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Mechanism and Modes of Microbial Minerogenesis of Polymetallic Nodules on the Ocean Floor

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Abstract This paper presents a quantitative analysis of the relations of the occurrence of polymetallic nodules with the geochemical actions of microbes in the seawater, pore water and sediments at the bottom of the eastern Pacific Ocean basin. Emphasis is laid on the relations of the activity intensity and biochemical transformation rate of aerobic bacteria (iron bacteria, *Thiobacillus thioparus*, halobacteria and manganese–oxidizing bacteria) and anaerobic bacteria (sulphate–reducing bacteria, denitrifying bacteria, *Thiobacillus denitrificans*) with minera–lization. The experimental research on the migration and accumulation of ore–forming elements caused by microbial and chemical actions shows that the microbes have changed the conditions of oxidation and reduction in the system, and their effect on the element precipitation is much stronger than the chemical actions and accelerates the enrichment of Fe and Mn. It demonstrates that the microbes can change the environment to promote the accumulation of ore–forming elements, thus leading to indirect mineralization.

It is first found under the scanning electron microscope (SEM) and transmission electron microscope (TEM) that there are fossil microbes of various sizes and forms in the shells of polymetallic nodules, and even ultramicrofossil bacteria at the cores. On the walls of some mineralized microbes there are sheaths of Fe and Mn oxides. After the death of the microbes, their bodies are accumulated on the interface of seawater–sediments and form polymetallic nodules. Microstructures of polymetallic nodules formed by microbes are also discussed, and two modes of microbial minerogenesis of polymetallic nodules, both direct and indirect, are suggested in the paper.

Key words: ocean basin in the eastern Pacific, mechanism of microbial minerogenesis, polymetallic nodules, palaeomicrobial minerogenesis

Polymetallic nodules on the ocean floor which contain rich metallic elements such as Mn, Fe, Cu, Ni and Co have significant economic value. Opinions vary as to their occurrence

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and the formation of both laminated and columnar microstructures. There are a number of views concerning the mechanism of polymetallic nodules. H.L. Ehrlich (1963, 1984) found bacteria that can cause oxidative precipitaion and reduction of Mn through experiments of bacterial separation and culture and considered the mineral deposits of sulphides, oxides and carbonates to be biogenous. Since the 1970s, more and more evidence and traces of the microbial minerogenesis have been discovered and a series of studies have been made for the mechanism of biological accumulation and precipitation of some metals (Идялегдинов, 1984). Rosson and Nealson (1982) studied the role of the Mn bacteria in the marine Mn cycle. Baturin and Sevchenko (1987) discussed the biogenetic composition of manganese nodules in the deep sea. In addition, some manganese–oxidizing bacteria can synthesize proteins, carbohydrates or other materials that bind, concentrate and thus enhance auto–oxidation of manganese in or on cells (Krumbein, 1983; Горшков, 1991). It is found through experiments that the Fe and Mn oxidizing bacteria can catalyse the oxidation of Fe and Mn ions. Generally, the study of the microbial minerogenesis of polymetallic nodules is still at a preliminary phase in the world. The concept about the seawater–rock–microbe system presented in this paper has not been reported before.

In recent years, the research on microbial minerogenesis has been carried out in China. Prof. Ye Lianjun and Chen Qiying have obtained fruitful results and published monographs on this subject, stressing the role of the microorganisms in the process of deposition (Ye Lianjun, 1996). Prof. Guan Guangyue et al. (1994) studied the microbial oxidation of Mn ores to confirm the effect of microbes, and Shi Junxian et al. (1989) experimented on the separation and oxidation capacities of Mn bacteria on Mn nodules and sediments in the Pacific Ocean. Prof. Yan Baorui et al (1992, 1994) first demonstrated the evidence of microbial minerogenesis of Mn nodules through the study of microbial transformation of ore substances in oceanic water, sediments and Mn nodules. But the above studies did not touch the minerogenesis of polymetallic nodules by palaeobacteria, and were weak on the microstructures of polymetallic nodules. Since 1993, the authors, through correlation of the microbial transformation rate with the chemical transformation rate of metallic elements, analyzed the relations between microbes and minerals on the ocean floor, where modern and ancient microbes existed in the nodules, and defined the mechanism and modes of occurrence of polymetallic nodules and their microstructures by microbes.

1 Mechanism of the Ore Element Transformation by Microbes

The factors of influence on the material transformation on the oceanic bottom include the pH and Eh values, material composition, and microbial geochemical actions. These factors are dynamic, so it is an active ecological system under interactions of seawater– rock–microorganism controlled by variations of chemical, physical and biological factors, in which microbes are the most sensitive because they have extensive contact with the environment and become the most active factor in the oceanic environment. They can divide by 65 times in 24 hours (Sun Liguang et al., 1995). This leads to their continuous material circulation with the surrounding media and participation in oxidation or reduction.

There are countless species of bacteria in the ocean. We have studied the iron bacteria and manganese–oxidizing bacteria which participate in the oxidation of Fe and Mn, and *Thiobacillus* and sulphate–reducing bacteria in the oxidation and reduction of sulphides of Fe and Mn. Meanwhile, we have studied the nitrobacteria and denitrifying bacteria in the transformation of nitrides and the halobacteria in the oceanic material circulation. Detailed studies have been made on the iron bacteria and sulphate–reducing bacteria (Yan Baorui, 1992; 1994). This paper only discusses the mechanisms of the manganese–oxidizing bacteria and halobacteria.

1.1 Manganese–oxidizing bacteria

The manganese–oxidizing bacteria are aerobic microbes, which are well bred in the Mn–bearing neutral pH media. The pH values for their survival are 7.0–7.3. They can oxidize low–valence Mn and form high–valence Mn compounds. The oxidizing reaction is

$$Mn^{2+}+1/2\,O_2+2OH^- \rightarrow MnO_2+H_2O$$

They are bacilli, separated out from seawater, submarine sediments and Mn nodules on the ocean floor and can sometimes produce dark brown oxidized manganese on the walls of cells (Plate I–12).

In the study area, manganese–oxidizing bacteria have been separated from the polymetallic nodules, bottom seawater and sediments. Their metabolism can speed up the precipitation and accumulation of Mn and Fe compounds. They play an important role in the nucleation of Mn nodules. In order to reveal the mechanism of manganese–oxidizing bacteria in the accumulation of ore–forming elements, we have made experimental studies.

Two sets of experimental systems have been established: one is the biological system containing the manganese–oxidizing bacteria; the other is the chemical system without participation of the bacteria. The No. 1 bacteria sample used for experiment I was separated out from the sediments in the West Area.

Variations of the experiment systems were observed and parameters measured during the experiment.

(1) Variation of the pH value

The pH value changed greatly during the two–week period of culture (Table 1). The table shows that the pH value becomes higher in the bacteria–containing solution, and changes little in the solution without bacteria. The rise of the pH value may be attributed to the fact that oxygen is consumed during the growth of bacteria, which reduces the H^+ concentration in the solution. The Eh value is reduced as the pH value increases and a weak alkaline condition is formed. That is favourable for the precipitation of metallic elements and their transformation to the solid phase.

Table 1 Variation of Fe and Mn precipitation rates (%) with time under the manganese–oxidizing bacteria and nonbacteria actions in the experimental systems

Experiment conditions	Time (d)	Precipitation rate of Fe (%)	Precipitation rate of Mn (%)	pH
With Mn–oxidizing bacteria	0	0	0	6.28
	7	22.7	5.4	7.0
	11	27.0	40.0	7.5
	15	82.0	69.3	7.8
Non–bacteria	0	0	0	6.28
	7	0	0	6.20
	11	0	5.5	6.00
	15	0	11.2	6.50

(2) Observation during the experiment

After 24 hours of inoculation of manganese–oxidizing bacteria, the solution became turbid. A few days later, a layer of manganese oxide was formed at the bottom of the vessel.

(3) Variation of ore–forming element content in the experiment systems

During the propagation of the Mn–oxidizing bacteria (Plate I–1 and I–2), the element concentrations were reduced, but the precipitation of Mn lagged behind that of Fe. In fact, the deposit of manganese appeared on the 11th day (Fig. 1). The precipitation rates of Fe and Mn were 82% and 69.3% respectively on the 15th day (Fig. 2). The other elements also became settled and turned into the solid phase.

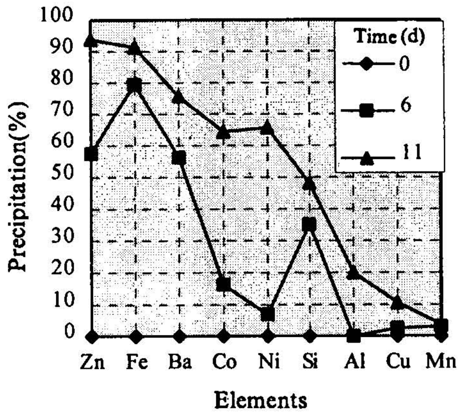

Fig. 1. Variation of element precipitation rates (%) with time under the Mn– oxidizing bacteria action.

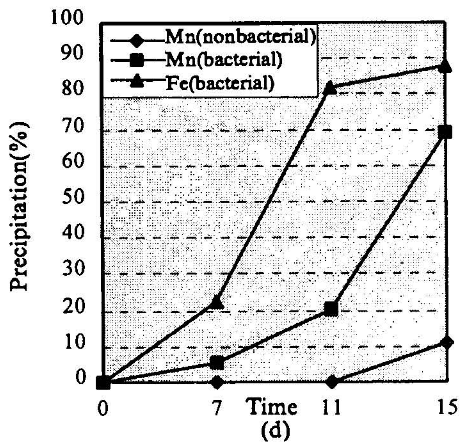

Fig. 2. Variation of precipitation rates (%) of Fe and Mn with time under the Mn–oxidizing bacteria and non–bacteria actions.

This phenomenon shows that in the metabolism, the bacteria cause the metallic elements to settle down, and the secretion may absorb some Fe and Mn and other trace elements which are co–precipitated. The experiments demonstrate that the manganese–oxidizing bacteria are closely related with the accumulation and metabolism of the ore–forming elements. In the ocean–floor environment, they can be the main biological factor in forming polymetallic nodules by catalyzing the precipitation of Fe and Mn elements.

1.2 Halobacteria

The halobacteria separated from the ocean water, sediments and polymetallic nodules on the ocean floor are bacilli (Plate I–11), which are widespread in the oceanic environment. A week of their culture in a medium of 35‰ salinity produced bacterial membrance with saline shell and accumulation of K and other metallic elements in the medium which became turbid. In order to reveal the effects of halobacteria on the transformation of ore–forming elements at the water–sediment interface, we set up four groups of experiment to study the seawater–halobacteria system and water–rock–halobacteria interaction system respec–tively. Subsystems with different organic matter contents are set up under these two systems.

The experiment (Table 2) shows that in the water–halobacteria and water–rock–halobacteria systems, the metabolism of halobacteria intensifies the accumulation and precipitation of Fe, Mn, Cu, Co, K, Na and Mg in the far from saturated saline solution. After the death of the cells, the high–valence oxidizing metals are separated out and precipitated, thereby speeding up the mineralization on the ocean floor (Figs. 3 and 4).

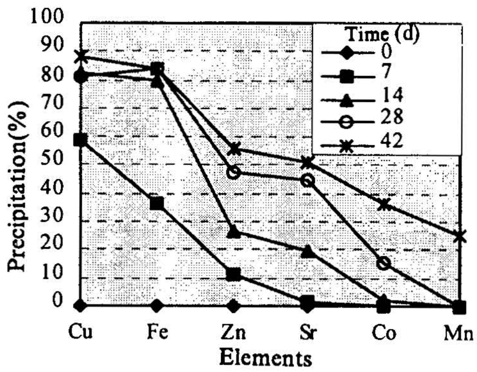

Fig. 3. Variation of precipitation rates (%) of Cu, Fe, Zn, Sr, Co and Mn with time under the halobacteria action.

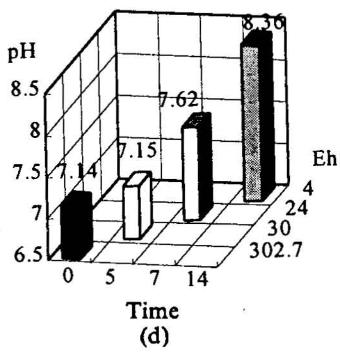

Fig. 4. Variation of pH and Eh with time under the halobacteria action.

Table 2 Variation of element concentrations (μg/ g) in the solid–phase system of the water–sediment–microbe interaction

Sample type	Element									
	Fe (%)	Ca (%)	Mn	Co	Cu	Ni	Pb	Zn	Sr	P
Sediment before experiment	4.41	2.01	7033	122.8	475.3	269.0	25.6	104.7	272.4	1676
Solid–phase sample after 35 days of halobacteria action	4.34	2.41	31940	363.1	730.3	950.0	76.5	104.8	24.6	2091

2 Microbial Minerogenetic Mechanism and Modes of Polymetallic Nodules

The study shows that the microbial minerogenesis consists of two modes(the direct and the indirect. The former includes accumulation and precipitation of elements, and transformation of element valence by microbes. The latter includes mineralization caused by microbial metabolism that changes the physico–chemical environment and causes biological decomposition and synthetization of organic compounds.

2.1 Direct polymetallic accumulation by microbes

Iron bacteria, manganese–oxidizing bacteria and halobacteria are capable of accumulating ore–forming elements during their metabolic processes. Sheaths of Fe and Mn oxides are formed on the cell walls, and sometimes adsorbed in the cells, which makes the bacteria mineralized.

The iron bacteria contain oxidase themselves that can catalyze the low valence Fe^{2+} and Mn^{2+} as their energy to produce high–valence Fe and Mn hydroxides or oxides, which can accumulate and deposit into minerals. It can also decompose the organic compounds to produce inorganic high–valence Fe and Mn compounds for mineralization.

The metabolic activities of Fe and Mn oxidizing bacteria can absorb and accumulate Fe and Mn on the cell walls of low valence Fe and Mn into high valence ones during the oxidizing process and form directly polymetallic nodules at the interface of the ocean water–sediment after the death of bacteria which contain large amount of Fe and Mn compounds. In addition, these bacteria containing metallic elements in the cells can form particles and continually absorb the surrounding elements as the core of the nodules. Therefore, metallic elements are enriched around the cells and then polymetallic nodules are formed. The accumulation of the microbes can form multilayered or laminated structures. SEM observation reveals many microbial tracks at the surficial and internal parts of the nodules (Plate I–10), which shows that almost all the microbes are subjected to Fe and Mn mineralization to some extent (Table 3). This is the evidence of mineralization through direct accumulation of microbes.

SEM photos show mineralized orbicular bacilli colonies appearing at the surficial and internal parts of the nodule. Also found are spherical bacteria cemented and mineralized from metabolic products, rod and spherical colonies, spherical bacteria with fine fibre, spherical bacteria enclosed with Fe and Mn, and the mineralized bacilli. These fossil bacteria are quite similar in shape and size with modern iron bacteria, manganese–oxidizing bacteria and halobacteria. Bacilli are dominant in the zone rich in Fe and Mn, and minor in the zone poor in Fe and Mn, which agrees with the deduction that the Fe and Mn oxidizing bacteria are the dominant species. At the core are also found very small (nm–sized) orbicular, chain and moniliform fossil bacteria, some of which still have a layer of sheath preserved. This is interesting and it shows that uncompressed fossils and even sheath around them are well preserved at the core.

Table 3 Element concentration (%) of minerals and bacteria of the polymetallic nodules (Station 5581)

No. of sample	Type of sample	Si	Ni	Co	Cu	Ti	Cr	S	Al	Mn	Fe	Ca
5581–D	Mn oxides at the core of the nodules	2.14	1.82	0.16	1.77	0.58	0.07	0.14	0.94	36.31	3.37	1.06
5581–3B	Fe and Mn oxides at the rims of the bacilli	3.34	1.57	0.16	1.73	0.82	0.02	0.18	1.28	32.60	4.79	1.12
5581–3A	Fe–Mn mineralized bacteria in the central part of the nodules	6.12	0.93	0.21	0.95	3.37	0.01	0.32	1.55	22.74	6.82	1.12
5581–F	Spherical bacteria at the core of the nodules	4.61	0.43	0	0.53	0.18	0.001	0.34	1.08	12.02	0.68	1.34
5581–J	Si mineralized spherical bacteria in the nodules	10.72	0.16	0.06	0.14	0.16	0.17	0.25	6.94	4.34	2.13	0.75

In the nodules, we have discovered very diverse microbial fossils (Plate I–10), and obtained direct evidence of the polymetallic nodules built up by microbes.

2.2 Indirect minerogenesis by microbial geochemical action which changes the oxidation–reduction conditions

The H^+ content, pH and Eh values in the media can be changed during the process of microbial metabolism, and the changes of pH and Eh values directly control the migration and precipitation of the metallic elements. Various acids and alkalis including organic acids and organic alkalis, CO_2, NH_4, and even strong acids like sulphuric acid and nitric acid may be created by metabolism, thus elements such as Pb, Zn, Cu, Fe, Mn, Ni and Co in the surrounding sediments are dissolved. The experiments show that *Thiobacillus thioparus* can change the sulphide into sulphate and form an acidic environment, which accelerates the migration of Fe, Mn and other metallic elements to the ocean bottom water. Here iron and manganese oxidizing bacteria can again speed up the precipitation and accumulation of Fe and Mn compounds. Meanwhile, other bacteria such as sulphur–reducing bacteria can reduce sulphate back to sulphide. The experiments show that the process of microbial metabolism results in the increase of the pH value and decrease of the Eh value to the low negative value (Yan Baorui, 1994). The deposit in the reducing environment can release Mn and Fe elements into the pore water. As the released Mn^{2+} migrates onto the surface of the deposit, and settles down when it encounters oxygen, then a large amount of H_2S is formed by sulphate–reducing bacteria, which is a favourable geochemical barrier to accelerate the precipitation and mineralization of metallic elements.

3 Discussion and Conclusions

The study of the occurrences of polymetallic nodules in the deep sea is very complicated, especially in the field of microbial minerogenesis. It involves a wide range of disciplines, especially the study of the effects of the microbes on the metallic element migration and modern and ancient microbes, and it is therefore rather difficult to achieve much in a short time. This paper, based on microbial geochemistry, aims to study the accumulation rule of the metallic elements caused by microbial ecology so as to describe the relations between polymetallic nodules formed by microbes and their microstructure, and thus to propose the minerogenetic mechanism of microbes.

(1) Our study is concentrated on the microbial geochemical action on the formation of polymetallic nodules and their microstructures. In particular, by means of SEM study for palaeobacterial tracks in polymetallic nodules, we have discovered their tracks which provide the evidence for microbial occurrences of Mn nodule microstructure.

The experiment shows that the microbial metabolism leads to differentiation of Fe and Mn. The precipitation rate of Fe differs greatly from that of Mn under the action of bacteria. The precipitation of Mn lags behind that of Fe. But in the experiment without bacteria, no difference is shown. That is the evidence for microbes accelerating the differentiation. The ecological successive actions of aerobic and anaerobic bacteria cause Fe and Mn to undergo the oxidation–reduction–reoxidation cycle, and rich Fe and Mn deposits occur alternately in the form of laminated structure.

(2) By comparison between the microbial and non–microbial experiments on ore–forming element transformation it is possible to know the direction of the element migration and the rules of precipitation–reprecipitation–redistribution. Based on this study, the microbial minerogenetic mechanism of mineral deposits in the deep ocean is established.

(3) The study of the oceanic media including the microbial ecology in nodules reveals a wide distribution of halobacteria, Mn–oxidizing bacteria, denitrifying bacteria and other new bacteria, which play an important role in the migration and accumulation of metallic elements in the media. The microbial metabolism can cause over ten elements to accumulate in the cells from the unsaturated seawater. The SEM observation also reveals that a large amount of microbes exist in the Mn nodules, which indicates that the oceanic envi-

ronments in both modern and ancient times are favourable for the reproduction of microbes. Therefore, we can conclude that microbes are active participants in the minerogenesis of Mn nodules. The intensive activity of modern microbes on the ocean floor further proves that microbial minerogenesis of the polymetallic nodules still continues. The discovery of new bacteria provides scientific evidence for microbial minerogenesis.

(4) Both in the experiments and under the SEM observations, we have found sheaths made up of high valence Fe and Mn on the cell walls. After the death of the bacteria containing rich Fe and Mn compounds, the dead bodies precipitate on the interface of water–sediment and form the polymetallic nodules.

(5) Two microbial minerogenetic modes can be summed up through comprehensive analyses: one is the direct minerogenesis of microbial accumulation; the other is the indirect microbial minerogenesis. These two modes coexist in the formation of polymetallic nodules on the ocean floor. This conclusion is of both theoretical and practical significance.

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References

Baturin, G. N., and Shevchenko, A. Y., 1987. *Oceanology*, 27(2): 193–196.

Ehrlich, H. L., 1963. Bacteriology of manganese nodules, 1. Bacterial action on manganese in nodule formation enrichment. *Appl. Microbiol*, 11: 15–19.

Ehrlich, H. L., 1984. Microbial Chemoautorophy, Chio St. Univ. Press.

Guan Guangyao, 1994. Supergenic geochemistry of Au deposit.

Krumbein, W. E., (ed.), 1983. Microbial Geochemistry. London: Blackwell Scientific Publications, 330p.

Rosson, R. A., and Nealson, K. H., 1982. Manganese bacteria and the marine manganese cycle. In: The Environment of the Deep Sea. J.G. Morin and W.G. Ernst, eds, pp. 206–216. New Jersey: Pentice–Hall Inc.

Shi Junxian, 1989. Microbial Abundance and Manganese Microbes in Sediments and Nodules of Northwestern Pacific. Beijing: China Oceanic Press (in Chinese).

Sun Liguang and Yan Xiaoyong, 1995. Introduction of Microbial Geochemistry.

Yan Baorui, Zhang Sheng and Hu Dachun, 1992. Microbial minerogenesis of polymetallic nodules in the Central Pacific Ocean, Progress in Geology of China—Papers to the 29th IGC. Beijing: Geological Publishing House.

Yan Baorui, Zhang Sheng, Zhang Xigen and Hu Dachun, 1994. Microbial Activity and Its Metallogenesis in Water–Rock System of the Central Pacific Ocean. Beijing: Geological Publishing House, 99p.

Ye Lianjun, 1996. The Significance of Organic and Organic Matter. Beijing: China Ocean Press.
Горшков, А.И., 1991. Извегстия, А.Н. СССР: Серия геологическая, 7: 67–74.
Идялетдинов, А.Н., 1984. Превращения Металлов. Алма–АТа: Изд. (Наука) Казахстан СССР.

Explanation of Plate

1. Mineralized bacillus, spherical arc–form bacteria, SEM × 5000 in western part of the east area.
2. Mineralized spherical bacteria at the surface of polymetallic nodules, SEM × 3100, section 5514.
3. Mineralized bacillus in pores of polymetallic nodules, SEM × 5000, in western part of the east area.
4. Mineralized bacillus and spherical arc–form bacteria at the surface of the nodule SEM × 3180, station 5740.
5. Sediment (0–10 cm), mineralized spherical bacteria and bacillus and bacterial filaments with fibrous minerals SEM × 5000, station 5525.
6. Core of the nodule, mineralized spherical and bacillus bacteria included by ferromanganese minerals, SEM × 9000, station 5740.
7. Core of the nodule, mineralized filamentous and spherical bacteria, SEM × 2600, station 5511.
8. Core of the nodule, mineralized bacillus and arc–form bacteria and bacterial filaments SEM × 6000, station 5660.
9. Core of the nodule, mineralized segmental bacillus, SEM × 5500, station 5660.
10. Core of the nodule, mineralized chain and grape form ultramicrobes, with bioshells, TEM × 150000, station 5687.
11. Ellipsoidal halobacteria cultured from sediment (30–40 cm), TEM × 14000, station 5687.
12. Manganese–oxidizing bacteria cultured from bottomwater, bacillus form with a definite direction, TEM × 10000, station 5552.

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Plate I