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Possible evidence for the biogenic formation of spheroidal ferromanganese concretions from the eastern Gulf of Finland, the Baltic Sea

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The fine structure of ferromanganese concretions from the Gulf of Finland has been investigated in detail by Energy Dispersive Spectrometry and Transmission Electron Microscopy. Numerous fine, almost filamental structures are observed within the concretions, many of which appear to be spirals several nm in diameter, which lie within the size range of nannobacteria. Black coarse structures have precipitated on the surface of capsular material on these structures. This material appears to consist principally of birnessite (7Å manganate) with minor amounts of manganosite (MnO). Manganosite is not the thermodynamically most stable form of the manganese oxides in the marine environment and has not been previously identified in either marine ferromanganese concretions or in capsular material on bacteria. The occurrence of fine, filamental structures within the concretions supports the idea that the formation of these concretions may, in part, be bacterially mediated. Bacterial processes may also play a role in the formation of the metastable manganosite phase.

□ *Gulf of Finland, Fe-Mn concretions, electron microscopy, bacterial processes.*

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INTRODUCTION

Since the discovery of manganese nodules in 1873, many scientists have studied the role of microorganisms in their formation. Thiel (1925) concluded that microorganisms, which precipitate manganese, are nearly universal in their distribution and may play a part in the deposition of sedimentary manganese ores. Wernadskij (1930) considered the formation of manganese concretions in fresh and salt water to be mediated by manganese-precipitating bacteria. The observations of Graham and Cooper (1959) supported the argument that manganese-rich deposits on the sea floor originate through biological rather than inorganic processes. Sorokin (1972) reported that bacterial life is more intensive on ferromanganese nodules than in the surrounding sediment, although no specific forms of iron- and manganese-oxidizing bacteria were found on the nodules. Subsequently, LaRock and Ehrlich (1975) identified various kinds of bacteria on the surface and within ferromanganese nodules from the Blake Plateau by means of scanning electron microscopy and culture tests. Baturin and Dubinchuk (1983) observed numerous ultra-microstructures in deep-sea ferromanganese nodules; the most characteristic structures among them were coccomorphic, tubular and broom-shaped forms. These are comparable in size and morphology with spores, cocci, sheaths of iron bacteria and hyphae of actinomycetes. Two ultra-microfossils, *Spirisosphaerospora pacifica* and *Miniactinomyces chinensis*, were identified in manganese nodules from the east Pacific Ocean sampled at a depth of about 5000 m by Lin et al. (1996), Bian et al. (1997) and Zhang et al. (1997). These ultra-microfossils are not cell-wall fragments. The nutritive hypha, reproductive hypha, spore, sporangium and colony have been distinguished in both cases. Recent studies describing the bacterial mediation of manganese and iron oxidation have been presented by Ghiorse and Ehrlich (1992), Ehrlich (1996a, b, 1998), Tebo et al. (1997), Konhauser (1998), Bargar et al. (2000) and Brouwers et al (2000).

The literature on the biogenic formation of shallow-water ferromanganese concretions is much less extensive than that of deep-sea manganese nodules (cf. Dean & Ghosh 1980; Dubinina 1980; Chapnick et al. 1982; Tipping et al. 1985; Ghiorse & Ehrlich 1992). Ghiorse (1980) and Ghiorse & Hirsch (1982) were amongst the first to identify manganese-oxidizing bacteria in Baltic Sea ferromanganese concretions. Subsequently, Zhamoida et al. (1996) reported the results of biochemical analysis of sediments and ferromanganese concretions from the eastern Gulf of Finland in the Baltic Sea. The protein content in individual sections of the spheroidal concretions ranged from 23 to 29 ppm which indicated very high levels of microbial activity. In a key study, Trokowicz (1998) showed that microorganisms play an important role in the cycles of iron and manganese in the Baltic Sea, in particular in facilitating the dissolution of iron and manganese in reducing environments and the precipitation of these elements in oxidizing environments such as on the surfaces of ferromanganese concretions. Three main groups of bacteria were identified: autotrophic, relatively autotrophic and heterotrophic. Four tables were presented listing the characteristics of the principal bacteria identified during that study.

These studies show that microbial structures are reliable indicators of past biogenic activity. In this paper, we investigate the microstructures of bacteria observed in spheroidal ferromanganese concretions from the eastern Gulf of Finland. Detailed descriptions of concretions from the eastern Gulf of Finland have been given by Zhamoida et al. (1996, 2002). Overviews of Baltic Sea concretions have recently been presented by Glasby et al. (1997) and Hlawatsch (1998).

SAMPLE DESCRIPTION AND OCCURRENCE

The eastern Gulf of Finland contains the highest known abundance of shallow-water ferromanganese concretions.

Sample N 95-8 was collected on June 3, 1995, at site N 95-8 (60° 03.40’ N; 27° 45.56’ E, 49 m) situated northeast of Moshny Island during a cruise of the R.V. Professor Logachev. Sampling was carried out using a Reinecke Kastengreifer box-corer. The superficial sediment was brown oxidized silty clay 10-20 mm thick which covered the concretion layer. The concretion layer had a complex structure. Down to a depth of 50 mm, it is olive-gray sandy-clayey silt containing dark brown, spheroidal concretions 2-30 mm in diameter (av. diameter 10-16 mm) displaying microgranular surface texture. The concretions made up to 70% of the sediment volume. Rusty brown iron oxyhydroxide cementation (1-2 mm thick) occurs to a depth of 60 mm. From 60 to 160 mm, a yellow gray sandy clayey silt is encountered which contains spheroidal brown concretions with smooth surface textures but displaying dissolution features. In the upper part of the interval, there are abundant microconcretions 2-3 mm in diameter. The bottom part of interval is enriched in larger concretions 15 mm in diameter and sand grains. The concretion layer at this site is underlain by soft gray early Holocene Ancylus lacustrine clays enriched in black amorphous Fe sulphides. A profile of the sediment column is shown in Fig. 1.

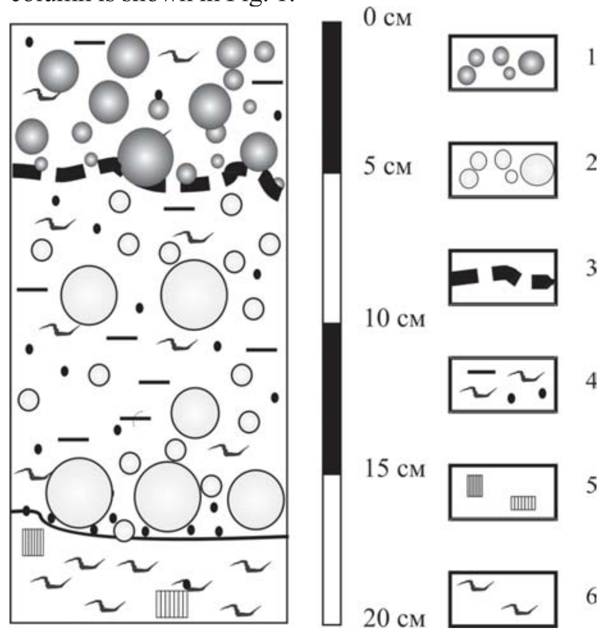

Fig. 1. Distribution of ferromanganese concretions and other minerals with depth in the sediment column at site N 95-8: 1 spheroidal concretions displaying microgranular surface texture; 2 spheroidal concretions displaying smooth surface texture; 3 iron oxyhydroxide cementation; 4 sandy-clayey silt; 5 amorphous Fe sulphides; 6 lacustrine clays.

Sample N 59-1 was collected on August 3, 1994, at site N 94-59 (60° 03.41’ N; 27° 45.18’ E, 51 m) situated northeast of Moshny Island during a cruise of the R.V. Academic Shuleikin. Sampling was carried out using an Ocean-0.25 grab-sampler which samples an area of 0.25 m^2. The description of concretion layer is almost the same as above since both sites are situated within a single concretion field within a distance of 0.19 km from each other. The abundance of the concretions is about 22 kg/m^2.

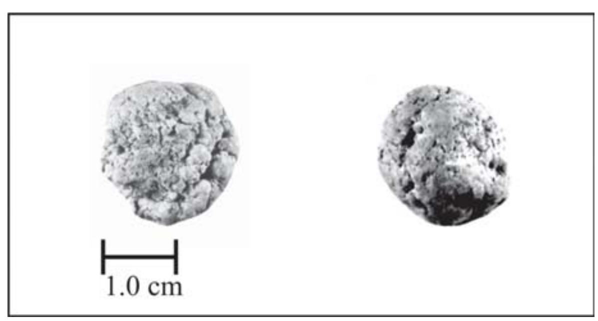

Fig. 2. Photograph of spheroidal ferromanganese concretions 95-8 from the Gulf of Finland.

At both sites, the spheroidal concretions (Fig. 2) selected for SEM (Scanning Electron Microscope) investigations were sampled from the upper part (10-50 mm interval) of the sediment layer containing the concretions.

METHODS AND OBSERVATIONS

Unpolished and polished sections of the spheroidal concretions were observed under the Polarizing Microscope ORTHOLUX-BK and the Scanning Electron Microscope Hitachi X-650 with Energy Dispersive Spectrometer EDAX PV9100.

The surfaces of the concretions display botryoidal growth patterns with individual botryoids about 500-800 mm in diameter (Fig. 3). Some of the larger botryoids appear to have formed as a result of the coalescence of several smaller ones. Particles of mineral such as phyllosilicates and some fossils are always observed in the spaces between the botryoids.

Polished sections of these concretions reveal concentric growth layers (cf. Glasby et al. 1997). Each layer is composed of a dense and a sparse sublayer. The thickness of the layers is about 100-250 mm (Fig. 4), sometimes up to 400 mm. After etching the polished section in an ion coater, these layers were seen to consist of many floccules (Fig. 4). These floccules are about 20-80 mm. Individual detrital particles displaying irregular features are scattered between the floccules. Occasionally, a pseudocolumn with a margin surrounded by discrete detrital particles (clastic sediments) was observed (Fig. 5).

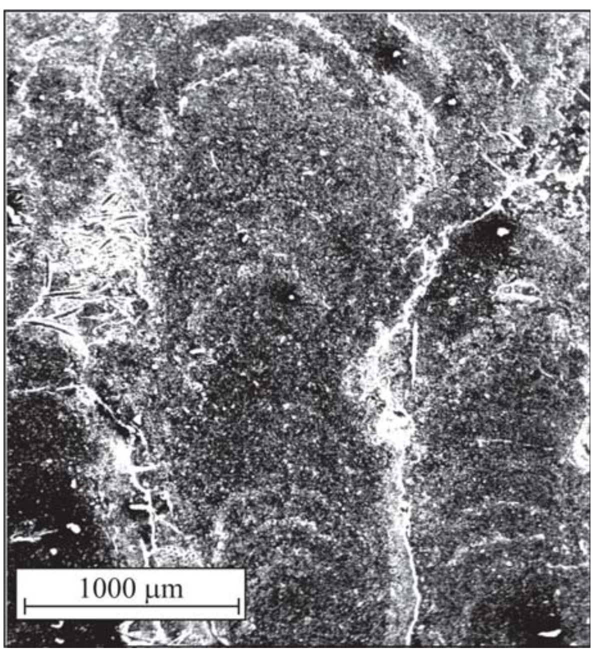

Fig. 3. Scanning electron micrograph (photo 988055) showing botryoidal surface texture in the spheroidal ferromanganese concretion 95-8 from the Gulf of Finland, x30.

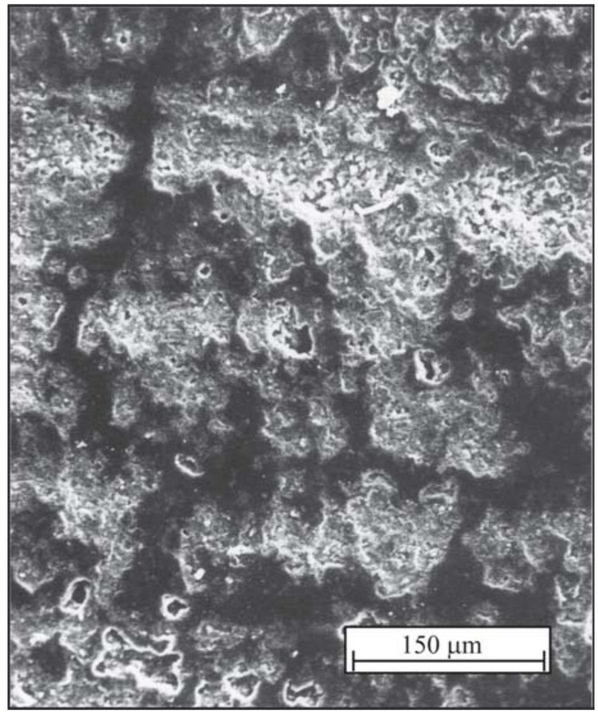

Fig. 4. Scanning electron micrograph (photo 950816) showing the floccules in the spheroidal ferromanganese concretion 95-8 from the Gulf of Finland, x200.

EDS (Energy Dispersive Spectrometer) analysis was carried out at 34 spots on the surface of the polished sections using an accelerating voltage of 20kV (Table 1). The data show that the composition of the concretions is heterogeneous even within an individual micro layer. Generally, the Mn/Fe ratios of these layers are in the range of 3-12 but sometimes can be as high as 44 and sometimes as low as 0.03 in a few layers, such as the bright layers in 970800 which are rich in Fe (Fig. 5). However, regular alternation of the Mn- and Fe-rich layers was not observed.

TEM (Transmission Electron Microscope) observations were performed using a JEM 200CX instrument with Energy Dispersive Spectrometer Link 860 operated at 200kV. Seven specimens for TEM were taken from the periphery to the centre of thin sections of the spheroidal concretions. The specimens was ground in an argon ion mill and coated with a thin carbon film. The TEM micrographs taken from different parts of the concretions show clear differences from any colloidal or crystalline minerals. Numerous fine, almost filamental structures can be seen in these photos, many of which appear to be spirals several nm in diameter (Fig. 6). These black coarse structures appear to be Mn oxyhydroxides which have precipitated on the surface of capsular material consisting of entombed bacteria (cf. Cowen & Bruland 1985; Ghiorse & Ehrlich 1992). The spiral structures are 7-20 nm wide and 30-250 nm long (Fig. 6). The spheroidal spore-like structures are about 5 nm in diameter, which is within the size range of nannobacteria (30-200 nm;

Table 1. EDS analyses of selected areas of the spheroidal ferromanganese concretions, 59-1 (*) and 95-8 (**). Because the loss on ignition during analysis was quite high, all analyses have been normalized to 100% and are expressed in percent. This does not affect the Mn/Fe ratios.

	SiO_2	TiO_2	Al_2O_3	Fe_2O	MnO_2	MgO	CaO	Na_2O	K_2O	Mn/Fe
	9.82		3.78	1.70	81.45		1.82		1.43	44.0
	4.32	0.11	2.18	5.39	83.86		2.34		1.48	14.3
Bright	7.59		3.03	7.37	77.98		2.36		1.57	9.72
	15.88		3.62	6.77	69.38		2.33		1.39	9.41
	6.44	0.02	2.86	17.20	66.97	2.39	1.29	2.04	0.78	3.89
	15.09	0.14	5.94	62.37	5.67	3.70	3.23	2.88	1.02	0.09
layers	14.68		5.63	62.98	6.16	3.67	2.34	3.48	1.07	0.09
(*)	16.95		6.02	63.24	4.30	2.42	2.44	3.92	0.71	0.07
	16.32		2.31	69.23	2.35	2.52	3.40	3.36	0.51	0.03
Dark	22.89	0.18	9.33	12.01	44.98	4.01	0.94	3.64	2.03	3.44
	13.71	0.05	1.83	4.45	73.49	2.13	1.38	2.02	0.94	16.5
layers	4.06		2.51	4.73	80.01	3.10	1.41	3.02	1.16	16.9
	18.40	0.23	5.94	4.62	60.11	3.70	2.64	2.26	2.10	11.93
Mixed	16.02		7.11	5.08	61.78	3.56	1.37	3.14	1.95	11.17
	19.15	0.24	8.23	5.14	57.40	3.39	2.35	2.03	2.07	10.38
bright	19.26	0.36	6.99	5.62	57.25	3.50	2.30	2.64	2.06	9.33
	16.51	0.03	6.80	5.94	60.15	3.68	1.97	2.97	1.95	9.30
and	20.27		8.53	7.13	59.65		1.97		1.88	7.68
	29.57	0.02	7.20	8.08	47.37	2.49	1.42	2.11	1.74	5.85
dark	21.11		6.29	13.29	51.11	2.62	1.29	2.70	1.59	3.85
	19.20		5.90	14.86	51.63	2.57	1.77	2.52	1.55	3.47
layers	18.62	0.38	6.18	13.60	51.20	3.02	2.68	2.63	1.70	3.46
(*)	19.77		8.42	15.52	51.80		2.14		1.58	3.07
	6.13	0.04	2.98	2.62	82.34	3.48	1.15		1.26	28.9
Mixed	9.81	0.12	3.59	2.77	77.21	3.36	1.00		2.15	25.6
	13.47	0.57	4.63	3.83	69.09	2.84	2.56	1.12	1.89	16.59
bright	7.56	0.50	3.47	5.10	74.43	3.14	2.72	1.41	1.68	13.4
	3.33	0.90	0.68	6.33	81.88	0.35	2.92	1.61	1.99	10.68
and	4.75	0.31	2.37	9.93	72.40	3.83	2.67	2.20	1.53	6.70
	8.35	0.35	2.87	11.07	69.30	2.88	2.53	1.27	1.37	5.75
dark	14.06	0.12	6.09	25.17	46.68	2.48	2.01	1.64	1.75	1.70
	15.77	0.23	5.86	25.96	43.17	2.43	2.71	2.40	1.46	1.53
layers	16.31	0.45	5.28	34.56	33.78	2.71	2.45	3.38	1.09	0.80
(**)	12.43	0.04	1.75	58.94	17.77	2.70	2.68	3.27	0.42	0.23

Jackson 1997) (cf. Folk 1997; Folk & Lynch 1997; Nealson 1997; Southam & Donald 1999; Alt and Mata 2000). Occasionally, spheroidal spore-like structures can be seen in the spaces between the filaments. No colonial-type structures or distinct morphologies leading to the identification of microbes were observed.

X-ray diffraction of a bulk sample of the spheroidal Mn concretion showed that the principal manganese oxide mineral present is birnessite (7Å manganate). Previously, Manheim (1965) had demonstrated the presence of todorokite (10Å manganate) in Baltic Sea concretions and Ingri (1985) the presence of birnessite (7Å manganate) in concretions from the Gulf of Bothnia. However, in the latter case, no attempt had been made to prevent the drying of the concretions prior to the study and it could be that the 7Å peak is simply an artefact of the collapse of the 10Å manganate phase (Glasby et al. 1997). A similar situation could have happened here.

EDS analysis demonstrated that the filaments consist of ferromanganese minerals. Electron diffraction studies confirmed that the minerals are poorly crystallized. Typically, 3 rings could be seen in the electron diffraction patterns, although 8 rings were seen in some patterns. Their d-values and intensities are in good agreement with the X-ray diffraction data of manganosite (Table 2). In the diffraction analysis, the lines which are ascribed to manganosite are just above the detection limit indicating that manganosite is a minor mineral within the concretion. The TEM micro-

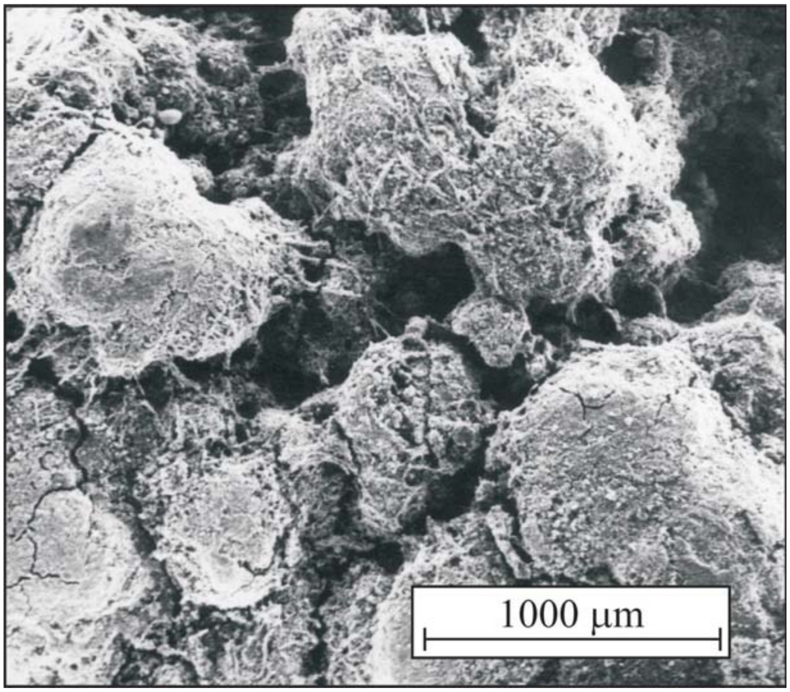

Fig. 5. Scanning electron micrograph (photo 970800) showing a botryoid surrounded by discrete detrital particles (clastic sediments) in the spheroidal ferromanganese concretion 59-1 from the Gulf of Finland, x30.

graphs show that the manganosite occurs as fine grains about 10 nm in diameter surrounding the filaments.

Manganosite (MnO-MnO_{1-15}) typically occurs as green to black octahedral or more rarely cubic crystals in metamorphic or low-temperature hydrothermal deposits (Frenzel 1980; Post 1992). It has only previously been identified and described very briefly in deep-sea nodules from the central Pacific Ocean by Shan (1993) and Zhang et al. (1997) with no explanation of its mode of formation given. In fact, manganosite is not thermodynamically stable in the marine environment and the reason for its occurrence could be quite important in establishing whether biogenic processes are involved in the formation of the concretions. The manganosite appears to occur only in isolated grains in the filamental structures within the concretions. Its formation may be bacterially mediated in a manner analogous to the formation of magnetite (Fe_3O_4) in magnetotactic bacteria (Stolz 1992) or of ferrihydrite (FeOOH) in ferritin micelles of bacteria or fungi (Ghiorse & Ehrlich (1992) or on bacterial surfaces (Fortin et al. 1998). It is possible that, as a result of microbial mediation, the thermodynamically most stable form of the manganese oxides do not necessarily form.

As is well known, there are clear differences in the morphology, mineralogy, composition and growth rates between shallow-marine ferromanganese concretions and deep-sea manganese nodules which makes direct comparison between the two difficult (Glasby 2000). We consider the high growth rates of shallow-water concretions (3-4 orders of magnitude higher than those of deep-sea nodules) to be an indirect argument in favour of their biogenic formation since their rate of formation from purely inorganic processes would not be expected to be sufficiently high to lead to the observed growth rates (cf. Glasby 2000).

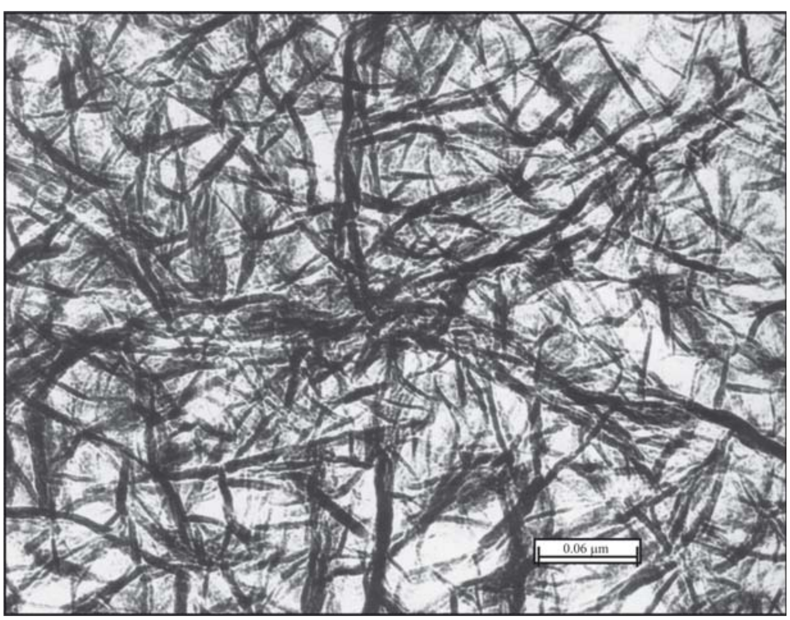

Fig. 6. Transmission electron micrograph (photo 22446) showing the filamental structures in the spheroidal ferromanganese concretion 59-1 from the Gulf of Finland, x150 000.

CONCLUSIONS

Spheroidal ferromanganese concretions from the eastern Gulf of Finland display irregular internal structures. In addition to ferromanganese floccules, clastic material composed of detrital particles, various types of fossils and a few authigenic minerals were always observed on the surfaces and within the concretions. These concretions generally grow concentrically outwards from the centre layer by layer. The process of concretion formation is discontinuous as shown by the irregular variations in the Mn/Fe ratios of the concretions. The occurrence of the concretions lying on the surface of or within the clastic sediments, the presence

Table 2. Electron diffraction data of manganosite in a spheroidal ferromanganese concretion.

manganosite		manganosite(JCPDS 7-230)		
d(Å)	I	d(Å)	I	hkl
2.57	m	2.568	60	111
2.23	vs	2.223	100	200
1.58	s	1.571	60	220
1.34	vw	1.340	20	311
1.28	vw	1.283	14	222
1.11	vvw	1.111	12	400
		1.020	10	331
0.99	vw	0.994	18	420
0.91	vvw	0.907	16	422
		0.855	14	511
		0.786	4	440

vs very strong, s strong, m medium, vw very weak, vvw very very weak

of concentric growth layers and the existence of various types of clastic material within the concretions demonstrate that the formation of these concretions is a separate and individual local phenomenon within the sedimentary environment of the marine basin.

The occurrence of floccules and botryoidal growth patterns in the concretions indicates that the formation of the ferromanganese concretions is not the result of purely physico-chemical precipitation. The microstructures in the concretions as revealed by TEM allow suggesting that these concretions are probably mediated by microbial processes.

Numerous fine, filamental structures with the size range of nannobacteria have been observed within the concretions. Black coarse structures have precipitated on the surface of capsular material which occurs on these filaments. This material appears to consist principally of birnessite (7Å manganate) with minor amounts of manganosite (MnO). The formation of the manganosite may be bacterially mediated.

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