Clays and Clay Minerals, Vol. 45, No. 2, 203–212, 1997.

BIOMINERALIZATION OF LAYER SILICATES AND HYDRATED Fe/Mn OXIDES IN MICROBIAL MATS: AN ELECTRON MICROSCOPICAL STUDY

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Abstract—The formation of layer silicates on capsuled bacterial cell walls was studied in freshwater microbial mats. The trends associated wtih Al, Si, Mn and Fe deposits with capsules are consistent with occurrence of layer silicates with 14, 10 and 7 Å X-ray diffraction (XRD) patterns. Scanning electron microscope and transmission electron microscope (SEM and TEM) observations of the microbial mats revealed the presence of microcolonies of rod- and coccus-shaped bacteria with layer-silicate thin films. Field measurements of pH, temperature and Eh indicated that these conditions for bacterial crystallization of layer silicates and hydrated Fe/Mn oxides in freshwaters are as follows: pH 6.3 to 7.8, 12 to 20 °C and Eh −24 to +200 mV. Glass slides kept for 3 weeks in the beakers with natural freshwater and river sediments were coated with brown materials. These materials were identified as layer silicates and colonized bacteria formed under photosynthetic conditions. The well-developed holdfasts on *Leptothrix discophora* bacterial cells are mainly associated with poorly crystalline layer silicates and hydrated Fe-Mn oxides. Semiquantitative elemental analyses of holdfasts using energy-dispersive X-rays (EDX) indicated that layer-silicate crystallization covers the cell at an early stage. Iron and manganese crystallization develops at a later stage, where aluminum substitution occurs in crystal structures. Laboratory experimental results indicated that layer silicates grew from a biochemical origin, rather than from inorganic origins in freshwater. Layer-silicate formation is linked with bacteria in microbial mats.

Key Words—Bacterial Cell, Electron Microscopy, Freshwater, Hydrated Fe-Mn Oxides, Layer Silicates, Microbial Mats.

INTRODUCTION

Various microorganisms have the ability to accumulate metallic ions such as Fe and Mn from their external aquatic environments (Emerson and Revsbech 1994a; Snowball 1994; Thamdrup et al. 1994). Manganese minerals specifically crystallize in deep sea sediments. Mn-bearing ground water, lakes, streams, hot springs and wetlands (Skinner and Fitzpatrick 1992; Tanaka et al. 1994; Thamdrup et al. 1994; Usui and Mita 1995) and acid mine drainage (Mann and Fyfe 1984, 1985, 1989; Mann et al. 1992; Skinner and Fitzpatrick 1992; Tazaki 1995; Tazaki et al. 1995). Dissolution and precipitation of Mn minerals are primarily mediated by microorganisms under natural surficial conditions (Larock and Ehrlich 1975; Beveridge and Murray 1976; Mustoe 1981; Chapnick et al. 1982; Burdige and Kepkay 1983; Cowen and Bruland 1985; Cowen et al. 1986; Ferris et al. 1988; Robbins et al. 1992; Schmidt and Robbins 1992). Laboratory and field studies have provided evidence that the Fe bacteria are found commonly in Fe-rich seeps under neutral-pH conditions, and are primarily responsible for most of the Mn and Fe oxidation. The presence of these elements appears to stimulate the growth of *Leptothrix ochracea* and *Gallionella* species (Nealson and Tebo 1980; Beveridge and Fyfe 1985; Payne 1993; Doyle and Marquis 1994; Emerson and Revsbech 1994b).

Numerous papers have been published on the formation of layer silicates in river sediments and freshwater systems. However, involvement of bacteria in layer-silicate crystallization has not been studied using electron microscopy. Ferris et al. (1987) reported the occurrence of a complex Fe-Al silicate forming on bacterial cells in a metal-contaminated lake sediment. The precipitates ranged from poorly crystalline granular material to a more well-developed crystalline phase. This polymorphic Fe-Al silicate was chamosite $[(Fe_5Al)(Si_3Al)O_{10}(OH)_8]$. Kohler et al. (1994) reported the formation of biogenic nontronite developed from marine white smoker chimneys. This hydrothermal nontronite is almost monomineralic, has a low Al content and formed at a temperature between 21.5 and 67.3 °C.

The objective of this study is to determine the natural occurrence of layer silicates in freshwater systems and conduct laboratory simulation experiments to understand the role of bacteria in nucleating and crystallizing them.

MATERIALS AND METHODS

Layer-silicate formation processes and bacterial activity were studied using an optical phase contrast microscope, SEM, EDX analyzer and TEM.

Laboratory simulation experiments used samples of water and sediment collected from a pond adjacent to Kanazawa University. Small streams drain into this pond where brownish microbial mats occur on the sur-

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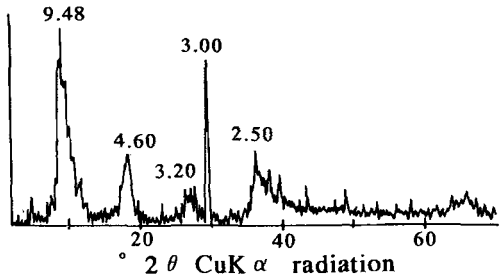

Figure 1. XRD pattern of orange-colored microbial mats from a pond adjacent to Kanazawa University.

face of the river sediments. The precipitation was cultured in a glass beaker with both water and sediment at pH 7–8 under photosynthetic conditions. A cover glass slide was kept in the water between a few weeks to a few months at room temperature. This was used to observe the precipitation of materials on the surface. The river water was filtered to remove the >0.45 μm fraction using membrane filter papers which were analyzed by atomic absorption.

The original sediments were analyzed using powder XRD. The results showed the presence of mainly quartz and feldspars. Iron oxide minerals, manganese oxide minerals and layer silicates were not detected in the original sediments.

Brown-colored holdfasts on the glass cover slide were observed with an optical microscope, JEOL JSM-5200 SEM equipped with a PV9800 STD energy dispersion system and a JEOL JEM 2000EX TEM. The pH and Eh were measured using a pH meter (Horiba M-8) and an Eh meter (Horiba D-13) during the laboratory experiment. Mineralogical compositions of the brown materials on the slide cover glasses were determined using a Rigaku X-ray diffractometer using Cu*K*α radiation. Atomic absorption was used to determine the elemental composition of the original river water. For comparison, 3 kinds of microbial mats from a hot spring, gold mine and river sediments, which are closely associated with bacterial layer silicates, were also studied.

RESULTS

Microbial Mats in Freshwater

pH, Eh, AND XRD RESULTS. The water chemistry of freshwater is as follows: Mn 1.03 ppm, Fe 0.25 ppm,

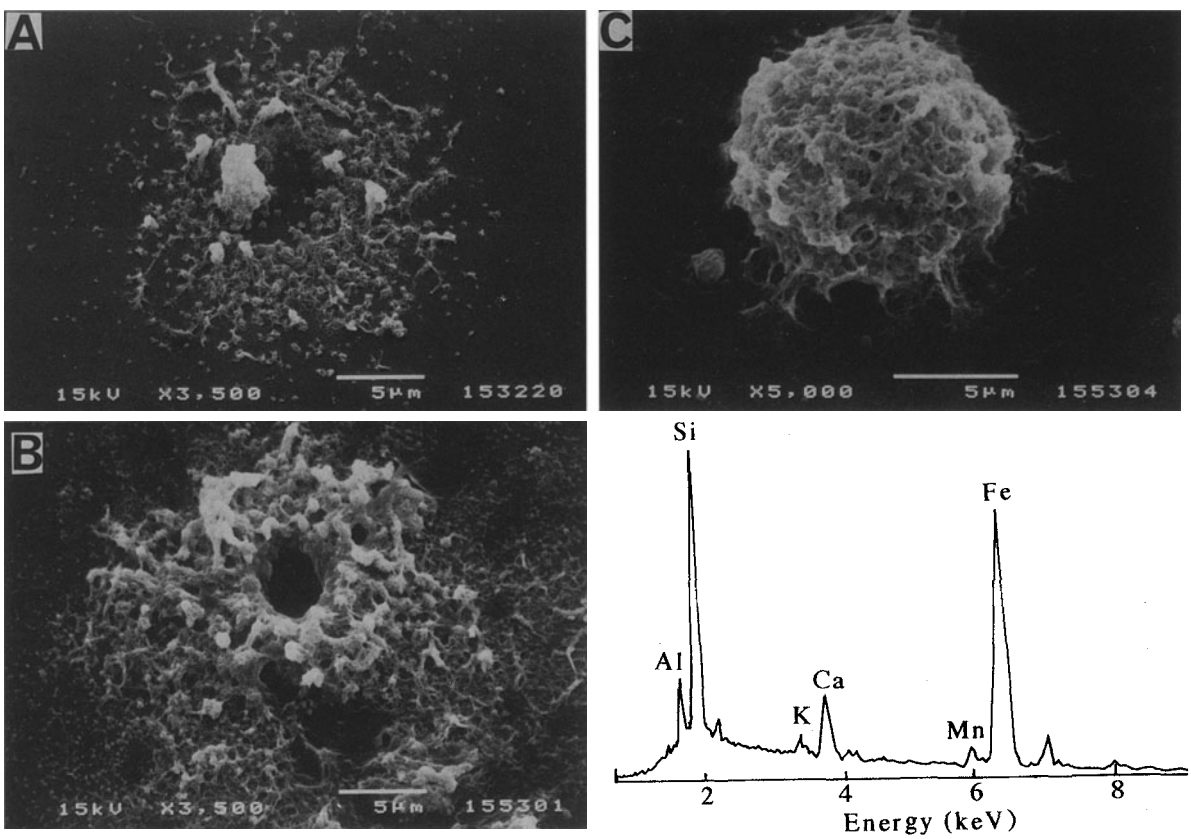

Figure 2. SEM micrographs of the holdfasts on the cover glass slide showing successive formation processes of mixtures of layer silicates and hydrated Fe/Mn oxides: (A) early formation stage; (B) doughnut-shaped holdfasts; (C) ball-shaped Mn nodule without holes in center. EDX data of the holdfasts indicated layer-silicate formation composed of Al, Si, Ca and Fe.

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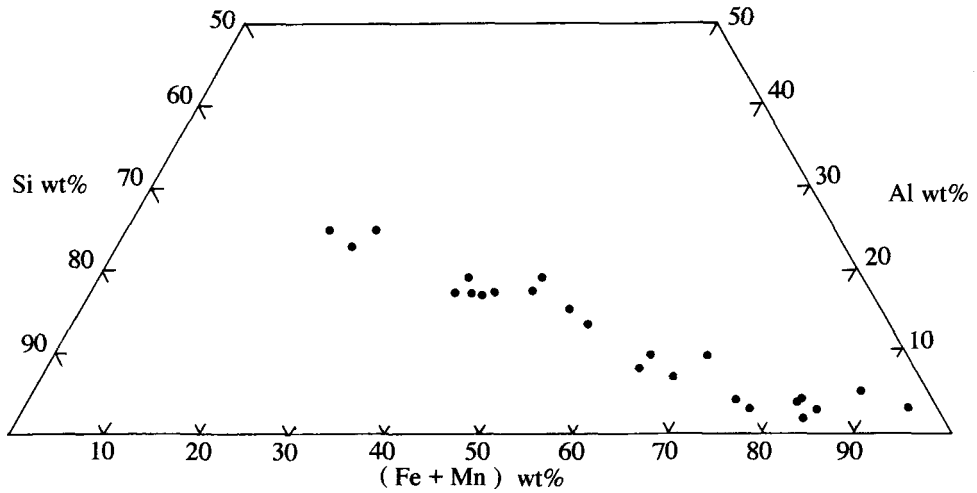

Figure 3. Distribution of Al, Si and Fe/Mn in microbial mats associated with bacteria showing, from left to right, a chemical tendency with experimental aging time at the periods 3, 5, 7 and 11 d. The graph indicates that Fe/Mn and Si contents increase, whereas Al contents decrease in the holdfast.

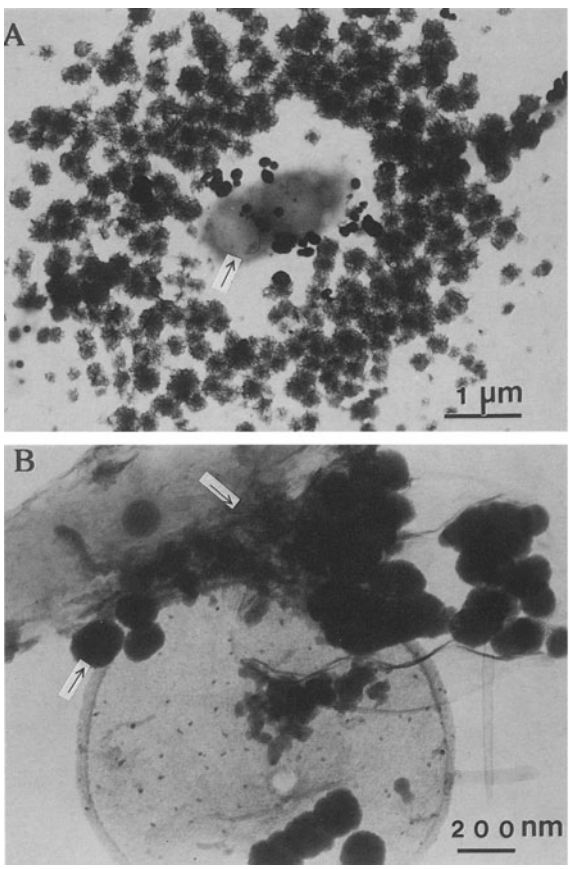

Figure 4. TEM micrographs of clay films attached to doughnut-shaped holdfasts with bacteria (arrow) (A). High dense spheres (arrow) with thin-film coatings of manganese oxide (arrow) (B).

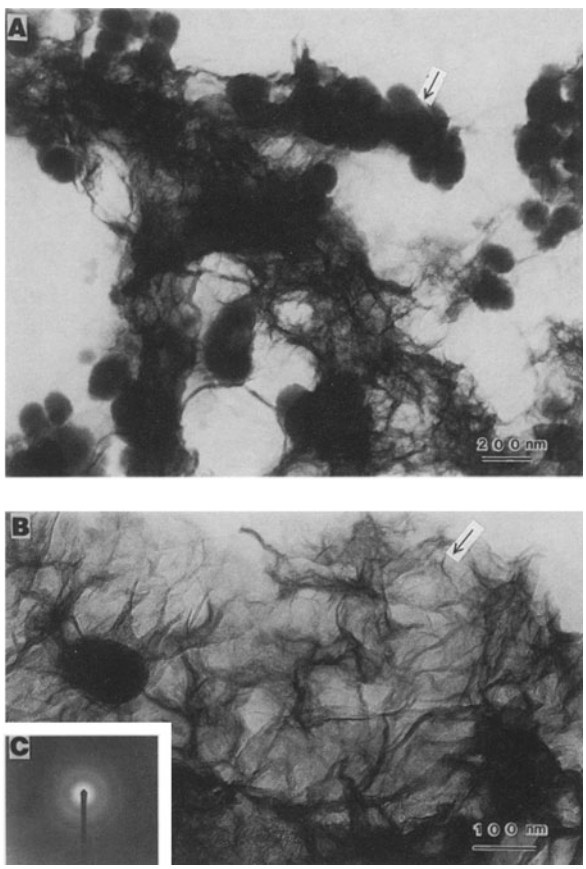

Figure 5. Diffuse electron diffraction rings at 2.76, 2.18 and 1.56 Å (inset C) of thin films (arrow) (B) and high dense spheres (arrow) (A) suggest that layer silicates and hydrated Fe/Mn oxides are present.

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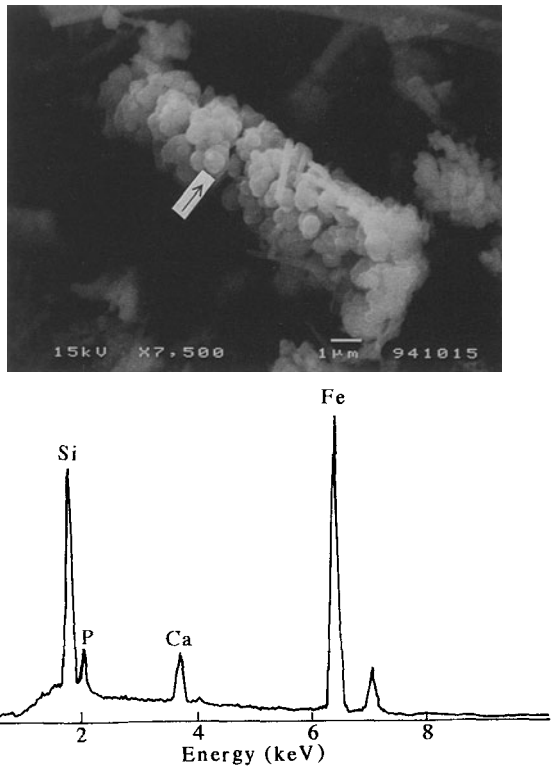

Figure 6. SEM micrograph of filamentous cyanobacteria collected from Azusa-gawa sediment in Nagano Prefecture. The EDX spectrum indicates layer-silicate formation on the cell wall (arrow).

Ca 76.00 ppm and K 18.00 ppm at pH 6.5–6.8 The freshwater pH ranges from 6.3–7.8 and the temperature from 12–20 °C. All samples in laboratory experiments showed a gradual increase in pH (7.2–8.1) and temperature (15–24 °C) within 13 d. The Eh of the water in the beakers ranges from −24 to +200 mV. The brownish precipitates formed on the cover glass slide after 13 d showed strong diffraction patterns for crystalline calcite (3.00 Å) and illite (9.48, 4.60, 3.20 and 2.50 Å) (Figure 1). No crystalline manganese and iron oxide minerals were detected by XRD. The XRD patterns of the thick brown precipitates indicated the presence of large amounts of amorphous and/or organic materials because of the high background. SEM-EDX data and TEM electron diffraction data identified these amorphous or poorly crystalline precipitates as hydrated Mn-Fe rich materials.

OPTICAL MICROSCOPY. The cover glass slides of both the thick- and thin-layered brownish precipitates showed a microstructure associated with the holdfasts of bacterial colony. These had a black and brown "doughnut shape" ranging from 5–50 μm in diameter. The diameter of the doughnuts enlarged over time during the experiment. At an early stage, brownish Fe materials with filamentous and/or coccoidal microorganisms precipitated on the surface. At a later stage, black and opaque Mn-rich materials precipitated near the center of the doughnuts. Black materials concentrated to form spherical Mn materials with experimental time. Under optical microscopy, the black Mn-rich color could be distinguished from the brown Fe-rich materials. Observations of the close-up microstructure of the holdfasts at the early stages of formation revealed a nucleation and radial growth pattern of the bacterial colonies with coccoidal bacteria (*Leptothrix discophora*).

SCANNING ELECTRON MICROSCOPY. The SEM micrographs of a cover glass slide kept in the water for 1 to 3 weeks (Figure 2) showed a stepwise formation process associated with the holdfasts ranging from an early stage (A; 1 week) to matured stage (B, C; 2 to 3 weeks). The holdfasts had a 1–5 μm hole in the center where bacteria emerged. The matured holdfasts showed a rounded morphology with no holes in the centers (Figure 2c). Some holdfasts were still intact but appeared to become more doughnut-shaped with attached layer-silicate thin films. The holdfasts on a slide kept in the water for the long-term experiment

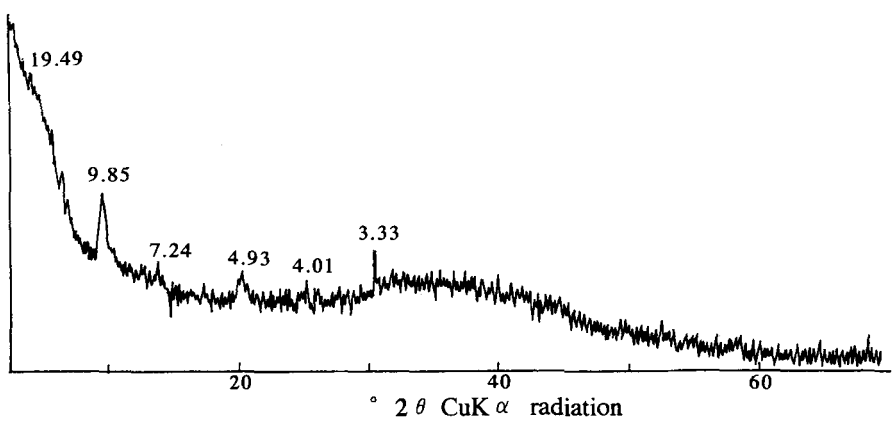

Figure 7. XRD analysis of the bulk microbial mats from Azusa-gawa sediment.

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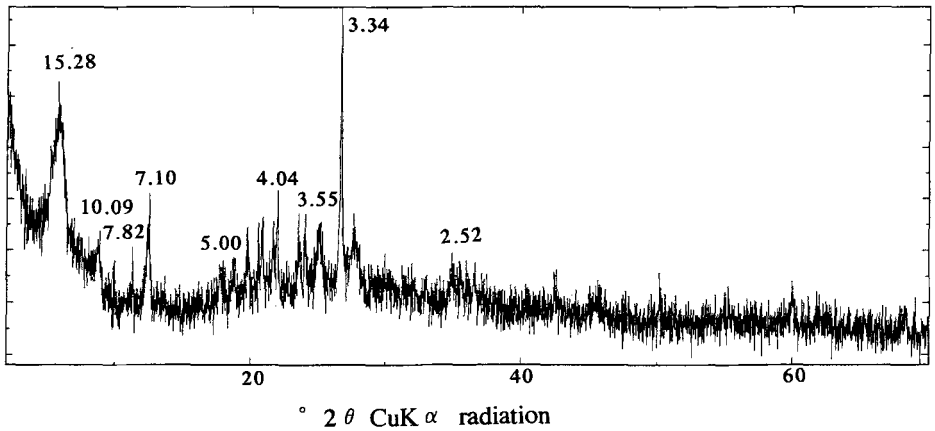

Figure 8. XRD analysis of the bulk microbial mats from Hishikari gold mine drainage, Kagoshima Prefecture, showing more layer-silicate microbial mats.

precipitated highly dense Mn materials with the circle almost filled with colonized precipitates. The doughnut-shaped holdfasts were 10 μm in diameter and contained concentrated layer silicates. Using EDX, the doughnut-shaped holdfasts were found to contain high amounts of Si and Fe with Al and Ca, which have a very similar composition dominated by layer silicates (Figure 2). In some samples, traces of K, Ca, P and S were also present. The small amounts of Si, K and Ca were caused by the underlying cover glass slide. These layer silicates were also identified by XRD (Figure 1) and electron diffraction.

EDX ANALYSIS. The EDX analyses of the holdfasts indicated that Si, Ca, Mn and Fe are dominant. These elements are the ones most likely to be found in layer silicates. The Si, Al, Mn and Fe concentrations in the holdfasts showed formation by chemical precipitation.

Although the amount of Fe, Al and Si in the accumulates surrounding the bacteria had variable concentrations, semiquantitative area analyses without an internal standard were carried out by EDX, providing some evidence for chemical precipitation of the doughnut-shaped holdfast with experimental time. The small amounts of Na, Mg, Al, P, S, Cl, K and Ti did not change with time, whereas Ca, Mn and Fe concentrations gradually increased. Mn and Fe concentrations in the holdfast at the periods 3, 5, 7 and 11 d are plotted in Figure 3. The data in Figure 3 indicate that (Fe + Mn) and Si contents increase, whereas Al content decreases in the holdfast. The Mn and Fe contents are almost saturated within periods 7–11 d. These Al-Si-(Fe,Mn) values are characteristic of poorly crystalline layer silicates. This observation parallels the results of earlier studies to simulate sedimentary diagenesis in the laboratory and in the field. The chemical composition of holdfasts was similar to those found for surrounding cells in the earlier stages of layer-silicate formation.

TRANSMISSION ELECTRON MICROSCOPY. The TEM micrographs showed that the doughnut-shaped holdfasts are associated with bacteria having coatings of thin films (Figures 4 and 5). The TEM micrographs of Figure 4a demonstrate the microstructure of the doughnut-shaped holdfasts, with a bacterial cell situated in the center where films and spheres are attached. The spheres surrounding bacterial cells indicate that Mn precipitation continues even after the initial layer-silicate deposition on the cell wall (Figure 4b). The bacterium is characterized by the intense development of granular Mn aggregates at the cell wall with internal layer-silicate structure (Figure 5). The holdfasts are composed thick mesh-like films and spheres showing electron diffraction patterns with diffuse rings at 2.76, 2.18 and 1.56 Å (Figure 5b, inset c) that reflect the poorly crystalline nature of layer silicates. Some electron diffraction spot *d*-spacing reflections are possibly due to calcite and quartz.

Other Case Examples of Bacterial Layer Silicates in Microbial Mats

A freshwater sample collected from a sediment in the Azusa-gawa River, Nagano Prefecture, showed bacterial layer silicates forming on filamentous cyanobacterial cells composed mainly of Si and Fe with traces of P and Ca (Figure 6) with XRD peaks occurring at 19.49, 9.85, 7.24 and 4.93 Å (Figures 6 and 7). Layer-silicate rich microbial mats were found in a Hishikari gold mine, Kagoshima Prefecture, drainage system and showed powder XRD peaks at 15.28, 10.09, 7.10 and 5.00 Å (Figure 8). Coccoidal bacterial cell walls coated with layer silicates composed of Al, Si, K, Ca, Fe and S were identified by EDX (Figure 9). Strong XRD peaks at 14.71 and 4.45 Å were found in a hot spring microbial mat from Iceland (Figure 10). Tubular algae were coated with granular layer silicates composed of C, O, Fe and Si around cell walls (Figure

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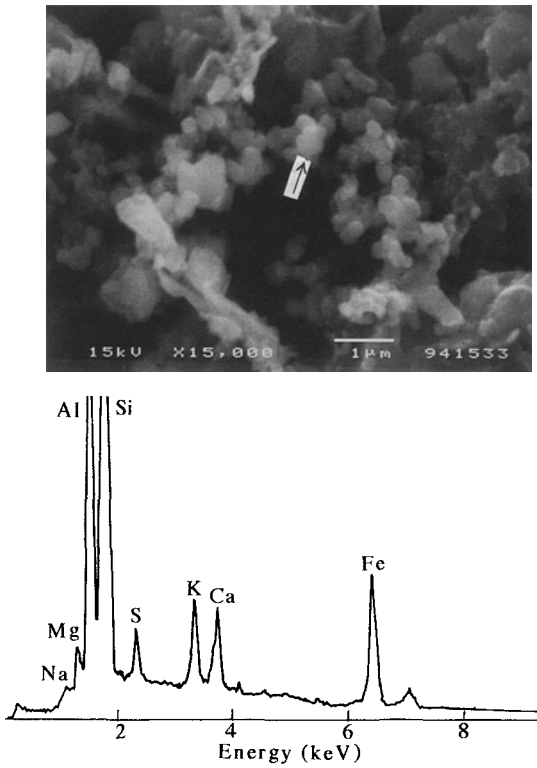


Figure 9. SEM micrograph of coccoidal bacteria (arrow) and the EDX showing layer-silicate formation on the cell walls.

11). The TEM and EDX of thin-sectioned specimens revealed the remains of bacteria inside the accumulations of Fe and Si (Figures 12 and 13). The coccoidal bacteria in the microbial mats showed successive stages of mineral preservation by Si, Al and Fe (Figure 13).

DISCUSSION

The microbial mats described here demonstrate that bacteria are capable of promoting both the absorption of elements and the crystallization of Al and Si in close proximity, so that layer silicates can be biogeochemically formed and immobilized simultaneously. Several studies of the synthesis and natural occurrence of layer silicates and siliceous ferrihydrites have provided considerable information about the nature of chemical reactions as compared to biomineralized reactions. Layer-silicate precursors may be precipitated directly on the bacterial cell wall, as shown in this study. The information about processes associated with the formation of Mn nodules (Schmidt and Robbins 1992; Konhauser et al. 1993) is useful to better understand the possible role of bacteria in the formation of layer silicates. The role of bacteria to nucleate elements for layer-silicate formation can be understood in terms of their ability to immobilize metallic ions.

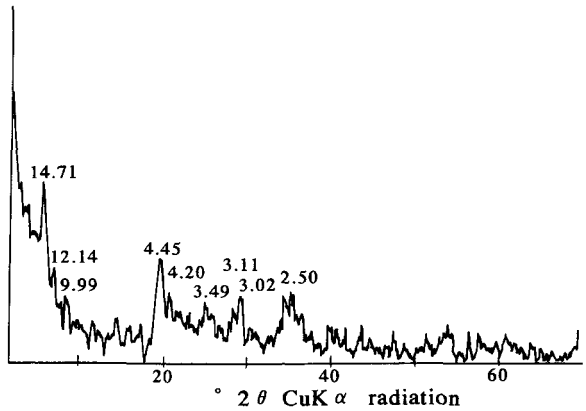
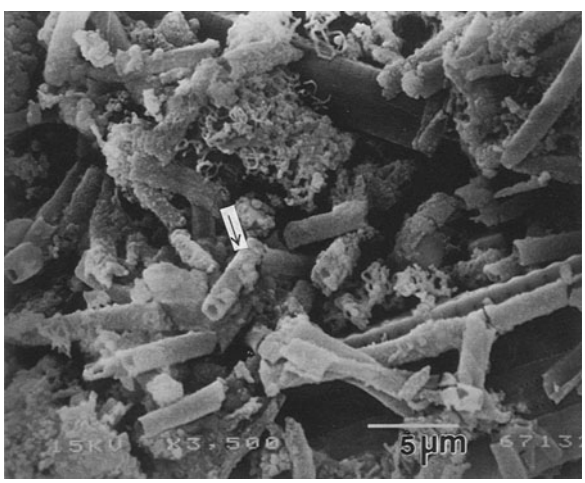


Figure 10. XRD analysis of the bulk microbial mats from hot springs in Laugarvatn, Iceland. Tubular algae coated by granular layer silicates.

From field observation and laboratory simulation experiments, the bacterial biomineralization processes have been traced through hydrated (Fe + Mn) oxides after the layer-silicate minerals have been formed. Alternatively, cationic colloidal species may form initially by surrounding bacterial cell walls that can be bound by the anionic surface polymers of the bacteria. The results indicate that layer silicates and hydrated



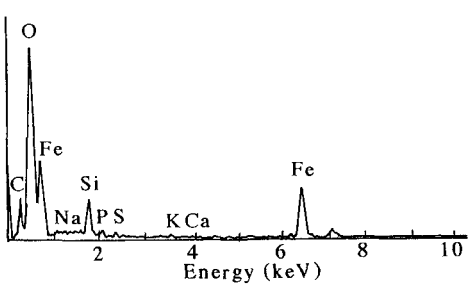


Figure 11. SEM micrograph of tubular algae (arrow) showing coatings of layer silicates and the EDX, from Laugarvatn hot springs.

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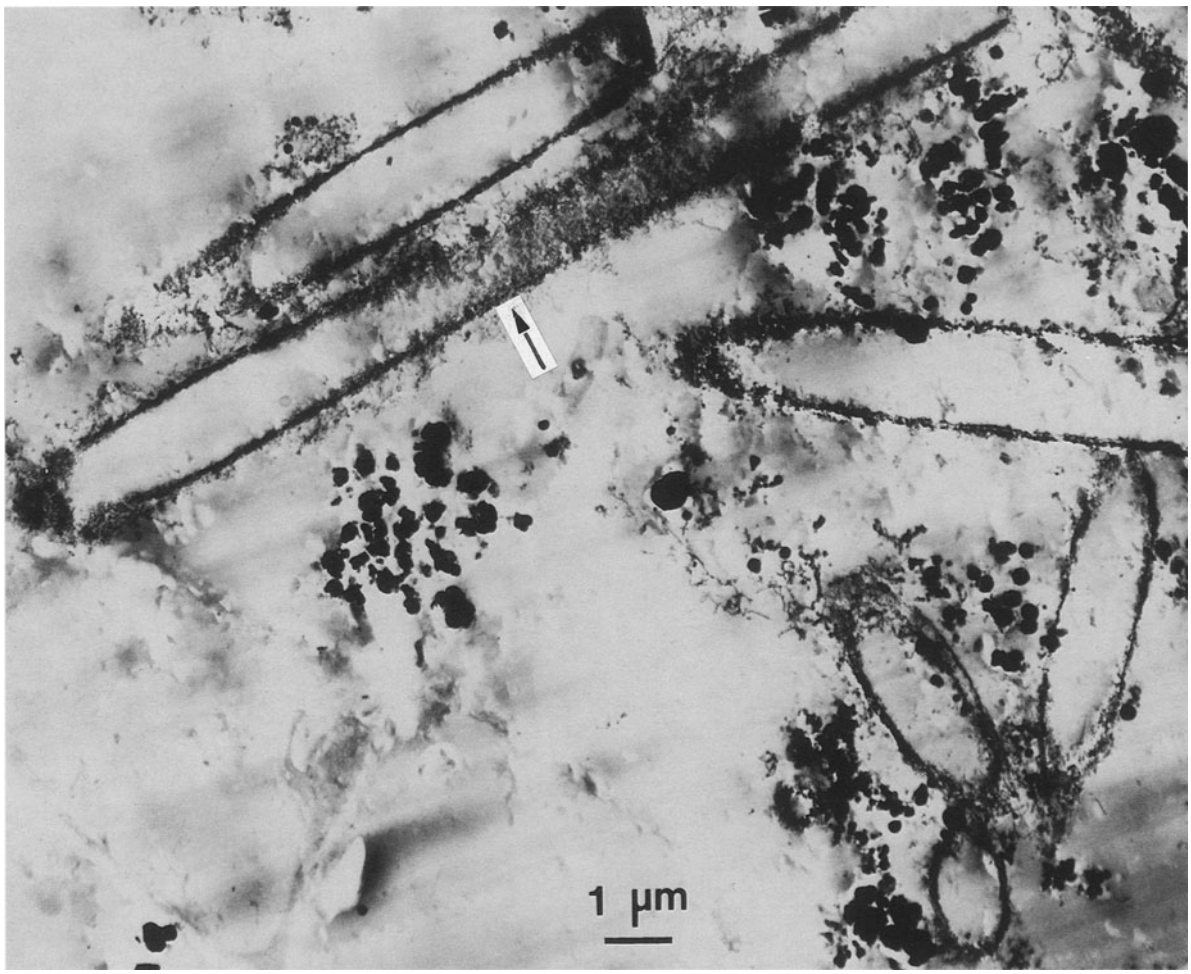

Figure 12. TEM micrograph of thin section of tubular algae showing coatings of layer silicates on the cell wall (arrow).

(Fe + Mn) oxides form via biochemical processes, rather than from inorganic processes. Doughnut-shaped bodies in the Mn ores resemble the open-centered holdfasts of modern Mn-precipitating Fe bacteria such as *L. discophora* (Schmidt and Robbins 1992). The admixture of layer silicates, Fe and Mn oxides is a contemporary microbial deposit. Hem and Lind (1983) have reported the thermodynamic replacement conditions for Mn and Fe phases in a diagram depicting Eh, pH and Fe concentration. Hydrous Fe-Al-silicate species could be precipitated directly by dissolved silicic acid from metals complexed by the bacterial cells. Cationic colloidal species formed initially in the sediment pore water systems could be bound. These processes, either separately or together, would account for the formation of the gel-like phase from which the crystalline forms typically evolve during structural rearrangement and layer silicate growth in the solid state (Amouric and Parron 1985). Iron probably precipitates as ferrihydrite and replaces the mobilized Mn. New Mn minerals, such as manganite [MnO(OH)], groutite [$Mn^{+3}O(OH)$], pyrolusite (β-MnO_2) were formed at a later stage in the development of secondary ores. From this study, at Eh values above 0 mV (horizontal boundary; pH-independent) and at pH values higher than 8 (vertical boundary; Eh-independent) Mn precipitation is enhanced, and the concentrations of both Fe and Mn elements in solution are directly linked.

On the glass slide left in the water during a long-term experiment, the Mn oxide oxidized ferrous Fe to form pseudomorphs of the Mn oxide mineral (Golden et al. 1988). Iron occurs both in divalent and trivalent ionic forms. However, Fe^{2+} is stable over a much larger Eh and pH range from Fe^{3+}. Generally, under natural conditions, Fe mobility is restricted to a relative acid geochemical environment. In the reaction, Mn oxidizes and dissolved Fe exchanges electrons; Mn is reduced from Mn^{4+} to Mn^{2+}. Although pyrochroite normally precipitates under alkaline conditions, Fe probably precipitates as ferrihydrite and replaces the mobilized Mn (Pracejus and Bolton 1992).

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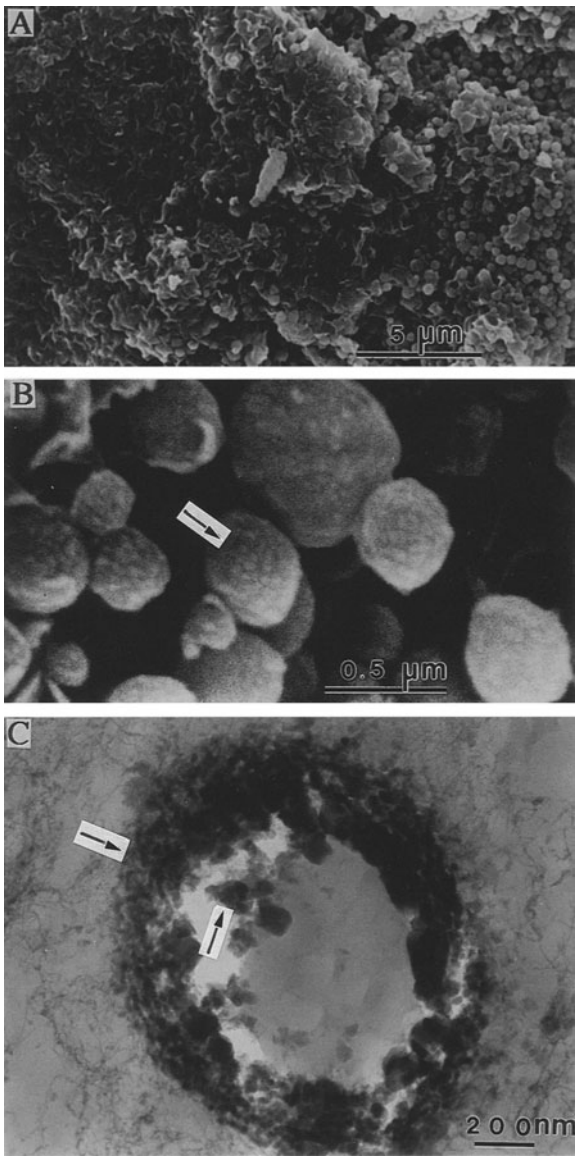

Figure 13. SEM (A, B) and TEM (C) micrographs of coccoidal bacterial cell showing coatings of layer silicates (arrow). Thin section shows clearly biomineralization of layer silicates on internal (arrow) and external cell (arrow) (C).

In a natural river water system, living bacteria reproduce on the surfaces of sediments and grow as colonies, layer-silicate films and spheres of hydrated Fe-Mn oxides. Schindler (1993) outlined the dynamics of *Bacillus* colony growth. Under appropriate conditions, colonies of bacilli, actinomycetes or clostridia and old colonies of other bacteria can develop varied forms with irregular structures and rough shrub-like radial sectors (Schindler 1993). In the *Bacillus* model, an active cell is randomly selected for each successive step of growth. A new cell is included into the set of active cells while the oldest cell is removed; thus, the number of living cells remains constant. A colony of bacteria is often regarded simply as a heap of individual microorganisms. The question is, what is the growth rate of bacterial colonies forming layer silicates? The factors that govern changes in cell morphology and metabolic activity are not well defined. One of the objectives of this study was to undertake laboratory simulation experiments to find the micrometer size of layer-silicate spherules that may have formed during stages within 2 weeks to form a hydrated (Fe + Mn)-rich precipitate at pH 7–8, Eh between −24 and +200 mV. This suggests growth up to ore-grade concentrations later on under biochemical conditions in freshwater systems. Tunnicliffe and Fontaine (1987) described extra-cellular accumulations of hydroxides by sheathed bacteria that colonize surfaces. As a result, poorly crystalline layer silicates on the thin films develop on the bacterial cell. It is suggested that bacteria may have been important in catalyzing the oxidation and precipitation of metallic ions from the freshwater system. Exchangeable cations on the layer-silicate surfaces can possibly be used for the regulation of toxic substances, such as heavy metallic ions in the environmental system (Filip 1979; Ehrlich 1981). A significant portion of the layer-silicate formation by bacteria serves to reduce dissolved heavy metallic content below toxic levels.

Electron microscopy supports the idea that layer-silicate formation is connected with the origin of life (Cairns-Smith 1982). He gives layer silicates a role that is more dynamic than mere adsorption and sequestration. That objection applies with equal force to organic polymerization. Cairns-Smith suggests that layer silicates are the vehicle for biopoesis because of their versatility and abundance on the earth. Detailed mineralogical research is required to justify this interpretation.

CONCLUSIONS

Using optical microscopy, SEM, EDX analysis and TEM, layer silicates formed in field and laboratory simulation experiments showed evidence for bacterial contributions to layer-silicate formation in freshwater. Cover glass slides aged in a beaker with natural freshwater and sediments produced coatings of brown-black-colored compounds. These compounds consisted of hydrated Fe-Mn oxides of doughnut-shaped holdfasts of colonized bacteria. The doughnut-shaped bodies in the Mn ores resembled open-centered holdfasts of modern Mn-precipitating Fe bacteria such as *L. discophora.* The TEM and SEM observations revealed thin layer-silicate films forming by interactions of hydrated Fe-Mn precipitation and bacterial activity. Under appropriate environmental conditions, colonies of bacteria can develop rough radial forms with an amorphous or poorly crystalline structure. Electron diffraction patterns showed that the holdfasts are com-

posed of a mixture of layer silicates and hydrated Fe-Mn oxides. This admixture of layer silicates and Fe and Mn oxides is a typical microbial response under conditions of pH 7 to 8 and Eh −24 to +200 mV. The extensive Al-Si-(Fe,Mn) mineralization associated with many of the bacteria in the microbial mats can be attributed not only to the high concentrations of soluble metals in the freshwater, but also to the high levels of bacterial activity to form layer silicates. The results of the laboratory simulation experiment indicate that layer silicates are mainly produced from a biochemical origin, rather than from an inorganic origin. Layer-silicate formation is strongly associated with bacteria in microbial mats.

ACKNOWLEDGMENTS

This work was supported by grants from the Ministry of Science, Culture and Education of Japan to this study. The author thanks students G. Zhou, K. Koiwasaki, T. Hattori and K. Yoshizu of Kanazawa University for their help. The reviewers of this manuscript have worked hard and made many excellent suggestions. They are sincerely thanked.

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(Received 23 May 1995; accepted 30 April 1996; Ms. 2563)