

Ferromanganese Nodules of the Baltic Sea: Composition, Helium Isotopes, and Growth Rate

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Abstract—Results of the study of shallow-water ferromanganese nodules in the Gulf of Finland of the Baltic Sea, which are of practical interest for metallurgical and chemical industries, are discussed. The nodules contain the following elements: Mn, Fe, Si, Al, Na, Mg, Ti, K, V, Cu, Ni, Zn, P, and Ba. Contents of Mn (~30%) and Fe (~10%) are virtually similar to those in deep-sea oceanic nodules. However, concentrations of Ti, Cu, and Ni are notably lower than average values in oceanic nodules. The helium isotopic composition was studied to reveal cosmic dust in the nodule substance. The measured ^3He and ^4He concentrations are $\sim 10^{-12}$ and $\sim 10^{-5}$ cm^3/g , respectively. The isotope ratio $^3\text{He}/^4\text{He}$ is approximately 10^{-7} . More than 60% ^3He is of cosmic (solar) origin, whereas ^4He is of terrigenous (radiogenic) origin. Based on the cosmic dust concentration and the space tracer method, the FMN growth rate is estimated at 8–9 mm/ka at the nodule age varying from ~800 to 1500 yr. The growth rate of nodule has negative correlation with its size. Based on literature data, the growth rate of FMN from the western Baltic Sea is twice as high. An independent calculation of the FMN growth rate based on the diffusion–sorption mechanism (DSM) yielded 8.1 mm/ka, which is very close to the result based on the space tracer method. This value is proposed as the average growth rate of the studied nodules. Comparison with our previous measurements of growth rates for oceanic nodules showed that these values differ only slightly and are equal to n mm/ka, where $n < 10$. It is inferred that the formation mechanism of both marine and oceanic nodules is based on the same principles that control the generation of mobile forms of Mn in the bottom layer of sediments, i.e., principles related to bioproductivity of sea and ocean basins. Fluxes of lithogenic forms of Mn are of minor importance.

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Ferromanganese nodules (FMN) with commercial concentrations of Mn, Fe, and other metals are regarded as perspective base metal ores for the metallurgical and chemical industries. After breakdown of the USSR, main commercial manganese deposits remained beyond the territory of Russia. Ferromanganese nodules of the Baltic Sea, like other seas of Russia, have long been known and much studied (Gorshkova, 1967; Strakhov et al., 1968).

Recently scientists of St. Petersburg discovered a ferromanganese nodule field (reserve 10n Mt) in the Gulf of Finland at a depth of ~50 mbsl not far from St. Petersburg. Mining of this ferromanganese nodule field eliminates to a certain extent the acuteness of manganese ore deficiency in Russia (Kurnygin, 2004). Ferromanganese nodules are known to be good sorbents of many metals (including the artificial ones) transported to the sea (Chelishchev et al., 1992; Hlawatsch et al., 2002a, 2002b). Therefore, it is important to know the growth (reproduction) rate of nodules under natural conditions. However, solution of this problem by standard radioisotope methods is hampered by serious difficulties. Traditionally used radioactive isotopes ^{230}Th , ^{231}Pa , ^{234}U , and ^{10}Be have a relatively long halflife, and

indirect signs show that Baltic nodules grow fast. Therefore, one of the main problems to be solved in this work was to establish the growth rate of FMN from the Gulf of Finland by the space tracer method based on the ^3He stable isotope delivered to sediments by cosmic dust. Cosmic dust particles are saturated with solar wind ions during the residence in open space. Therefore, the particles transport to terrestrial sedimentary rocks solar helium with a higher isotope ratio $^3\text{He}/^4\text{He} \sim 10^{-4}$ compared to helium from rocks of the Earth's crust, for which this ratio makes up 10^{-8} – 10^{-7} . As a result, ^3He isotopes in FMN samples are mainly of the solar (cosmic) origin. This phenomenon can be used for establishing the growth rate and age of nodules without a priori assumption on the constancy of the FMN growth rate (Anufriev et al., 1996). It is only within this assumption that application of widely used methods of nuclear geochronology is possible (Kuznetsov, 1976). Solution of problems mentioned above requires knowledge of the chemical composition of FMN. This was also one of the purposes of the present work.

Table 1. Results of chemical analyses of the Baltic FMN

Element	Gulf of Finland, wt %	Western Baltic Sea*, wt %	Element	Gulf of Finland, wt %	Western Baltic Sea*, wt %
Mn	32	23.8 ± 12.8	K	0.81	–
Fe	9.15	14.7 ± 12.8	V	0.012	–
Si	5.14	–	Cu	0.01	0.002 ± 0.00042
Al	2.7	0.7 ± 0.3	Ni	0.03	–
Na	0.56	–	Zn	0.116	0.0125 ± 0.0316
Mg	1.28	1.41 ± 0.4	Pb	≤0.01	–
Ti	0.105	–	Ba	0.235	–

Note: (*) FMNs of the western Baltic Sea region also contain Ca, Li, Co, and Mo that are not included in Table 1. (–) Not analyzed.

Table 2. Results of the helium isotopic study in FMN samples from the Gulf of Finland

No.	Weighed sample, g	$^4\text{He} \times 10^6$, cm ³ /g	$^3\text{He} \times 10^{12}$, cm ³ /g	$(^3\text{He}/^4\text{He}) \times 10^7$	Object
1	0.5435	13.7 ± 1.4	1.3 ± 0.13	0.95 ± 0.15	Powder of four nodules, diameter ~25 mm
2	2.1423	16.4 ± 1.5	1.3 ± 0.13	0.815 ± 0.11	Single nodule, diameter ~25 mm
3	0.6199	11.7 ± 1.1	4.5 ± 0.4	3.8 ± 0.4	Nodule surface, diameter ~25 mm
4	0.4011	13 ± 1.3	1.3 ± 0.13	1.0 ± 0.14	Powder of four nodules, diameter ~25 mm
5	1.9319	15.6 ± 1.5	1.37 ± 0.13	0.88 ± 0.12	Powder of small nodules, diameter ~5–10 mm

MATERIALS AND METHODS

According to the available data (Kurnygin, 2004), FMNs of the Gulf of Finland lie on the seafloor as a continuous bed up to 1.5 m thick. Nodules are mainly irregular spherical and up to 30 mm in size.

The chemical composition of nodules was determined by the standard chemical method using the high-frequency ICP-MS spectrometer (PC 1000) at the final stage. The calibration of mass spectrometer was based on standard solutions of elements. Reliability of the analysis was checked by comparing the data on different weighed samples. The relative error of analyses was ±4%.

The procedure of sampling preparation for analyses was as follows.

Four nodules of nearly same diameter (~25 mm, ~40 g) were ground to a grain size of 1 mm or less. One portion of the material was used for the chemical analysis, while the second portion was used for the helium isotopic analysis. This procedure allows us to obtain average values for both concentrations of chemical components and the amount of cosmic dust particles in the analyzed samples.

The helium isotopic analysis was carried out using the high-resolution magnetic resonance mass spectrometer (MRMS) operating in the static exhaust regime (Anufriev et al., 2006). Helium was extracted from samples by heating them in vacuum with the subsequent getter purification from chemically active gases. The extraction device (Anufriev et al., 1977) was

connected with the mass analyzer chamber. This technique simplified the procedure of helium introduction into the ionic source of mass analyzer.

RESULTS

Chemical composition. Table 1 presents results of chemical analyses. For comparison, the table also shows data on analyses of FMN from the western Barents Sea (Hlawatsch et al., 2002a). It is evident that the concentration of major rock-forming elements Mn and Fe (within error limits) in the studied FMN is nearly the same as in nodules of the western Baltic Sea. Similar Mn and Fe concentrations are also typical of the Pacific FMN (Volkov, 1979; Baturin, 1986; *Atlas...*, 1990; Andreev, 1994). According to the accepted classification (Volkov, 1979), the Mn/Fe ratio (3.5) in the studied nodules suggests that they can be referred to the type of ferromanganese nodules.

Isotopic composition. Table 2 presents results of the helium isotope study. In runs 1 and 4, we used weighed samples taken from the same material obtained by grinding four nodules (Table 1). Fair coincidence of results in the analyses indicates a sufficiently complete averaging of cosmic material concentration (as a result of FMN grinding) in the whole powder volume.

When comparing with published results of isotope analyses of helium in oceanic FMN (Sano et al., 1985; Baturin, 1986; Anufriev et al., 1989), one can note that

Table 3. The solar component of ^3He , growth rate, and age of FMN from the Gulf of Finland

No.	$^3\text{He}_s \times 10^{-12}, \text{cm}^3/\text{g}$	$r, \text{mm/ka}$	t, yr	Object
1	0.89	8.4	1500	Powder of four nodules, diameter ~25 mm
2	0.82	9.1	1400	Single nodule, diameter ~25 mm
3	4.1	1.8	–	Nodule surface fragment, diameter ~25 mm
4	0.91	8.2	1500	Powder of four nodules, diameter ~25 mm
5	0.90	8.3	780	Powder of small nodules, diameter ~5–10 mm

nodules from the Baltic Sea are characterized by lower (by two orders of magnitude) isotope ratios $^3\text{He}/^4\text{He} \sim 10^{-7}$. This is related to the fact that the concentration of terrigenous ^4He is an order of magnitude higher, while the concentration of cosmic (solar) ^3He is an order of magnitude lower than in the oceanic FMN. It should be pointed out that high ^4He concentration indicates both an old age of the Baltic terrigenous material (carrier of ^4He isotope) and, probably, a high growth rate (r) of Baltic nodules relative to the growth rate of oceanic FMN. To determine the r value (Anufriev et al., 2005) in the case of low isotope ratios $^3\text{He}/^4\text{He} \sim 10^{-7}$, it is necessary to separate the cosmic (solar) share of helium He_s in the measured (bulk) He_{mes} value. Based on study of the helium isotopic composition in lunar dust (Anufriev et al., 1983; Anufriev and Boltenkov, 2005), it is taken into account that all cosmic helium represents solar wind-implanted helium. The solar wind component of helium He_s can be identified within a two-component model (terrigenous helium He_t and solar helium He_s according to the expression reported in (Anufriev, 1985; Anufriev and Boltenkov, 2005):

$$\frac{^3\text{He}_s}{^3\text{He}_{\text{mes}}} = \left(1 - \frac{(^3\text{He}/^4\text{He})_t}{(^3\text{He}/^4\text{He})_{\text{mes}}}\right) \cdot \left(1 - \frac{(^3\text{He}/^4\text{He})_t}{(^3\text{He}/^4\text{He})_s}\right)^{-1}, \quad (1)$$

where s is solar parameters, t is terrigenous parameters, mes is measured parameters and values.

The share of terrigenous helium $^4\text{He}_t$ in the measured helium $^4\text{He}_{\text{mes}}$ within the two-component model can be found from the equation:

$$\begin{aligned} & \frac{^4\text{He}_t}{^4\text{He}_{\text{mes}}} \\ &= \left[\left(\frac{^3\text{He}}{^4\text{He}} \right)_s - \left(\frac{^3\text{He}}{^4\text{He}} \right)_{\text{mes}} \right] \cdot \left[\left(\frac{^3\text{He}}{^4\text{He}} \right)_s - \left(\frac{^3\text{He}}{^4\text{He}} \right)_t \right]^{-1}. \end{aligned} \quad (2)$$

According to published data (Krylov, 1984), the $(^3\text{He}/^4\text{He})_t$ value ranges within 10^{-8} – 10^{-7} . Moreover, if U and Th concentrations are equal and the preservation of helium is identical, the isotopic ratio $(^3\text{He}/^4\text{He})_t$ has negative correlation with the age of rocks. Rocks of the Baltic Shield surrounding the Gulf of Finland are ranked among the oldest ones in the Earth's crust. Therefore, the terrigenous helium isotopic ratio can be

close to the lower limit of the range mentioned above, i.e., to $(^3\text{He}/^4\text{He})_t \sim 10^{-8}$. To define more exactly the $(^3\text{He}/^4\text{He})_t$ value, we carried out the following investigations. We measured the isotopic composition of helium in the eolian dust sampled over three months at the coast of the Gulf of Finland [Lisitsyn, 1974]. It was found that $(^3\text{He}/^4\text{He}) = 3 \times 10^{-8}$. This value was for $(^3\text{He}/^4\text{He})_t$ in Eq. (1). According to different estimates (Geiss et al., 1970; Anufriev et al., 1983; Anufriev and Boltenkov, 2005), the $(^3\text{He}/^4\text{He})_s$ value is $(2-4) \times 10^{-4}$. The mentioned uncertainty of the $(^3\text{He}/^4\text{He})_s$ value does not affect appreciably results based on formulas (1) and (2). The $(^3\text{He}/^4\text{He})_{\text{mes}}$ values obtained for different samples are given in the fifth column of Table 2. The solar and terrigenous components can be obtained from Eqs. (1) and (2). The results of calculations are presented in Table 3.

The analysis shows that the solar ^3He and terrigenous ^4He in the sedimentary rock sample account for more than 60 and 99.9%, respectively. The growth rate r of ferromanganese nodules can be found from the following expression (Anufriev et al., 1996):

$$r = k \cdot F / \rho \cdot ^3\text{He}_s \quad (3)$$

where $k = 0.5$ is the coefficient of cosmic dust accumulation (Anufriev and Boltenkov, 1996), F is the flux of ^3He isotope. Let us assume that the $^3\text{He}_s$ value is equal to $2.4 \times 10^{-15} \text{ cm}^3/(\text{cm}^2 \text{ yr})$ (Anufriev et al., 1996a) obtained for the Pacific Ocean; FMN density $\rho = 1.6 \text{ g/cm}^3$; and $^3\text{He}_s$ is the solar helium concentration in the sample (Table 3). Table 3 presents results of the calculation of the growth rate r . The growth rate value (8–9 mm/ka) obtained is close to the value reported from the western Baltic Sea (20 mm/ka) in (Hlawatsch et al., 2002a, 2002b).

DISCUSSION

We assume that the FMN growth rate should be nearly equal in different regions of the Baltic Sea. The growth rates (r) obtained for FMNs from the Gulf of Finland and the western Baltic Sea in (Hlawatsch et al., 2002) show a nearly twofold difference (8–9 and 20 mm/ka, respectively). In this connection, the question arises as to whether the twofold difference of the r

value is an artifact owing to the application of as yet exotic methods for the determination of the growth rate of Baltic ferromanganese nodules. Let us analyze values of parameters used to calculate the r value. The most vulnerable value in Eq. (3) is the $F(^3\text{He})$ flux in the calculation of the growth rate by the space tracer method. Other existing data (Marcantonio et al., 1998, 1999) yield approximately two times lower $F(^3\text{He})$ values that depend little on geographic coordinates. The use of this value in Eq. (3) diminishes the r value (Table 3) and increases discrepancy of the comparable values. We determined the FMN density ρ many times, and this parameter never exceeded 2 g/cm^3 . These results coincide with the value of 1.95 g/cm^3 reported in (Greenslate, 1977). Substitution of this density value in Eq. (3) does not change the r value. The $^3\text{He}_s$ value was calculated based on three different $^3\text{He}/^4\text{He}$ ratios determined experimentally. Uncertainty of these values may change the $^3\text{He}_s$ value by no more than 15%. This parameter also has an insignificant influence on the r value. Hence, another choice of parameters in Eq. (3) may either decrease or slightly increase the r value, but does not change the discrepancy of the comparable values.

The method used in (Hlawatsch et al., 2002a) is based on the analysis of the Zn concentration profile in the nodule body and the following assumptions: zinc in Baltic ferromanganese nodules is mainly of the sorption and man-caused origin and the first considerable discharge of technical Zn into the western Baltic Sea, which provoked the peak of Zn concentration in the profile, took place approximately 100 years ago in 1870. In this method, the growth rate r is assumed as constant and found from the equation:

$$r = l/t, \quad (4)$$

where $l = 2 \text{ mm}$ is the distance from the nodule surface to peak in the Zn profile (presumably, 100 years ago). Hence, $r = 2 : 100 = 20 \text{ mm}/10^3 \text{ years}$. It should be noted that the nodule considered in the work is not spheroid but platy. Therefore, its growth rate in different directions cannot be constant, and the relationship between parameters l and t is not unambiguous enough to fulfill the requirement for model (4). Moreover, since nodules are porous bodies, it is likely that the used deep peak of Zn actually represents a peak of the present-day highly concentrated Zn sorbed into deep zones of nodules over a long indefinite period. In other words, the results obtained cannot be considered as unambiguous.

In order to check the reliability of values obtained, we used an independent method of the calculation of the growth rate (Anufriev and Boltenkov, 1996; Anufriev et al., 1999) based on the Mn flux and the diffusion-sorption mechanism of nodule formation. Efficiency of the method was tested on Pacific nodules (Anufriev and Boltenkov, 1996; Anufriev et al., 1999).

In this model, the growth rate of a spherical nodule is determined by the following equation:

$$r = \frac{DC}{\rho f R}, \quad (5)$$

where D is the constant of Mn diffusion, C is the Mn concentration in interstitial water, ρ is the density, f is the relative weight content of Mn, and R is the nodule radius.

The value $D = 2.3 \times 10^{-6} \text{ cm}^2/\text{s}$ was based on data from (Li and Gregory, 1974) assuming that the annual mean temperature of bottom seawater equals 8°C . A choice of another (similar in value) temperature will change but slightly the constant D . In accordance with data in (Hlawatsch et al., 2002a), concentration $C = 6.7 \times 10^{-6} \text{ g/cm}^3$ was chosen for the upper 2-cm layer of sediments at Station 9 with maximal values of Mn concentration. The nodule substance density ρ is 1.6 g/cm^3 . This is the minimal value among the measured ones. The relative concentration of Mn $f = 0.25$ was chosen according to data in Table 1. Let us consider that the radius of a nodule, which is similar to the studied variety (Tables 2 and 3) and is growing in the upper 2-cm layer of sediments, is equal to 1.5 cm . Using Eq. (4), we shall get $r = 8.1 \text{ mm/ka}$. This value is almost identical with the growth rate based on the concentration of cosmic ^3He (Table 3) and is nearly twice as low as the value given in (Hlawatsch et al., 2002a). The analysis showed that maximal r values were used as parameters in Eq. (5). Hence, another choice of parameters in (5), which would nearly double the growth rate (up to 20 mm/ka) seems to be impossible. Thus, if we assume that the FMN growth rate in the Baltic Sea basin is constant or it can slightly vary in different regions, then it is reasonable to take the value of 8 mm/ka as the average one.

CONCLUSIONS

Study of the chemical composition of ferromanganese nodules in the Gulf of Finland (Baltic Sea) demonstrated that the Mn and Fe contents in FMN of the gulf are nearly similar to those in oceanic nodules. However, concentrations of Ti, Cu, and Ni are noticeably lower than average values in oceanic nodules.

Isotopic studies of helium carried out to reveal the cosmic component in FMN samples from the Gulf of Finland showed that the characteristic value of the helium isotope ratio in the nodules was $^3\text{He}/^4\text{He} \sim 10^{-7}$, which is nearly two orders of magnitude less than the ratio in deep-sea oceanic nodules. In eolian dust collected on the gulf coast, the terrigenous component of nodules yielded $^3\text{He}/^4\text{He} = 3 \times 10^{-8}$. Concentrations of solar and terrigenous helium were calculated based on the model of two-component, i.e., terrigenous (radiogenic) helium and solar (cosmic) helium composition of helium in FMN. The solar $^3\text{He}_s$ concentration accounts for nearly 70% of the measured ^3He concen-

tration. The remaining amount of ^3He (~30%) is of terrigenous origin. By contrast, the major amount of ^4He (virtually 100%) is of terrigenous origin. It should be pointed out that the surface layer of relatively large nodules (diameter ~25 mm) comprises an elevated amount of solar $^3\text{He}_s$ (up to ~90%).

Study of shallow-water ferromanganese nodules from the Gulf of Finland revealed that they comprised cosmic dust with implanted solar corpuscular radiation. Measurements based on the space tracer method, demonstrated that the FMN growth rate in the Gulf of Finland is 8–9 mm/ka. This value is supported by the growth rate (8.1 mm/ka) calculated for the Baltic FMN based on the diffusion–sorption model.

A substantial decrease in the growth rate in near-surface layers of nodules (Sample 3, Table 3) is likely to indicate growth deceleration at increasing nodule size, i.e., variation in this parameter during the growth of nodules. The obtained ages of FMNs from the Gulf of Finland (~800–1500 yr) suggest that the process of their formation is intensely continuing at present.

Comparison of the growth rate of Baltic nodules (this work) and Pacific nodules (Anufriev et al., 1996; Anufriev and Boltenkov, 1996) shows that these values are equal to n mm/ka, where $n < 10$. Hence, mechanism of the formation of both marine and oceanic FMN (Volkov, 1979; Anufriev et al., 1999) is governed by the same processes that govern the formation of mobile forms of Mn in the bottom layer of sediments. The works cited show the role of detritus in the formation of mobile forms of Mn. Hence, the FMN growth rate is governed by bioproductivity and the related rate of reducing processes in the bottom layer of sediments. The influx of lithogenic forms of Mn is of minor importance in this process.

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