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Ocean manganese nodules as stromatolite with a fractal like-signature

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ABSTRACT

Deep-sea manganese (Mn) nodules are problematic in terms of factors such as their characteristic form and genesis. There are many reports of bacterial species from manganese nodules. However, the genesis of these nodules has not been fully confirmed. Samples, mainly from the Clarion Clipperton Fracture zone in the Pacific Ocean, were examined by mineralogical methods and X-ray CT. Thin sections of these samples showed columnar stromatolite structures with rhythmic bands. Mineralized bacteria were observed by SEM and TEM. Surface morphology could be described as having a fractal-like nature. The fractal characteristics of spherical to dome-like forms were fundamentally composed of at least four ranks. The 4th order form corresponds to the stromatolite dome top shapes. Similar granular domain units and porous characteristics in manganese nodules were clearly observed by X-ray CT sections. Mathematical simulation based on fractal models reproduced similar morphological characteristics to the natural samples. So, we arrived at the concluding hypothesis that manganese nodules are aggregated stromatolite with fractal-like characteristics. Furthermore, we discussed the possibility that the nature of the layer manganese oxide minerals as the major component of the nodule and associated Fe-oxyhydroxide minerals may become an absorber/scavenger of strategic heavy metals and also toxic metals in the environments.

1. Introduction

In previous reports, there have been many studies on manganese (Mn) nodules (Glasby, 1977; Harada, 1978; Dymond et al., 1984; Usui et al., 1989; Zhang et al., 1997; Han et al., 2003; Ver-Laan et al., 2004; Mukhopadhyay and Ghosh, 2010; Choi et al., 2011). Ocean manganese nodules widely spread across deep sea floors are in strict chemical composition ferromanganese nodules with various heavy metals such as Fe, Co, Ni, and Cu (e.g., Baturin, 1988; Nicholson and Eley, 1997; Usui and Someya, 1997; Hein et al., 2000; Rona, 2008). These manganese nodules, together with manganese (Mn) crusts and microconcretions, represent the main manganese (Mn) oxide deposition in the ocean. In this respect, manganese nodules are important metal resources. Manganese nodules are very problematic materials since their first finding in 1873 during the voyage of HMS Challenger (Murray and Renard, 1891). Why are the shapes nodular or potato-like? Why are they not buried: sedimentation rates of the surrounding deep sea floor are much faster than the growth rate of the nodule. The growth rates of the nodules are very slow and variously estimated to be 1–5 mm/1000 years or slower than these values (Berger, 1974; Skornakova, 1979; Kadko and Burckle, 1980; Kennett, 1982; Prospero, 1996). Some additive occurrences of metal contents in ferromanganese deposits have been reported (e.g., Baturin, 1988; Nicholson and Eley, 1997; Usui and Someya, 1997; Hein et al., 2000; Rona, 2008). Principal sediments types are calcareous and siliceous ooze and clay minerals. Where do the metals of Mn, Fe, Co, Ni, etc. come from? Possibilities include continental runoff, sea water, or hydrothermal, volcanic activities at midocean ridges and hydrocarbon-rich fluid venting in continental margins (Hein et al., 1997; Post, 1999; González et al., 2009). Is their origin fundamentally biogenic or abiogenic? What is the reason why thin rhythmic banding is present in the nodules? These questions remain unsolved.

Varieties of manganese minerals can be identified from ocean manganese nodules. Manganese oxide minerals are essentially complexes based on different Mn oxidation states of +2, +3, and +4. Natural manganese minerals commonly have low crystallinity and often comprise mixtures of some minerals. Manganese minerals from ocean manganese nodules have been variously described as todorokite, buserite, birnessite, 10 Å-manganate, 10 Å- and 7 Å -phyllomanganates, δ-MnO_2, vernadite, akhtenskite, nsutite (γ-MnO_2), etc. (Burns et al., 1974; Turner et al, 1982; Turner and Buseck, 1983; Manceau et al., 1997; Kim et al., 2003; Bargar et al., 2005; Drits et al., 2007). In these situations, using a simple mineral name may be difficult. Furthermore, in this paper we do not deal

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with the detailed crystal structures of each of the component minerals, but mainly describe the textures and morphologies. So here, we do not use special mineral names but refer to them as 10 Å phyllomanganate (phase) and/or 2.5 Å manganate (phase), and so on. These manganese oxides minerals are chemically active and become strong scavengers of heavy metals (Feng et al., 2005; Han et al., 2006; Wang et al., 2009). Geochemical analyses of the bulk nodule samples have reported the major, minor and trace elements and classification according to ternary diagrams (e.g., Bonatti, 1972). Many biosignatures containing bacteria have been found and reported on the surface and within nodules (Burnett and Nealson, 1981; Burnett and Nealson, 1983; Mann et al., 1988; Ehrlich, 2002). Bacterial oxidation by microbes has been widely studied and clarified recently (Nealson and Ford, 1980; Greene and Madgwick, 1991; Tebo et al., 2004). Three types of bacteria have been reported from the manganese nodules; Mn(II) oxidizers, Mn(IV) reducers and bacteria groups independent from metabolism of manganese (Sorokin, 1972; Ehrlich, 2000).

Growth rates of bacteria under high hydrostatic pressure (~500 atm) and low temperature (ca. 4 °C) are estimated to be very slow (Ehrlich, 1972). Not only bacteria but also other organisms, such as benthic foraminifera and other protozoa have also been reported (Nealson and Ford, 1980). They may feed on these Mn(II)-oxidizing bacteria. Thus, Mn(II) oxidizing bacteria may have two roles; manganese accretion on the nodules and to serve themselves as food (Nealson and Ford, 1980). Thin concentric layering and laminar growth pattern in manganese nodules are characteristic. Han et al. (2003) examined them from standpoints of radiometric dating and interpreted the cycles of laminae bands due to Milankovitch orbital cycles. Layer structure of manganese oxides is known to absorb heavy metals (Feng et al., 2005; Wang et al., 2009).

Based on the results of this study and the summation of previous studies, here we arrived at the concluding hypothesis that manganese nodules are a kind of stromatolite on the deep ocean floor with a fractal signature. Furthermore, we discuss the role of manganese oxides minerals as accumulator of useful and toxic heavy metals.

2. Samples and experimental methods

We used manganese nodule samples mainly from the Clarion-Clipperton Fracture zone in the Pacific Ocean, which are contained in the Mineral Collection of the Department of Geology, Niigata University. Four other samples were partly examined for comparative purposes. The samples from the Clarion-Clipperton Fracture Zone 13°N 127°W were ca. 5500 m in depth (Locality-A: 5 samples); samples from this area have been previously described (Han et al., 2003). The samples from four other samples (Locality-B, -C, -D and -E) are as follows: Sample from Marcus-Wade Seamount ca. 4000 m in depth (Locality-B); Sample from Peru Basin northern sector of Nazca Plate, South of the Galapagos Rise, ca. 5000 m in depth (Locality-C); Sample from South East of Hawaii MMAJ TRC (Locality-D); Sample from Izu Rise 29.00°N, 139.3°E, and 2150 m in depth (Locality-E). They are shown in Fig. 1. Samples were examined by standard mineralogical methods; polarizing microscopic observation, X-ray diffraction (XRD), Scanning Electron Microscope (SEM), and Transmission Electron Microscope (TEM) with Energy Dispersive Spectrometer (EDS).

Polarizing microscopic observations were carried out using thin sections of the samples with thickness of ca. 0.03 mm. XRD analysis was carried out using X-ray powder diffractometer (Rigaku ULTIMA IV), equipped with Cu Kα (40 kV, 40 mA) radiation, graphite monochrometer, slit system 2/3° – 0.45 mm – 2/3° and scanning speed 2 deg/min. Powder samples were prepared from small pieces of the sample with agate mortar. SEM images were taken using JSM-5600 (JEOL) with accelerating voltage of 15 kV. Samples for SEM observation were prepared by coating Au on the specimens. TEM used is JEM-2010 (JEOL) with EDS of Voyager IV (Thermo Fisher). TEM was operated at 200 kV. EDS has an ultrathin window. Furthermore, three-dimensional inner micro-structures of the manganese nodules were obtained by the X-ray CT. The specimens were imaged by a microfocus X-ray CT scanner, ELESCAN NX-NCP-C80-I (4) (Nittetsu Elex Co.) at Osaka University. The CT scanner has a microfocus X-ray tube (6 × 8 μm) with a W target and a CCD camera (34 × 72 mm and 480 × 640 pixels) as the X-ray detector. Details of this scanner have already been described (Ikeda et al., 2002).

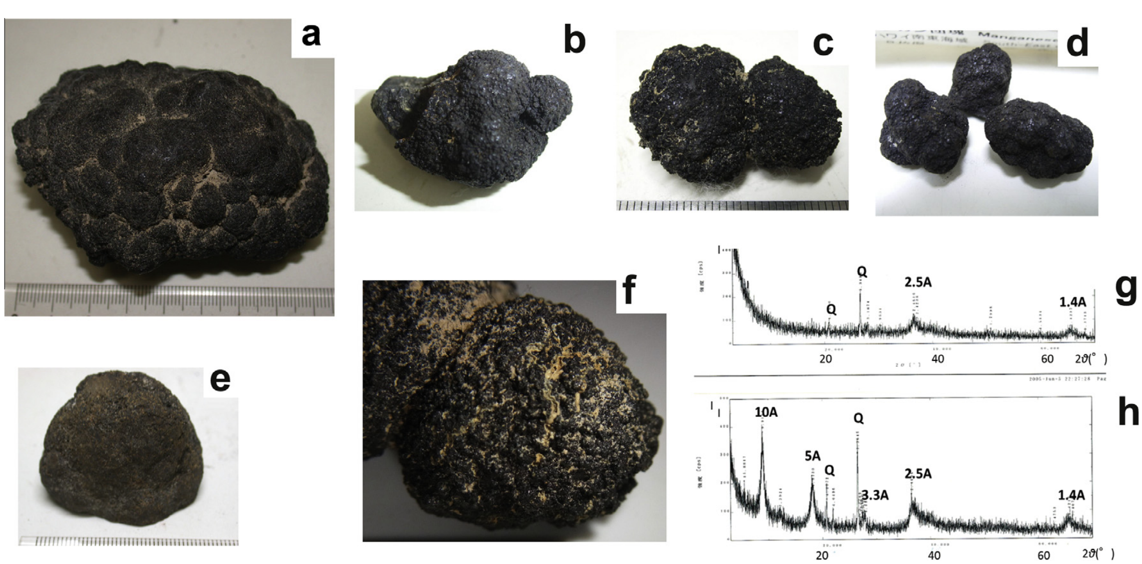

Fig. 1. Photographs of manganese nodule samples from five localities in the Pacific Ocean. (a) Sample from Clarion-Clipperton Fracture Zone 13°N, 127°W ca. 5500 m in depth (Locality-A). Lateral size of the sample is 8.5 cm. (b) Sample from Marcus-Wade Seamount (Locality-B). Lateral size of the sample is ca. 3 cm. (c) Sample from Peru Basin northern sector of Nazca Plate, South of the Galapagos Rise, (Locality-C). Lateral size of the sample is 3 cm. (d) Sample from South East of Hawaii MMAJ TRC (Locality-D). Lateral size of the photograph is 4c. (size of each sample ~2 cm). (e) Sample from Izu Rise 29.00°N, 139.3°E (Locality-E). Lateral size of the sample is 4 cm. (f) Close-up photograph of surface of the sample from Peru Basin (c) indicating tube-building worm. Lateral size of the photograph is 2 cm. (g) XRD pattern of the Mn nodule from South East of Hawaii (d). (h) XRD pattern of the manganese nodule from Clarion-Clipperton Fracture Zone (a). Samples from Locality-A were most typical, examined in detail and were mainly described here.