Synthesis of Manganese Oxide Spherules in Gels—An Approach to Understand Growing Process of Manganese Nodules

Hitoshi MOMOI*, Masami NAKAMOTO** and Kazuko KAMATA***

Abstract: Spherical aggregate of manganese oxide has been known to occur in nature as manganese nodules on deep sea floor and as manganese oolites in giant manganese ore deposits on land. Syntheses in gel were carried out to elucidate growth process of spherical manganese ores. An agar-agar gel containing sodium hydroxide was prepared in a glass test-tube, and a manganese chloride solution was poured on the gel. Diffusing manganese ion in the solution combines with the hydroxyl ion in gel, and manganese oxide precipitates. The products consist of X-ray amorphous gel with minor amount of hausmannite and pyrochroite. Under an adequate condition the precipitate forms Liesegang bands composed of many spherical particles. The particles generally have a concentric internal texture similar to those of oolites. Some particles are ellipsoidal, spindle-shaped, or irregular, having undulating cortices like those of manganese nodules. The precipitated particles have either smooth or undulated concentric texture in spite of a quiet environment of formation. The complex fluctuating diffusion is an important process for the formation of manganese oxide spherules, and a change of periodical sedimentary environments is not always necessary.

Introduction

Two typical occurrences of manganese oxide spherules are known in nature. One is manganese nodule on and in deep-sea sediments and the other is oolite occurring in giant manganese ore deposit, such as Nicopole in South Ukraine and Groote Eylandt in Australia (BOLTON et al., 1988).

Since the voyage of the H. M. S. Challenger, it has been well known that manganese macronodules on deep sea bottom have a concentric and laminated internal texture (GLASBY, 1977; SOREM and FEWKES, 1979). The manganese micronodules in modern marine sediments have the similar texture to those of macronodules (FRIEDRICH, 1976; OHASHI, 1985; SAWADA, 1988). The major and minor element chemistry of macro- and micronodules (SOLEM and FEWKES, 1979; DYMOND et al., 1984; UCHIO, 1979; OHASHI, 1985; SAWADA, 1988, 1989 etc.) and for their growth rates (KU, 1977) have been clarified.

Modern and ancient oolite deposits are dealt with in innumerable papers (e. g., PETTIJOHN, 1975; SCOFFIN, 1987). Calcareous oolites such as in the Bahama beach seem to be the product of direct precipitation on nuclei of dissolved materials in a turbulent free-rolling environment which is subjected to strong tidal current action. OSTWALD (1980) mineralologically and BOLTON et al. (1988) sedimentologically have studied manganese oolites from the Groote Eylandt deposit in Australia. The manganese oolite is thought to form in shallow water and relatively low-energy marine environment (BOLTON et al., 1988). Many ambiguous points remain, however, in the growth mechanism of spherules.

Synthesis of manganese nodule was firstly made in sulfuric acid solution by RAAB and MEYLAN (1977). Their product was a spherical aggregate of fine hair-like particles. The idea of growth of oolites in gel has been discussed since a review by BUCHER (1918). Recently, HENISCH (1970, 1988, 1991) has succeeded single crystal growth in gel. The diffusion of ions in gel often results in a Liesegang ring (LIESEGANG, 1913). However, the growth pro-
cess of the ring has not been theoretically established (KAI, 1985, 1986). The gel-method was applied to synthesis of spherulitic rhodochrosite (MOMOI et al., 1988). We used the same technique for synthesis of manganese oxide and successfully obtained spherules with a concentric internal texture. This paper presents experimental approach to growth of spherules at a room temperature and one atmospheric pressure. The results can be a clue to understand the growth process of natural manganese nodules and oolites.

**Method of Experiments**

Silica gel is effective for the crystal growth (HENISCH, 1970), but the control of hydroxyl ions in silica gel is very difficult. Therefore, agar-agar gel was used in the experiments. Manganese oxide in agar-agar gel was precipitated from solutions of manganese chloride and sodium hydroxide of various concentrations as the diffusing reagents. Another reason is that both ions of sodium and chlorine remain in the solution and the gel after reaction, forming sodium chloride solution resembling to sea water. NaOH and MnCl₂ were used as starting reagents. Another set of experiments were carried out together with additional 500 ppm Ni, because todorokite in natural manganese nodules always contains minor amount of nickel or copper as essential elements (USUI et al., 1978). An ammonia solution was also used in some additional experiments in weaker oxidizing condition than sodium hydroxide solution.

Gel solutions were prepared by adding 2.5% agar-agar to distilled water at 80°C throughly mixing for 10 min. At the same temperature, NaOH was dissolved into the gel solution to make up various concentrations (0.05 – 0.125 mol/l). Then the solutions were transferred into pre-heated glass test-tubes (inner diameter of 5 mm) at 70°C. The test-tubes were kept still overnight at 25°C for the solution to gelatinize. MnCl₂ solutions of varying Mn concentration (0.02 – 0.20 mol/l) were prepared. The Mn solution was poured onto the gelatinized gel in the test-tube. All the experiments were finished within about one month when the manganese ion in the solution was depleted. Most experiments were carried out at the controlled temperature of 25°C and some were in a refrigerator at 0°C.

**Results**

(1) Progress of diffusion

Manganese ions in the upper solution start to diffuse into the lower gel in the test tube. The yellow-colored diffusion front is visible in the colorless gel. The distances from the solution-gel boundary to the diffusion front were plotted to the experimental duration time in Figs. 1a and 2a. The calculated diffusion coefficients are also plotted to the duration time (Figs. 1b and 2b). Both figures typically represent experimental conditions under which either of the two diffusing ions has a fixed concentration; 0.1 mol/l NaOH (Fig. 1) and 0.4 mol/l MnCl₂ (Fig. 2). Fig. 1b shows...
that the diffusion coefficients stay almost constant with time and increase with the increase in concentration of manganese ion. The diffusion of manganese ion obey a simple diffusion equation \( l = DT^{1/2} \), where \( l \) is distance of diffusion, \( T \) duration time and \( D \) diffusion coefficient. Such behavior of diffusion into gel has been reported in the experiments using lead iodide by Müller et al. (1982). Fig. 2b shows that the diffusion coefficients gradually increase with the increase in the concentration of hydroxyl ion. When the concentration of hydroxyl ion is low, the diffusion rate of manganese ion in gel seems to be accelerated, due to the decrease of hydroxyl ion in gel with the progress of precipitation. The rate of increase in the distance decrease gradually after one month and the diffusion stops when manganese ion in the upper solution is depleted.

Fig. 2 Diffusion process of manganese ions in gels under various hydroxyl concentrations in solutions at a fixed manganese concentration in gel before reaction. a) relation between distance and time, and b) relation between diffusion coefficient and time.

(2) Patterns of precipitation
The formation of precipitation takes place according to the following chemical equation: \( \text{MnCl}_2 + 2\text{NaOH} = \text{Mn(OH)}_2 + 2\text{NaCl} \). The manganese oxide precipitation in gel changes its color with time; firstly yellow, brown, and finally black. The change is controlled by ion concentration and duration time. When either ion in solution or gel is low in concentration, the precipitation remains as yellow in color without changing to brown. The difference in color is related to the degree of oxidation, the solution being in contact with air. The precipitation is thought to change from Mn(OH)\(_2\), through MnO·OH, to MnO\(_2\)·nH\(_2\)O.

The precipitation pattern includes often more than one layer textures, that is, the Liesegang ring. There are two types of layers: one is homogeneous layer in which no particle is recognized under a scanning electron microscope, and the other is composed of particles. The particles do not always form layers, but in some cases they are dispersed throughout the column. Also, the particles generally appear in places at some distance from the solution-gel boundary, and their size become larger with the approach to the diffusion front.

The patterns of precipitate are classified into six types (see also Fig. 3).

Pattern A: The color of the precipitation is
pale yellow to pale brown, and a pale colored layer is clearly observed. The pattern appears when the manganese concentration in nickel-bearing solution is low.

Pattern B: The precipitation is formed in a single thick layer in gel near the solution-gel boundary. After one month reaction, the upper solution changes in color to brown due to reverse diffusion of hydroxyl ion into the solution from the gel.

Pattern C: Two broad layers of precipitate are formed in gel. Many spherical particles are dispersed in gel between two broad layers of precipitate.

Pattern D: One thick layer of precipitate is formed below the boundary. A few thin layers of pale brown color are observed in gel further below. These layers are called Liesegang rings or bands (Fig. 4-b). No particles are observed.

Pattern E: The pattern resembles to the pattern D. Many spherical particles are randomly
dispersed below the thick layer without layer texture (Fig. 4-c).

Pattern F: This is also similar to the pattern D. Many thin layers under the broad layer consist of many particles, forming the Liesegang bands (Fig. 4-a).

(3) Relation of patterns to experimental conditions

The variability of precipitation patterns are plotted with the initial concentration of NaOH as abscissa and of MnCl₂ as ordinate (Figs. 5 and 6). Fig. 5 shows the result of nickel-free solutions and Fig. 6 of nickel-bearing solutions. In the figures, both lines of concentration difference \( \Delta = [\text{Mn}^{2+}] - 1/2[\text{OH}^-] \) and concentration product \( \sigma = [\text{Mn}^{2+}] \cdot [\text{OH}^-]^2 \) are drawn (Muller et al., 1982).

In the experiments over 0.1 mol/l of manganese chloride, all the patterns show the Liesegang bands and change from non-particle-bearing (pattern D) to particle-bearing pattern (pattern F) with the increase of hydroxyl ion. The sequence of the change is similar to that observed in the pattern for progress of time. On the other hand, the patterns change from one band (pattern B), through broad bands (pattern C) to particle-bearing Liesegang bands (pattern F) with the increase of manganese ion concentrations. The course of the change crosses a line where the concentration difference is equal to 0, that is, the environment of precipitation at the lowest supersaturation. The particle-bearing Liesegang pattern (pattern F) is plotted in the higher concentration region of both diffusing ions, and the precipitation forms in a place where the concentration product is large as pointed out by Muller et al. (1982).

As shown in Fig. 6, the experiment using nickel-bearing solution is characterized by the appearance of pattern A in lower concentration region of NaOH. The effect of nickel is obvious, but the reason is not clear at the moment.

The experiments were also carried out in a refrigerator at 0°C to reduce diffusion rate of manganese ions. The results are shown in Fig. 7. The particle-bearing Liesegang patterns were observed in the field of more dilute hydroxyl solution than those in the experiments at a room temperature.

A spacing among the typical Liesegang bands has been known to obey a simple spacing law; \( X_n = aP^n \), where \( X \) is a distance (mm) from the boundary, \( n \) an order from the upper band, and \( a \) and \( P \) constants. The spacing between the lower bands becomes broader. As shown in Fig. 4-b, over eighty bands were observed in our experiment, where \( a \) and \( P \) being 32 and 1.025, respectively. Generally, formation of a well-developed Liesegang pattern is rather rare, most of layered patterns are irregular and do not obey simple spacing law (Kai et al., 1982 and 1983).

(4) Identification of products

As mentioned above, the products include particles and particle-free precipitates. After the gel was dissolved in hot water, the products were separated from gel solution by filtration. During the separation, the products are often oxidized by air. To prevent the products from oxidation, hand picking was sometimes used.

The products were examined with an X-ray diffractometer and a Gandorfi camera. An XRD result is shown in Fig. 8. The particle-free precipitates include minor amount of hausmannite (\( \text{Mn}_3\text{O}_4 \)) and pyrochroite (\( \text{Mn(OH)}_2 \)). However, the diffraction pattern is of an amorphous material as a whole, reflection peaks being weak and broad (Fig. 8). The
diffraction patterns of the particle-containing precipitates consist of four weak reflections of hausmannite. Except for those peaks, the patterns are similar to those of the particle-free precipitates. The synthesis of todorokite was not achieved in spite of added nickel in some experiments.

(5) Morphology of particles
The forms of particles are classified into two types: one is spherical and the other ellipsoidal, spindle-shaped or irregular. The former occurs as dispersed particles (pattern E) and the latter as layer-forming one in gel (pattern F). The forms were examined with a scanning electron microscope (Fig. 9), and the internal textures with a back scattered electron images (Fig. 10).

The spherical particle has two or more cortices (Fig. 9-A) showing concentric texture. The back scattered electron images (Fig. 10-C and D) of sections of particles reveal a manganese containing layer (light part) and a manganese-free layer (dark part) that form alternating bands. The texture is closely similar to natural manganese oolites. Some ellipsoidal particles have undulating surfaces similar to those of manganese nodules (Fig. 10-E and F). The material consisting of manganese-free layer is not identified, but it is probably agar-agar. Each manganese-containing layer seems to consist of minute radiating crystals.

Surface texture of spherules is feather-like, and shows a network composed of many thin platy crystals (Fig. 9-B and D). The feature is almost identical to hydrothermal manganese oxides in Fig. 4 of Usui et al. (1989). The ellipsoidal particles also have two or more similar thin layers to those of spherules (Fig. 10-E). They also show feather-like surface texture.

Particles synthesized in the ammonia-bearing gel as an additional experiment are composed of pyrochroite, and show the typical radiating spherulite texture. The particles are grown in a weaker oxidation environment than those in the sodium hydroxide-bearing gel.

Discussion
The experimental results reveal that the spherules of manganese oxide are easily synthesized in gel at a room temperature or lower and at one atmosphere pressure. The synthesized spherules are very similar to natural manganese micronodules and oolites in the following points: (1) The surface texture of the spherules is of a network which resemble to those of manganese nodules as shown in SEM photographs by Uchio (1979), Ohashi (1985) and Usui et al. (1989). (2) Laminated in-

---

**Fig. 8** X-ray diffraction pattern of a precipitate.
Experimental conditions: Cu–Kα radiation filtered by Ni, 35 kV – 12 mA, slits 1° – 0.4° – 1°, scanning speed 1/4°/min, chart speed 5 mm/min, range 200 cps and time constant 2 sec. Initial concentrations: 0.125 mol/l MnCl₂, 0.20 mol/l NaOH and 500 ppm Ni. H: Hausmannite. P: Pyrochroite.
Fig. 9 Scanning electron photomicrographs of precipitated particles of manganese oxide. A: Spherical particle with a concentric internal texture (Bar scale: 10 μm). B: Close-up of the surface of A (5 μm). C: Spherical particle with feather-like surface (10 μm). D: Enlarged surface of C (5 μm). E: Ellipsoidal particle (100 μm). F: Close-up of the surface of E (10 μm). Initial concentrations: A and B 0.10 mol/l MnCl₂ and 0.10 mol/l NaOH; C and D 0.18 mol/l MnCl₂, 0.095 mol/l NaOH and 500 ppm Ni; E and F 0.18 mol/l MnCl₂, 0.12 mol/l NaOH and 500 ppm Ni.

Fig. 10 Back scattered electron images of precipitated particles. A: Spherical, ellipsoidal and bar-like particles (Bar scale: 100 μm). B: Irregular particles (100 μm). C: Spherical particles with a concentric internal texture (100 μm). D: Spherical particle (10 μm). E: Ellipsoidal particle with an undulated cortex (100 μm). F: Close-up of undulated cortex of E (10 μm). Initial concentrations: 0.20 mol/l MnCl₂ and 0.125 mol/l NaOH.

The texture is inferred to have grown under the influence of a complex fluctuating processes in diffusion. The fact that such particles form a layer structure (pattern F) means that the complex diffusion in gel took place along with the progress of the Ostwald ripening, after the Liesegang bands have been formed.

The synthetic alternating layers composed of manganese oxide and agar-agar correspond to the natural concentric texture consisting of manganese oxide and siliceous minerals. The

ternal texture is observed in natural as well as synthesized specimens. Natural manganese oolites commonly have concentric layer composed of minute radiating crystals perpendicular to concentric cortex (OSTWALD, 1980). (3) The undulating cortices of some synthesized spherules are similar to dendritic structures which are observed in the bottom surface of marine manganese nodule (USUI et al., 1978).
agar-agar gel in the experiments corresponds to clay sediment in nature (KRAUSKOPF, 1967). It is said that manganese oolites grow in near shore, estuary, or inlet environment (BOLTON et al., 1988). The experimental data show that the environment for the growth of concentric spherules does not necessarily require a violent, free-rolling, shallow marine environment as envisaged for calcareous oolites (SCOFFIN, 1987). Similarly, a periodical change of specific sedimentary condition is not necessary for the growth of manganese nodules on modern deep sea floor. The concentric texture of the spherical manganese oxide can be formed also in the quiet geological environment, because the fluctuating diffusion of manganese ions in gel also yields similar texture. The cause for the fluctuation of diffusion is an important unsolved problem.

Acknowledgment: We would like to thank Dr. N. KASHIMA of Ehime University for the use of scanning electron microscope, Dr. K. FUJINO and Dr. T. MINAKAWA of Ehime University for their critical discussion and Miss. K. NAKAI, Mr. M. INOUE and Miss. N. NAKAGAWA for their assistance in experiment. This paper has benefited from critical review comments by Dr. Y. KAJIWARA of Tsukuba university and Dr. A. USUI of Geological Survey of Japan. The work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

References


