocks do not typically contain traceable clastic material and clay. At present, most researchers agree that banded iron formations can be subdivided into two categories. These are small deposits (e.g., Algom), definitely associated with volcanites, and deposits such as that of Lake Superior, which are large in size and localized in a narrow stratigraphic interval (Kholodov, 1993).

Of various hypotheses of the accumulation of banded iron formations, the terrigenous-sedimentary and volcanic-sedimentary hypotheses have the most support. These hypothesis offer different explanations of the sources of iron, modes of iron and silica transportation into the sedimentary basin, and modes of precipitation leading to characteristic thin lamination.

The classical variant of the terrigenous-sedimentary hypothesis suggests that the weathered rocks of ancient landmasses provided necessary sources of iron and silica. Various authors suggest that the sedimentary basins were either narrow, deep troughs, or wide, enclosed basins (Mel'nik, 1973; Drozdovskaya, 1990). In their opinion, products of continental weathering experienced strong differentiation during their transportation to the sedimentary zones, whereas iron and silica migrated as colloid solutions and were deposited outside the zone of accumulation of terrigenous sediments, activated by electrolytes of seawater, or by mutual coagulation. According to this theory, the laminated structure of banded iron formations was produced by different rates of coagulation and precipitation of iron and silica hydroxides from solution. However, it is strange that such a simple mechanism did not also take place in subsequent geological epochs.

Supporters of the volcanic-sedimentary hypothesis suggest that iron and silica were produced by underwater volcanism. In primary sediments, iron carbonates and silicates, and gels of siliceous acid were precipitated from the seawater, which was additionally mineralized by volcanic emanations. Along with iron silicates and carbonates in the siderite and shamosite facies, iron oxides were also deposited in zones of increased Eh of water. This change of oxygen and carbon dioxide regimes was responsible for rhythmic alternation of siliceous–siderite bands with iron–silicate bands with siliceous intercalations (Drozdovskaya, 1990; *Iron–Siliceous Formations...*, 1991). The most popular modern hypothesis suggests a hydrothermal origin of iron, which was transported to the shallow zones of the ocean from the area of central oceanic ridges, which were located at much shallower depths than now. This hypothesis is supported by the very high rates of deposition of banded iron formations, which cannot be explained by weathering on the landmasses alone. The peak of their deposition was 2.3–2.4 Ga, while the mean rate of deposition within the period of 1.8–2.7 Ga (the main period of their accumulation) was 10^{12} g/yr. Supposedly, the rate of the hydrothermal cycle, which was three times the present rate, produced the necessary amount of leached iron (Isley, 1995). Kholodov and Butuzova (2001) also concluded that hydrothermal processes played a significant role in the formation of Precambrian ores. In their view, the combination of a low rate of occurrence of rare earth elements (which are similar in composition in the deposits of both the Algoma and Lake Superior types) with a positive anomaly of europium supports the theory of the hydrothermal influx of chemical elements, at least until 2.3 Ga. This also suggests that both types of deposits were produced by both endogenous and exogenous factors.

Some features of banded iron formations cannot be explained by just chemical or mechanical processes of their formation, but suggest some biological influence. The study of metamorphic iron band formations, performed by Fonarev (1987), allowed the recognition of noticeable variations (even in the outwardly homogeneous layers of iron quartzites) in the iron content of minerals, chemical composition of rocks, and values of oxygen fugacity corresponding to rhythmic lithological alternations in the less metamorphosed and nonmetamorphosed rocks. Such variations are difficult to explain by the changes in the redox conditions and pH of the accumulative environments. Fonarev's data on oxygen fugacity agree with the results obtained by Mel'nik (1973) on the isotope composition of oxygen in iron minerals from iron quartzites. Mel'nik discovered some features that are difficult to explain by the purely chemical processes of iron oxide precipitation. These are: (1) primary heterogeneity of isotope compositions of $\delta^{18}O$ in iron oxides; (2) iron oxides form a continuous series of isotope content with a similar isotope content of magnetite and hematite, although within the same bed, at levels a few dozen centimeters apart, the isotope content of magnetite varies considerably (differ by 1–2‰, whereas $\delta^{18}O$ of hematite and magnetite vary from +1.3‰ to –6.8‰); and (3) iron oxides with the lowest values of $\delta^{18}O$ are confined to beds that formed in reductive environments with high fugacity of CO_2.

All the above features of the isotope distribution of oxygen indicate possible participation of bacteria in the accumulation of banded iron formations. However, this assumption requires several constraints. The role of bacteria in the formation of iron ores manifests itself by their capacity to concentrate elements from the environment and overcome kinetic barriers, i.e., to be catalysts of chemical processes. It is evident that noticeable microbial activity occurs at the earliest stages of formation and diagenesis of sediments. A number of questions concerning the genesis of banded iron formations (source of iron, transportation pathways, sedimentation of iron along with silica) are presently not resolved, and they can hardly be resolved using the biogenic theory.

The banded texture characteristic of modern cyanobacterial mats, which are considered to be equivalents of the Precambrian communities preserved as stromatolites (Zavarzin, 1989), results from the metabolism of oxygen-producing cyanobacteria and a large group of anaerobic microorganisms decomposing organic matter and producing gases (H_2S, CO_2, CH_4, H_2). The distance between the aerobic and anaerobic zones does not exceed a few millimeters and is characterized by sharp gradients of O_2 and H_2S content. The accumulation of alternating manganese and iron beds is observed in lacustrine sediments and results from the activity of iron- and manganese-oxidizing bacteria (Perfil'ev and Gabe, 1964). The study of biofilms on granite showed that bacterial metabolism is responsible for the leaching of iron from the iron-containing silicates and its precipitation as ferrihydrites, hematite, or siderite, depending on the local physicochemical environment created by bacteria. The distances between the beds with siderite and ferrihydrite do not exceed a few millimeters. Silicon contained in porous waters is also set down on biofilms, but is not involved in microbiological processes (Brown *et al.*, 1994). The possibility of a closed cycle where Fe^{2+} is leached from magnetite, biotite, and ilmenite to form a colloid suspension of Fe^{3+} and is later reduced by iron reducers was shown for biofilms by Brown *et al.* (1999).

All ore minerals of banded iron formations could have been of biological origin because, for both oxidized (hematite) and reduced (magnetite and siderite) minerals, a direct mechanism of bacterial production has been shown by microbiologists. On the other hand, these conclusions are not supported by experimental and native observations. The most debated origin is that of magnetite, biologically produced mainly by dissimilatory iron-reducers. Magnetite is thought to be of metamorphic origin. Organic matter (Walter and Hofmann, 1983) or siderite (Mel'nik, 1973) could be the main reducers for its transformation from hematite during metamorphism. Based on geochemical, isotopic, and physicochemical studies, Mel'nik concluded that magnetite had a complex polymorphic character and recognized the primary sedimentary, diagenetical, and metamorphic types of magnetite. Primary sedimentary magnetite could be deposited in a sharply reductive environment from supersaturated solutions. However, in Mel'nik's opinion, this process wasunlikely to have played a significant role. Periodical changes of Eh and low partial pressure of CO_2 are needed for chemical precipitation of magnetite from iron hydroxides during diagenesis. At the same time, the diagenesis of oxide-carbonate-silicate sediments does not lead to the formation of magnetite. Mel'nik did not discuss the role of iron-reducing microorganisms in the reduction of iron hydroxides, because this group was only discovered relatively recently.

In the present day, the formation of iron quartzites has ceased completely. The mass accumulation of biogenic magnetite is not observed either, although iron reducers are shown to be widespread (Lovley, 1995). At the same time, in laboratory experiments, magnetite is the main reduced product of the metabolism of iron reducers. The understanding of the factors controlling the formation of biogenic magnetite in the present day may be decisive in solving the problem of the role of dissimilatory iron reducers in the origin of this mineral in banded iron formations.

We conducted a laboratory study to elucidate the physical and chemical factors influencing the formation of magnetite by the anaerobic thermophilic acetate-oxidizing iron-reducing bacterium "*Thermoincola ferriacetica*," strain Z-0001, obtained from samples of iron-containing sediments at the hydrothermal source on Kunashir Island. A thermophilic bacterium was chosen for a purpose. The process of the thermophilic reduction of Fe(III) to magnetite (Slobodkin *et al.*, 1995) agrees well with the theory that states that iron reducers take part in the accumulation of banded iron formations because: (1) apart from the terrigenous washout, volcanic–hydrothermal processes are suggested as the main sources of silica and iron for iron quartzites (Mel'nik, 1973; Isley, 1994; de Ronde *et al.*, 1994; Kholodov and Butuzova, 2001); (2) many thermophilic microorganisms represent evolutionary early taxa and are phylogenetically close to the progenot (Vagras *et al.*, 1998).

Firstly, we studied the mineralogy of the products of metabolism of thermophilic iron reducers at early diagenetic stages in a changing physical and chemical environment. Secondly, we investigated sediments of biogenic ferrihydrite as the most likely natural acceptor of electrons for iron reducers in the modern environment. In this case, it was necessary to reveal the factors prohibiting the formation of biogenic magnetic in the present environment.

A synthesized amorphous hydroxide of Fe(III) or residue of natural biogenic ferrihydrite were used as electron acceptors, whereas acetate was used as an electron donor. The experiment was performed in strictly anaerobic conditions at $t = 60°C$. The formation of reduced mineral phases was studies at varying CO_2 contents in the gas phase and varying volume proportions of gas and liquid phases. Mössbauer spectroscopy analysis has shown that the increase in partial pressure of CO_2 in gas phase causes a formation of doublets characteristic of siderite (Fig. 1).

The composition of reduced products changes depending on the initial content of iron hydroxide, in the atmosphere of $N_2 + CO_2$ (80 + 20%), while the proportions of the gas and liquid phases are constant (Fig. 2). The formation of magnetite was observed when the level of amorphous hydroxide was very excessive. If the amount of initial material was reduced twice or four times, siderite was the only reduced phase. This resulted from the relative increase in concentration of CO_2. Interestingly, unrelated to the initial amount of amorphous hydroxide, iron reducers reduced approximately the same proportion of Fe(III) (approximately one-third).

Until now, biogenic magnetite was precipitated in the laboratory only when the synthesized iron hydroxide, chemically obtained using strict rules of residue preparation, was used as an electron acceptor (Lovley, 1987; Zhang *et al.*, 1997; Fredrikson *et al.*, 1998). At the same time, in nature, biogenic ferrihydrite is the most beneficial electron acceptor for iron reducers. Because of this, the study of the process of reduction of ferrihydrite by thermophilic iron reducers, which could provide information about the possibility of biogenic

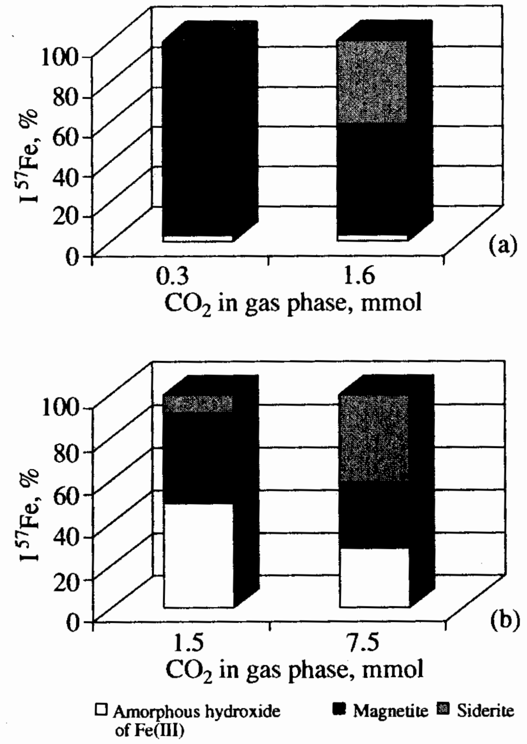

Fig. 1. Dependence of proportions of mineral phases after 14 days of incubation of "*T. ferriacetica*" from the partial pressure of CO_2: proportions of liquid and gas phases 1 : 2, (b) proportion of the liquid and gas phases 1 : 6.

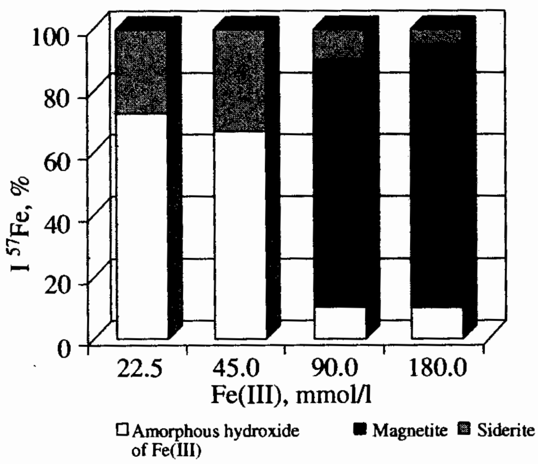

Fig. 2. Relationship between the proportions of the mineral phases after 14 days of incubation of "*T. ferriacetica*" strand and the initial content of amorphous hydroxide of Fe(III).

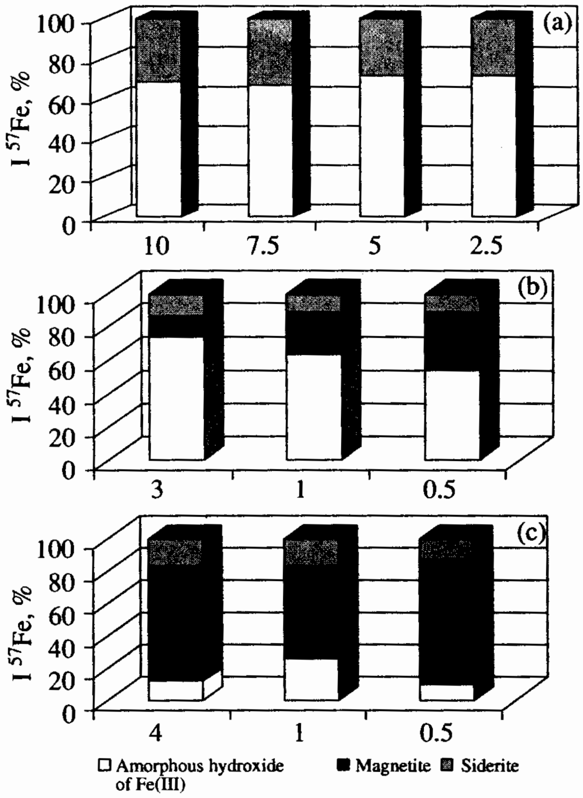

Fig. 3. Relationship between the proportions of mineral phases after 14 days of incubation of "*T. ferriacetica*" and the content of inert organic matter (G/l): (a) agar, (b) beef extract, and (c) microcrystalline cellulose.

magnetic formation in modern hydrotherms, was particularly interesting. Experiments have shown that the only phase formed during the reduction of ferrihydrite residue by "*Thermoincola ferriacetica*," formed by *Leptothrix*, is siderite. This possibly resulted from the presence of organic matter (sheaths of *Leptothrix* and plant remains), which could not be separated from the ferrihydrite residue. To check this hypothesis, inert organic matter, which is not used by "*Thermoincola ferriacetica*" for growth (agar, beef extract, or microcrystalline cellulose), were added to the synthesized amorphous iron hydroxide. Agar was added as an equivalent of mucous sheaths of iron bacteria, while beef extract and cellulose were provided as equivalents of very soluble organic matter and plant foliage, respectively. As a result, a clear relationship was observed. Siderite was formed when agar was added, magnetite and siderite were formed when beef extract was added, and magnetite and siderite were formed when cellulose was added (Fig. 3).

Experiments have shown that the dissimilatory reduction of Fe(III) into Fe(II) by thermophilic acetate-utilizing bacterium is possible with a subsequent formation of magnetite as a stable product. The formation of magnetite as a final reduced phase by iron reducers depends on many factors, including CO_2 concentration, presence of complex organic compounds, electrical surface properties of minerals of Fe(III). All these factors that are present in different combinations in natural environment are responsible for the modern formation of biogenic Fe(II)-containing minerals. Further experiments are needed to establish which of the above factors is working in each case. At present, there is a possibility that, in the modern natural environment, siderite, vivianite, Fe(III) oxides are the final mineral phases in the metabolism of iron reducing microorganisms, while the formation of magnetite may be a laboratory artifact. However, such a hypothesis does not exclude the possibility of the formation of magnetite by iron reducers in different environments, e.g., in the Precambrian.

Experiments conducted suggest that several factors were necessary for accumulation of magnetite in Precambrian banded iron formations by thermophilic iron reducers. These are: (1) excess of iron hydroxide, (2) low content of organic matter, and (3) partial pressure of CO_2 similar to that in the modern environment.

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