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ORIGINAL

Organized bacterial assemblies in manganese nodules: evidence for a role of S-layers in metal deposition

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Abstract Polymetallic/ferro-manganese nodules (Mn-nodules) reach sizes of up to 10 cm in diameter and are abundantly found on the seabed. To date, the origin of Mn-nodules remains unclear, and both abiogenic and biogenic origins have been proposed. In search of evidence for a contribution of microbial processes to the formation of Mn-nodules, we analyzed those spherical nodules which contain a concentrically banded texture in their interior. The Mn-nodules were collected at a depth of 5,152 m from the Clarion-Clipperton Zone. Our high-resolution scanning electron microscopy analyses reveal first published evidence that endolithic microorganisms exist and are arranged in a highly organized manner on plane mineral surfaces within the nodules. These microorganisms are adorned on their surfaces with S-layers, which are indicative for bacteria. Moreover, the data suggest that these S-layers are the crystallization seeds for the mineralization process. We conclude that the mineral material of the Mn-nodule has a biogenic origin, and hope that these data will contribute to the development of biotechnological approaches to concentrate metals from seawater using bacteria in bioreactors.

Introduction

Recent developments have documented that, for the formation of inorganic polymers, e.g. of silica in diatoms or in sponge spicules, organic matrices are required for their deposition or even for their synthesis (Cha et al. 1999; Krasko et al. 2000; Müller et al. 2008). As a consequence, it became possible to apply those basic findings for the in vitro fabrication of bio-silica for a variety of potential biotechnological applications (Morse 1999; Schröder et al. 2008). The present study approaches the question whether also a further natural inorganic resource of high economical importance, the polymetallic/ferro-manganese nodules (Mn-nodules), is of biogenic origin, and might be sustainably exploited by biotechnological processes. The commercial value of marine Mn-nodules as resource of essential ingredients (Mn, Ni, Co, Mo) is well established, e.g. to obtain iron for steel production. Due to the global demand for these important metals present in Mn-nodules, the elucidation of their formation has gained increasing scientific attention. However, to date it is unknown how the Mn-nodules are formed. Evidence has been presented that the growth rate of Mn-nodules is low, and even slower than the accumulation rates of the adjacent sediments (Jauhari and Pattan 2000). Several theories have been proposed for their formation, including precipitation of the metals from terrestrial and sub-seabed sources (abiogenic origin), or deposition of the metals through microbial/enzymatic processes (biogenic origin; Chester 2000; Morgan 2000; Zhang et al. 2002).

Steps pointing to a biogenic origin of Mn-nodules have been the findings of Thiel (1925), who concluded that microorganisms can precipitate manganese, and suggested that these organisms also play a role in the deposition of Mn in sediments. Such a role has been experimentally

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demonstrated by Wernadskij (1930), notably for bacteria. Ultra-microfossils, e.g. *Spirisosphaerospora pacifica* and *Miniactinomyces chinensis*, have been identified in Mn-nodules by Lin et al. (1996). More recently, the enzymatic Mn and Fe oxidation by bacteria has been demonstrated (see Ehrlich 1998; Brouwers et al. 2000). These studies on the biochemistry of biotic oxidation of Mn by bacteria in culture suggest that a similar mechanism proceeds also during the formation of solid Mn-nodules. However, concrete evidence for the existence of distinct bacterial communities in Mn-nodules, by high-resolution and, likewise, sensitive scanning electron microscopy imaging techniques, is still lacking. First indications have been achieved recently by application of the technique of high-resolution scanning electron microscopy (Wang et al. 2008). This procedure was also used in the present study to identify those probable microorganisms which are arranged on pronounced laminated and concentrically organized layers.

Materials and methods

Mn-nodules

Different specimens of Mn-nodules from the same area have been studied. They had all been collected from the Eastern Pacific Ocean basin, within the Clarion-Clipperton Zone, by the research vessel *Haiyang 4* during cruise DY85-1 in the Eastern Pacific Ocean basin in 1991, from a depth of 5,152 m (cf. Wang et al. 1998). The location was at 9°22′N and 151°44′W. The element composition of the nodules (Mn, Cu, Ni, Fe and Co) was determined as described by Wang et al. (2000).

One oval Mn-nodule, studied in detail, has a diameter of 55 mm (Fig. 1a) and a major axis of 100 mm (Fig. 1b). In order to stabilize the integrity of the nodules, they had been tied in a rubber-net (Fig. 1b). The internal texture shows regular, concentrically banded zones of different reflectivity. This difference can be attributed to changing contents of Mn and Fe, whereby the lighter layers are richer in Mn and poorer in Fe (Halbach et al. 1988). Based on the classification by Wright et al. (2005), these nodules belong to the elongated, oval morphotype. The cross element composition is, for Si, 2.14%, Ti 0.23%, Mn 16.4%, Fe 4.25%, Co 0.21%, Ni 1.01%, Cu 1.26% and Zn 0.083%. Recent analytical data from Mn-nodules, collected from the Clarion-Clipperton abyssal plain (Duliu et al. 2008), add a series of rare elements to this dataset.

Digital light microscopy

The analyses were performed with a VHX-600 Digital Microscope from KEYENCE (Neu-Isenburg, Germany), equipped with a VH-Z25 zoom lens (magnification from 25 to 175×).

Electron microscopy

High-resolution scanning electron microscopy (SEM) analyses were used to study the morphology of the nodules. For this purpose, cleaned parts of nodules were mounted onto aluminium stubs (SEM-Stubs G031Z; Plano, Wetzlar, Germany). Electron microscopic inspection was performed with a Gemini Leo 1530 high-resolution field emission scanning electron microscope (Oberkochen, Germany).

Spectroscopy

Energy dispersive X-ray spectroscopy (EDX) was performed with an EDAX Genesis EDX System attached to a scanning electron microscope (Nova 600 Nanolab; FEI, Eindhoven, The Netherlands) operating at 10 kV with a collection time of 30 s.

Results

Microscope study shows that the concentrically arranged, Mn-enriched laminae are interspersed with 100- to 450-µm-sized micro-nodules, which are glued together by a whitish interstitial material (Fig. 1c). Those micro-nodules had already been imaged by Murray (1891) in Mn-nodules collected close to New Guinea. Figure 2a shows an SEM view of a polished section through an Mn-nodule, displaying the region with micro-nodules and the region of

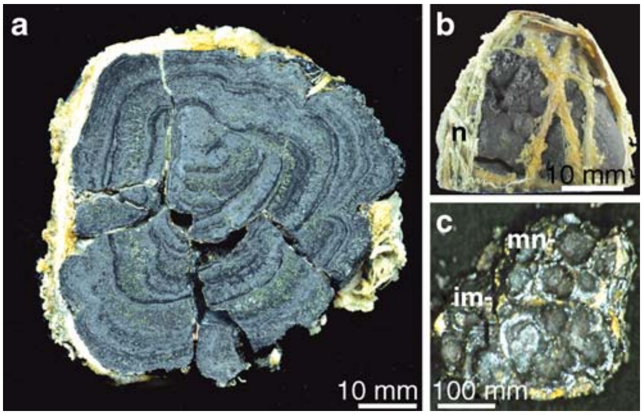

Fig. 1 Nodule morphology. The Mn-nodules were collected within the Clarion-Clipperton Zone (Eastern Pacific Ocean basin). **a** Photomicrograph of a section through an Mn-nodule with typical regular, concentrically banded zones of different reflectivity. **b** View to the major axis of a nodule, grouped to the elongated morphotypes. The rubber-net (*n*) stabilizes the nodule. **c** Digital light microscope image of a surface fracture of a nodule, displaying the micro-nodules (*mn*) dispersed within the interstitial, whitish material (*im*)

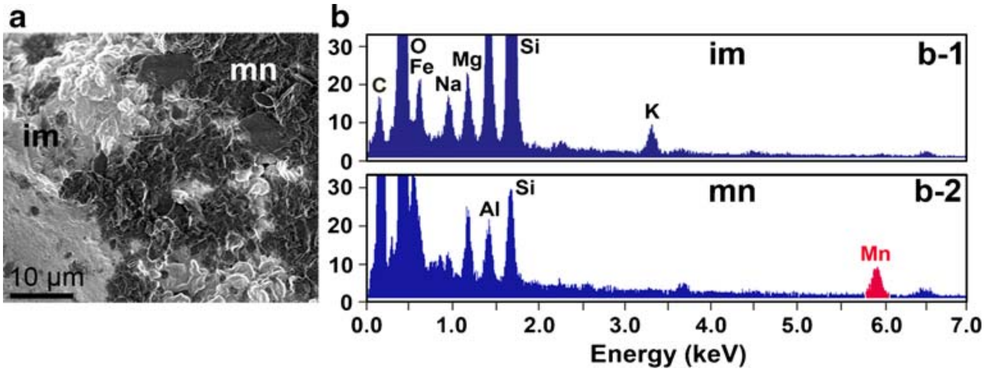

Fig. 2 Nodule analysis. **a** SEM image of a cross section through an Mn-nodule, indicating the micro-nodules (*mn*) and the region comprising the interstitial material (*im*). **b** EDX mapping. X-ray energy spectrum for a region enclosing the interstitial material (*im*; **b-1**) and a region within micro-nodules (*mn*; **b-2**). Only in the latter spectrum is a peak corresponding to Mn detected. Also present are the elements C, O, Fe, Na, Mg, Al and Si

interstitial material. EDX spectrometry spectra (Fig. 2b) reveal a distinct Mn peak for the region including the micro-nodules, in addition to Fe and six other elements (Fig. 2b, bottom), whereas no Mn was detected in the interstitial material (Fig. 2b, top).

In order to detect any assemblies of endolithic micro-organisms, we focused our high-resolution SEM analyses at first onto plane boundary areas within the sections, considering these had the highest likelihood for the existence of organized mono-layered microorganisms. Surprisingly, almost 20% of the surface of the flat boundary layer selected (in Fig. 3a) is covered by arrays of cones of 0.8–1.0 µm average size. It is striking that these small piles are linearly arranged with an interspacing of 1.0–1.5 µm. A closer view of the “substratum” on which these phalanxes of cones are seen discloses further organized structures. Parallel to the plane surface comprising the phalanx-like cones, three to five layers are seen, deeper in the mineral deposit, which display aligned holes of 0.8–1.0 µm with an interspacing of 1.0–1.5 µm (Fig. 3b). At the rim of two planes, forming a fissure, these organized structures of arranged cones become less distinct, and a loosely mineralized zone appears (Fig. 3c). In some regions of a fissure, one plane can be identified which comprises the phalanx of cones, whereas the opposite plane shows a negative imprinting, a mirror image (Fig. 3d). Again, the dimensions of the cone structures and their arrangement match with those seen in the other images. Intriguing is also the occurrence of a cavernous texture at the end of a fissure, where the two planes of these ruptures merge (Fig. 3e). Those few holes existing here have an average diameter of 1 µm. In rare cases, a break up of deeper layers can be observed, which shows regularly arranged, phalanx-like cones without a large interspacing (Fig. 3f). These horizontal views of those structures likewise show the 1-µm-sized cones, which are also visible in corresponding vertical images (Fig. 3g).

An even more detailed analysis of the morphology of the cone-like structures was possible with the high-resolution SEM technique. Frequently, the interpreted endolithic microorganisms were well visible on the surfaces of planes within the nodules, enabling a description of their distinct and in-depth morphology. In fissures, solitary cones are aligned at the surface of one plane, in a highly ordered manner (Fig. 4a). Their sizes are uniform in a given area, ranging between 0.8 and 1.0 µm; their surfaces vary from paracrystalline to crystalline. The characteristic forms of the interpreted endolithic microorganisms are depicted in Fig. 4a–g, where it can be seen that their surfaces are covered by crystal-like scale bricks. Their shapes range from ellipsoid (Fig. 4a), via pillar-like (Fig. 4b and c) to cone-like (Fig. 4d and e). In Fig. 4g, the top protrusions are stripped off, opening up the locular interior. At higher magnification, the scale bricks on the surfaces (Fig. 4f), and the locular internal structures (Fig. 4g) of the ellipsoid microorganisms become even better visible.

Independent evidence for the existence of bacteria in the Mn-nodules comes from images revealing that the surfaces of the flat boundary layers comprise definite, nevertheless unusual S(surface)-layers (Fig. 4h and i). Such crystalline structures have been described for gram-negative archaea, as well as gram-positive and gram-negative bacteria (see Sleytr and Messner 1983; Sleytr et al. 1999). S-layers are planar assemblies of identical protein or glycoprotein subunits. The morphological units are composed of one, two, three, four or six identical subunits, and have a centre-to-centre spacing of approx. 2.5–35 nm. They cover the bacterial cells completely, and are organized in the form of crystalline lattices exhibiting oblique (p1, p2), square (p4) or hexagonal (p3, p6) symmetry. S-layers with hexagonal lattice symmetry are predominant among archaea; those of bacteria are generally 5–20 nm thick, with a smooth outer and a corrugated inner surface. Based on high-resolution REM analysis of the Mn-nodules, we succeeded to identify

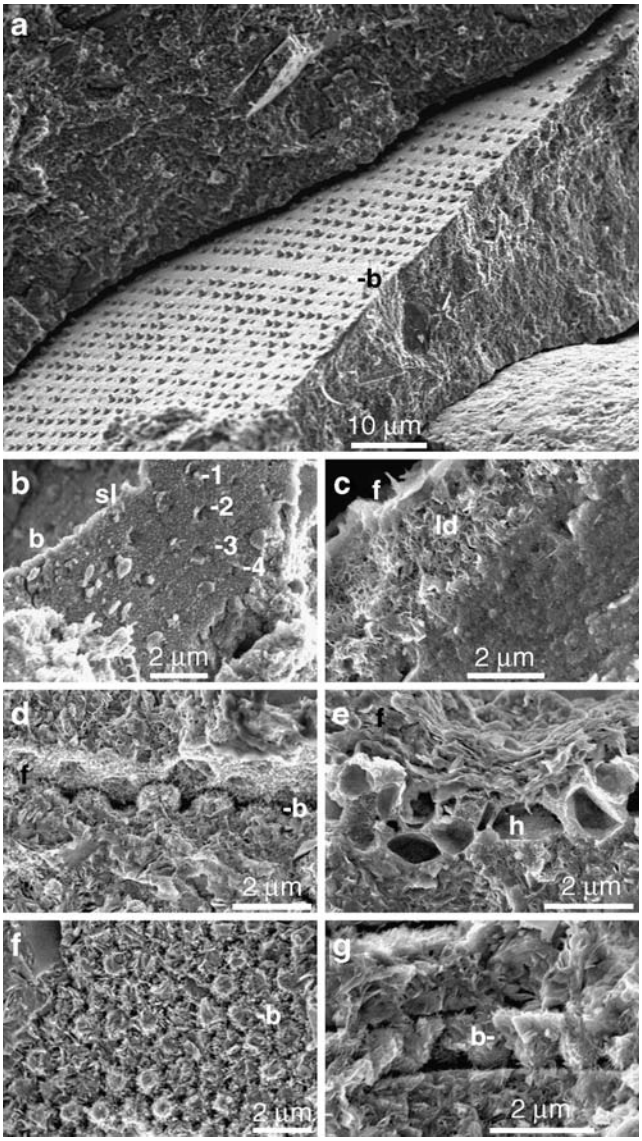

Fig. 3 Cone-like structures (operationally abbreviated here with *b*, denoting bacteria, and identified as such below) on plane areas within Mn-nodules (high-resolution SEM images). **a** Phalanx of cones, arranged in parallel lines, on surfaces of plane structures within the nodules. The individual cones (*b*), with sizes of 0.8–1.0 µm, are regularly arranged in a pattern with an interspacing of 1.0–1.5 µm. **b** Below the surface layer (*sl*), into which the cones (*b*) are embedded, an organized lamellar zonation of four layers (designated *1* to *4*) can be recognized. These are delimited by a line of 1-µm holes, with an interspace of 1.0–1.5 µm between each hole. **c** At the rim of the planes, this organized arrangement ends, and loosely mineralized deposits (*ld*) are formed rather on solid mineral. **d** Two planes including a fissure (*f*) which is split along one subsurface structure, displaying a line of phalanx-like cones (*b*). One side (*lower*) shows the cones (*b*), whereas the corresponding side comprises the mirror imprints. **e** Towards the end of two planes of a fissure (*f*), where the planes merge, holes (*h*) appear. **f** Horizontal view onto a subsurface layer, comprising the cone-like structures (*b*). **g** A front view from this area displays the cones (*b*)

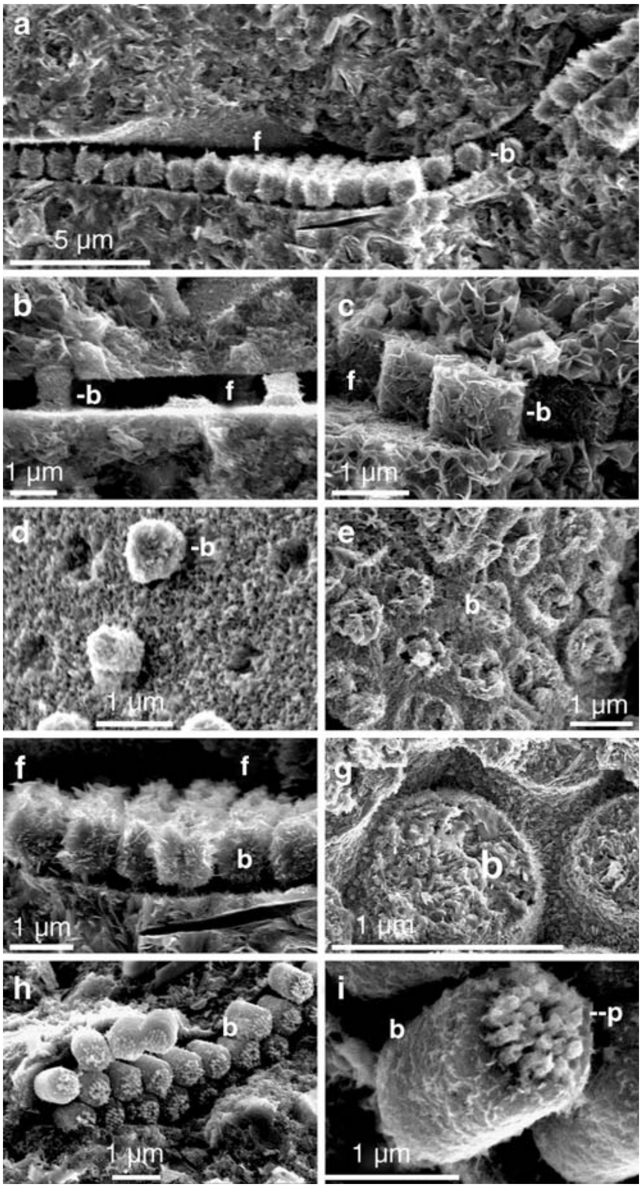

Fig. 4 Identification of the cone-like structures (suggested to be endolithic microorganisms) as bacteria with S-layers (high-resolution SEM images). **a** In most fissures (*f*) within Mn-nodules, solitary cones (*b*) exist which are arranged in a phalanx line. **b**, **c** The microorganisms, existing in close vicinity to the two planes of fissures (*f*), have a pillar-like shape. Their surfaces are covered by crystal-like scale bricks. **d** The ellipsoid morphotype of the cones (*b*) is seen on non-covered "open surfaces" of planes. **e** The cone-like structures (*b*) have lost their protrusions, opening up their locular interior. **f** A phalanx of ellipsoid microorganisms (*b*), aligned along one plane of a fissure. **g** An ellipsoid cone which has lost part of its top, showing its fissured internal structure. **h** Final determination of the suggested endolithic microorganisms as bacteria, based on the existence of S-layer crystalline structures. The batteries of bacteria (*b*) are piled up at a wall. **i** Each individual bacterium (size: 800×300 nm) is decorated on its outward-directed surface, with 20–25 pillar-shaped protrusions (*p*; size: 75×45 nm), the S-layers. The arrangement of the protrusions essentially shows an oblique to square pattern

several nests of microorganisms with a surface cover of S-layers. These pillar-shaped protrusions are all oriented in the same direction, and concentrated to that side which is not attached to the mineral surfaces (Fig. 4h). The elongated microorganisms, now more precisely identified as bacteria within the Mn-nodules, measure—uniformly—800 nm in their longitudinal axis and 300 nm in their cross axis. The pillar-shaped protrusions, arranged on the surfaces of the bacteria in an organized (oblique to square) manner, measure 75 nm in their longitudinal dimension and 45 nm in their transverse (Fig. 4i). Hence, in terms of their morphology/appearance and size, these pillar-shaped protrusions resemble crystalline proteinaceous S-layers. In all, 20–25 pillar-shaped protrusions can be counted per bacterium.

Discussion and conclusions

Biomineralization is one of the most booming branches in the field of marine biotechnology (Morse 1999; Schröder et al. 2007, 2008). Two categories of biomineralization—biologically induced mineralization and biologically controlled mineralization—have been distinguished (see Weiner and Dove 2003). Whereas the former can help to understand the "passive" deposition of mineral onto organic matrices, the latter category serves to explain the direction of nucleation, growth and morphology, as well as the final deposition of minerals via organic matrices and organisms. In the present study, we suggest that the formation of Mn-nodules can best be characterized as a biologically controlled mineralization process. Previously, this important ore material supply in the ocean had been assumed to originate from terrigenous and/or volcanic, and also hydrothermal processes (cf. Elderfield 2006). It was Goldberg (1958) who recognized that the absolute masses of some metals in the ocean exceed their supply from continental rock weathering over geological time. Even though Butkevich (1928) and Wernadskij (1930) reported already on the presence of particular iron bacteria in Mn-nodules, the function of these microorganisms in these nodules, and their mechanism of oxidation have remained unclear until today. The major hurdle in improving our understanding was the fact that—apparently—Mn-nodules grow very slowly, with the consequence that only little organic material can be expected there, and that sufficiently sensitive detection techniques for microorganisms in the nodules were lacking.

At present, and based on the presented SEM images alone, it is not advisable to decide to which kingdom (Archaea or Eubacteria) we should attribute the bacteria identified. Due to the uniform size of the cone-like structures (suggested to be endolithic microorganisms) and of the bacteria with S-layers, we propose that these organisms belong to one, or a few related taxa. Hence, the morphotypes would vary from (1) pillar-like structures, decorated with crystal-like scale bricks, via (2) cone-like structures, with an interior of small cavities/compartments of mineralized walls, to (3) characteristic bacteria comprising, on their surface, outward-oriented S-layer crystalline components. This variation might reflect different stages of mineralization of an endolithic bacterial species existing in the Mn-nodules.

This view is supported by the known biochemical components of S-layers of other bacteria (Kandler and König 1993; Beveridge 1994; Sleytr and Sara 1997). These layers are composed of glycoproteins of high molecular weight (≈200 kDa), acidic and exhibiting many sulphate residues per molecule, in addition to unusual sugars (methylated galacturonic acid and furanosidic galactose).

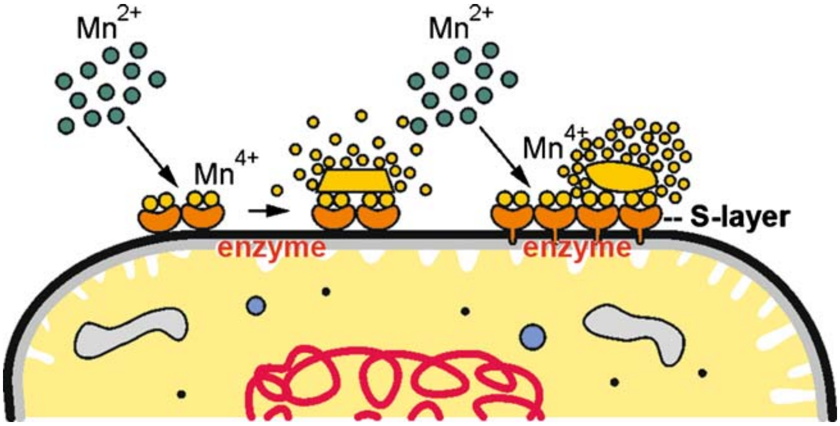

Fig. 5 Proposed biogenic deposition of minerals onto bacteria, from which the growth of nodules originates (schematic). (Ecto)enzymes, proposed to exist on the surface of the microbes, oxidize Mn^{2+} to Mn^{4+}, which is largely insoluble and forms the seeds for subsequent mineralization processes. In addition, it is proposed that these enzymes are arranged at the particles (nm-sized) comprising the *S-layer* (surface *layer*) of the bacteria

In Archaea, the sugars are linked to a polysaccharide backbone consisting of GalNAc-GalA–GlcNAc linear repeats and asparaginyl–GalNAc linkage units. In general, the S-layers are composed of acidic proteins (or glycoproteins) with isoelectric points between pH 3 and 6. Furthermore, the S-layer proteins usually have high amounts of glutamic acid and aspartic acid (together approx. 15 mol% of total amino acids). According to these properties, S-layers have been recently successfully introduced in biotechnological processes. To exploit the high density and defined position of the carboxy groups located on the surface of S-layer lattices, immobilization (covalent attachment) of different (macro)molecules has been achieved (reviewed by Sleytr et al. 1999). Furthermore, also organized non-covalent binding of macromolecules (e.g. polycationic ferritin) to the S-layers has been demonstrated. S-layers have been shown to function as templates in natural mineralization processes, e.g. fine-grain mineral formation (Schultze-Lam et al. 1992), celestine or strontianite nucleation (Schultze-Lam et al. 1992) and iron precipitation (Brown et al. 1998). Building on this information, S-layers have been successfully used to chemically produce Pd-nanoclusters from bound Pd(II)-complexes (see Fahmy et al. 2006).

Considering these data, it is conceivable to accept the crystallization of minerals on bacterial S-layers as the mechanistic basis for mineralization via protein templating, also for the formation of mineral deposits in Mn-nodules. It is experimentally proven that bacteria, especially the endolithic forms, acquire their energy through aerobic lithoautotrophic metabolism (sulphide oxidation, Fe(II) oxidation, Mn(II) oxidation) or anaerobic lithoautotrophic metabolism (anaerobic iron oxidation). These enzymic reactions result in the precipitation of metal oxides (Ehrlich 1966; Edwards et al. 2005).

In our group, we are approaching to isolate and sequence (potential) fragments of bacterial DNA from nodules. However, it is difficult to provide conclusive data that the sequences that might be obtained indeed originate from those bacteria existing within the metal of the nodules, as already stressed by Ehrlich (2002). What we learnt from the present study is that bacteria with S-layers exist in Mn-nodules, providing reasonably solid evidence that mineral formation in Mn-nodules is of biogenic origin. The organic matrix, the surface of the bacteria, provides at least the crystallization seeds for the mineralization. In addition, exo-enzymes (Kellogg et al. 2006) might be proposed which mediate the oxidation of metal ions. Adopting this view it can be understood why, quantitatively in the water/sediment interface at abyssal depths, more Mn is present in Mn-nodules (10^{11} tons for the entire Pacific Ocean) than in the surrounding seawater (10^9 tons). It is reasonable to assume that the enrichment of elements in Mn-nodules, from e.g. 10 ng Mn/l seawater to 100 g Mn/kg nodule (Kennish 2001), is organic template-mediated (causative agent for nucleation) and biologically controlled (compartmentalized crystallization).

This new concept implies (1) supply of sufficient amounts of seed crystal at which nucleation can occur (S-layers) and (2) accelerated velocity of metal ion oxidation (exo-enzymes). Hence, in view of the arguments given, it appears highly likely that initial mineral deposition proceeds on the surface of the bacteria, on the S-layers (driven mainly by the oxidation of Mn(II) and Fe(II) to Mn(III, IV) and Fe (III); Fig. 5), and these deposits are largely amorphous. Considering these data, it is conceivable to accept the crystallization of minerals on bacterial S-layers as the mechanistic basis for mineralization via protein templating, also for the formation of mineral deposits in nodules (Fig. 5). In a second phase, crystallization of the deposits proceeds during an “aging” process, as proposed by Ehrlich (2002). The bacteria remain permanently trapped within the deposited minerals, enabling an abiotic oxidation of the metal oxides.

Studies are in progress to isolate endolithic bacteria from the outer zones of Mn-nodules. It would be advisable to start not only from the surface of the nodules alone (i.e. from the biofilm communities colonizing the nodules; Edwards et al. 2005) but also from the mineralized subsurface regions where endolithic bacteria have been abundantly detected in the present study. If this goal is successfully reached, then new biotechnologies can be developed to accumulate and precipitate the trace amounts of soluble metal ions existing in the marine environment, at a large scale in bioreactors. These novel technological/biotechnological processes can serve for the harvesting, from marine waters, of components required for the steel industry.

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