

THE ORIGIN OF NICKEL COMPONENT IN MARINE SEDIMENTS

By

Kazuo YAMAKOSHI

Department of Physics, Faculty of Science, Kyoto University, Kyoto, Japan

(Received December 4, 1970)

ABSTRACT

The origin of nickel component of the deep sea sediments is discussed. The extraterrestrial nickel fraction is thought to be supplied through grain sedimentation and the terrestrial nickel fraction is through ionic (or colloidal) sedimentation into deep sea sediments. The nickel, iron and manganese contents in various size groups of pelagic red clay, globigerina ooze and gray ooze, off the Torishima Island are obtained. A few examinations show that ionic supply of nickel component overcomes grain supply in deep sea sediments.

1. Introduction

In pelagic deep-sea sediments nickel and manganese components are contained in higher concentration than in igneous rocks.

The origin of these excess parts has been discussed and investigated by many workers¹⁻⁹⁾.

Moreover vertical distributions of nickel, iron and manganese components in deep-sea sediments are revealed by the studies of long cores raised from the Swedish Deep Sea Expedition with the Albatros in 1947-1948^{2,3)}.

The typical patterns of vertical distributions of these elements in a long red clay core are shown in Fig. 1^{2,3)}. The NiO content varied from a maximum of 0.089 wt% to a minimum of 0.041 wt%. Five distinct maxima occurred at various depths, and average value was 0.056 wt%. Except one minimum no correlation between the variation of three oxides is evident from the curves. Four sources of nickel content in red clay were considered by H. Petterson^{2,3)}. The extraterrestrial supply (meteoric dust) was considered as the most considerable source by him. While high manganese concentration in red clay was considered as to be supplied through volcanic matters.

This interpretation of the origin of nickel component was objected by Smales and Wiseman⁴⁾, Laevastu and Mellis⁵⁾ and Smales, Mapper and Wood⁷⁾.

Laevastu and Mellis⁵⁾ separated magnetic spherules from the various depths in the same core which is studied about the vertical distribution of nickel, iron and manganese components by Petterson and Rotschi³⁾. The size of the separated spherules ranged from 10 to 230 microns. And they obtained the relation between spherule concentration and depth in the core. In Fig. 2 a concentration of magnetic spherules in upper three meters of the core is shown, compared with the nickel content in the same depth. In the paper by Laevastu

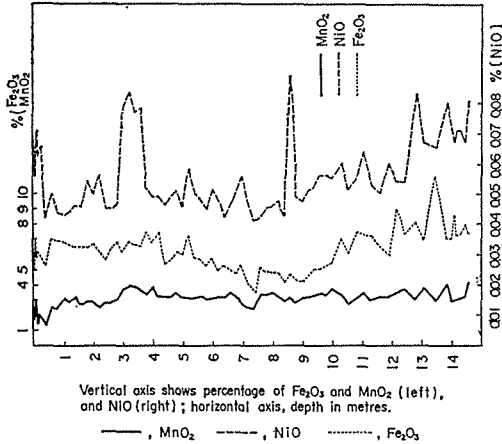


Fig. 1. The vertical distribution of nickel, manganese and iron contents in the sedimental core 72, obtained by Petterson and Rotschi^{2,3)}.

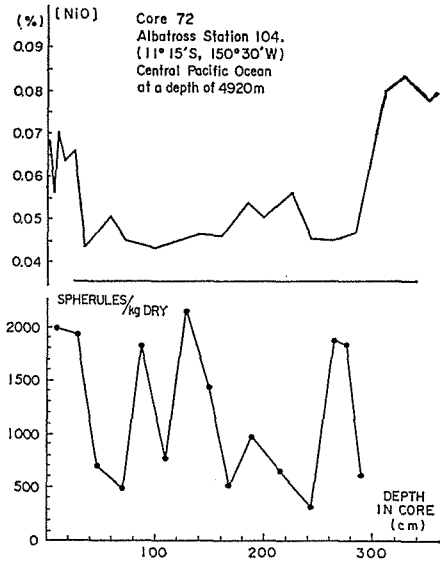


Fig. 2. Comparison of the vertical distribution of nickel contents* with metallic spherule concentration** in the same sedimental core. (* Petterson and Rotschi^{2,3)}, ** Laevastu and Mellis⁵⁾)

and Mellis it is emphasized that no correlation between the spherule concentration and nickel content in the core is present.

Smales and Wiseman pointed out that the ratio of nickel to cobalt and nickel to copper in red clay is similar to the ratio in igneous rocks and extremely different from the ratio in meteorites. The ratios in various materials is shown in Table 1⁴⁾.

Table 1. Average ratios involving nickel, cobalt and copper by Smales and Wiseman⁴⁾.

	(Ni/Co)	(Ni/Cu)	(Cu/Co)
Red Clay	3.1	0.85	3.7
Globigerina ooze	4.1	0.77	5.4
Manganese Nodules	4.3	1.2	4.3
Oceanic Rocks	2.3	1.6	2.7
Average for Igneous Rocks (Rankama & Sahama, 1950)	3.5	1.1	3.0
Meteorites (Stones and stony irons)	22.7	100	0.24
Average for Meteorites (Rankama & Sahama, 1950)	13.1	92	0.14

Moreover the same opinion was repeated in the investigation by Smales, Mapper and Wood⁷⁾. In that work nickel, cobalt and copper contents in igneous

rocks, marine sediments and meteorites were determined using neutron activation analysis.

Oepik discussed also about this problem⁶⁾. He stated that comparisons of the ratios of nickel to cobalt and copper is not so important and the ratio of nickel to cobalt in solar atmosphere is rather similar to the ratio in red clay than to the ratio in meteorites.

In 1954 Goldberg¹⁰⁾ proposed a idea of the scavenging of various trace elements into the sediments by the hydrated oxides of manganese and iron.

Amano, Okada and Shima⁹⁾ examined soluble and insoluble nickel fractions by 1 N HCl in a long deep-sea core. They considered, soluble nickel was brought as Fe-Ni alloy from cosmic material and insoluble nickel was supplied as a camouflage element in the silicate minerals of terrestrial origin.

In § 2 of this work the objections by Laevastu and Mellis and also by Smales and his coworkers are discussed. In § 3 the relations between nickel, iron and manganese components in deep-sea sediments are examined. In § 4 the amount of nickel fractions of terrestrial and extra-terrestrial origins are estimated.

2. Comments to the objections by Laevastu and Mellis and also by Smales and his coworkers

The objections by Laevastu and Mellis is not so effective against Pettersson's hypothesis. Nickel content in red clay must be compared with the weight, not the number, of spherules of all sizes per unit volume. Therefore the values of spherule concentration limited in size from 10 to 230 microns per unit volume, which were compared with nickel content in red clay in that paper, is meaningless.

If the total weights of spherules ranging from 10 to 230 microns in size were used, however, it may be difficult to compare them with nickel contents in red clay. Because a fairly amount of nickel is present also in the size fraction of smaller than 10 microns in red clay.

In this work the nickel, manganese and iron contents in a size fraction of smaller than 6 microns in a red clay sample^{*)} are obtained.

Table 2. The nickel, manganese and iron contents in a red clay sample^{*)} in fraction of smaller than 6 microns in size.

[Ni]=0.020	[Mn]=0.48	[Fe]=6.28
(percent by weight)		

According to Sverdrup's data²²⁾ the fraction of smaller than 6 microns in size exceeds 90 % of total red clay. Therefore in that fraction the nickel content exceeds $(0.020/0.023) \times 0.9 = 0.78$ of total nickel in red clay, where the average nickel content is 0.023 % in this red clay sample.

And next, the (Ni/Co) ratios, which are obtained by Smales and his coworkers⁷⁾ using neutron activation analysis are distributed widely from 1.4 to 7.1.

Furthermore the average ratios of nickel to cobalt contents in sea-water are estimated 26.7 and 30.5 in the Central and Eastern Pacific Ocean respecti-

^{*)} This red clay sample was dredged up at the location (0°00'N, 150°05'E) in 1968.

vely¹¹⁾. These values are larger than the ratio in meteorites. And the average ratio of nickel to copper contents in sea-water is estimated 0.146 for 28 samples¹¹⁾.

These complicated differences may be not so cleared up by a simple hypothesis.

3. Studies on relations between nickel, iron and manganese components in deep-sea sediments

Nickel, iron and manganese contents in red clay, globigerina ooze and ferro-manganese nodules, which were obtained during the cruise KH-67-5 with the Hakuho-Maru from December 1966 to February 1967 in the North Pacific Ocean, are determined and shown in Table 3^{*)}. The data determined in many investigations and in this work are plotted in Figs. 3 and 4. From the results of Figs. 3 and 4 it can be said nickel component is coprecipitated on the whole with the hydrated oxides of manganese and iron into the bottom-sediments. It is a noteworthy fact that similar ratios of nickel to iron and manganese components are found also in the ferro-manganese nodules. It may suggest the origin or the growth-process of ferro-manganese nodules.

Next it is the problem, which occurs as the supply process of nickel component to the deep-sea sediments the ionic (or colloidal) precipitation or grain sedimentation.

From Pettersson's curves, which are shown in Fig. 1, it can be said, that the nickel fractions at the peak positions may be supplied through grains but the nickel fractions at the other plain positions through ionic precipitation.

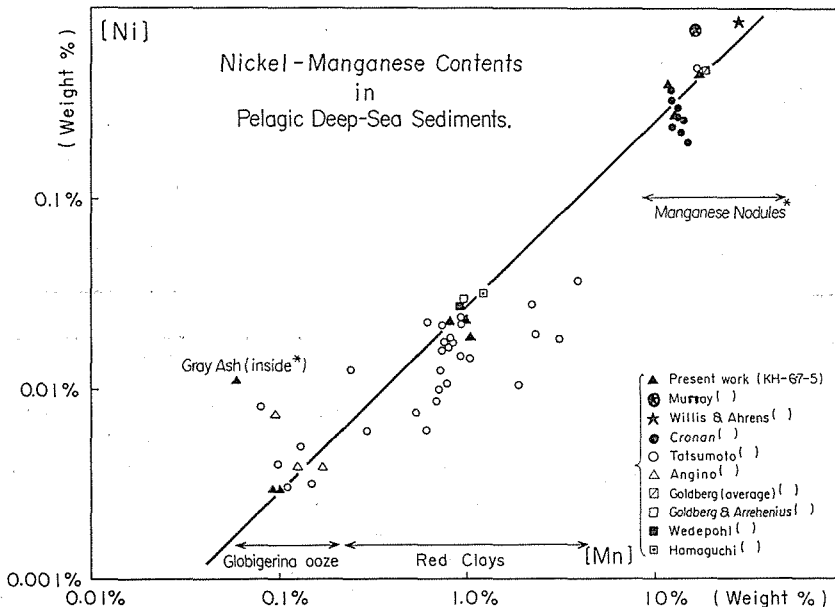


Fig. 3. Nickel-manganese contents in pelagic deep-sea sediments.

^{*)} The experimental errors of chemical analysis in this work do not exceed $\pm 15\%$.

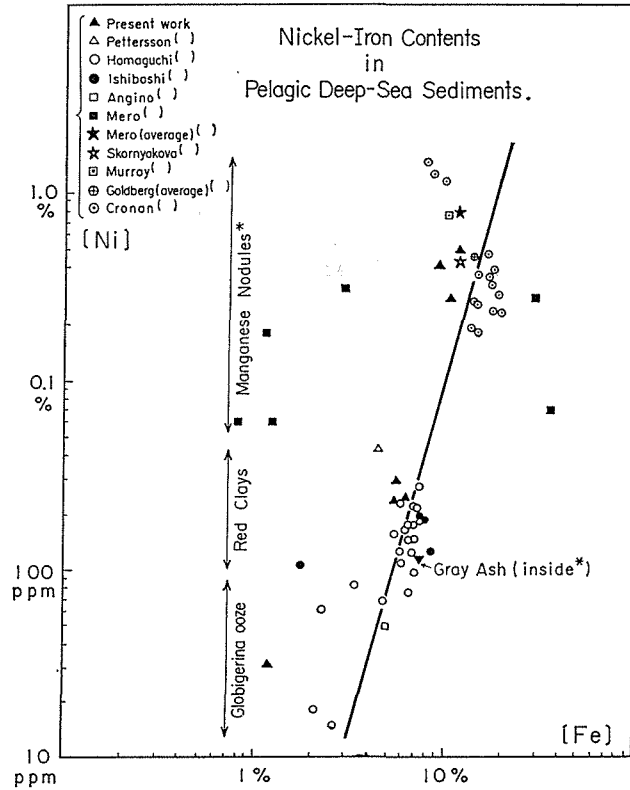


Fig. 4. Nickel-iron contents in pelagic deep-sea sediments.

Table 3. Nickel, iron and manganese contents (percent by weight) and (Ni/Mn), (Ni/Fe) ratios in red clay, globigerina ooze and ferro-manganese nodules. (this work)

Sample code	Sample	[Ni]	[Fe]	[Mn]	(Ni/Mn)	(Ni/Fe)
St-17*	red clay	0.023	6.01	0.96	0.024	0.0038
St-34**	red clay	0.029	5.47	1.08	0.027	0.0053
St-36***	red clay	0.023	5.49	0.84	0.027	0.0042
St-25****	globigerina ooze	0.003	1.18	0.10	0.03	0.0025
St-34	ferro-manganese nodules	0.498	11.29	16.21	0.030	0.0042
St-34	ferro-manganese nodules	0.401	8.79	12.10	0.033	0.0045
St-36	ferro-manganese nodules					
	(manganese crust)	0.277	10.23	13.43	0.021	0.0027
	(gray ash)	0.011	7.29	0.059	0.19	0.0015

* St-17 (0°01.3'S, 150°04.2'E), depth 5245 m.

** St-34 (09°16.3'N, 179°20.5'W), depth 6000 m.

*** St-36 (11°30.8'N, 177°19.9'W), depth 5400 m.

**** St-25 (02°17.6'N, 167°00.0'E), depth 4260 m.

If the empirical relation of "cosmic spherules", $VN = \text{constant}$ is reliable, where V is volume of a single spherule in a given size group and N is the number of spherules in this size group²¹⁾, it can be considered, that relatively higher content of nickel is present in larger size groups of pelagic deep-sea sediments, in which relatively lower contamination of terrigenous matter is expected.

And if no supply of terrestrial nickel to deep sea sediments is present and each size group of the sediments has the same size interval, the total weights of nickel component contained in any size group are expected to be equal, because we have the modified relation $\rho CVN = \text{constant}$ in any size group, where ρ is the density and C is the nickel content of the "cosmic spherules". In this work nickel, iron and manganese contents of red clay, globigerina ooze and gray ooze, obtained at the location, off the Torishima Island separated in six size groups are obtained. At first the size distributions of the samples are determined. These samples are mechanically separated with sieves of various meshes in distilled water and ethyl-alcohol into six particle size groups. The results are given in the Table 4.

Table 4. Size distributions of red clay, globigerina ooze and gray ooze*²⁾ (wt%)

Size group	Size interval	Red clay (St-17)	Globigerina ooze (St-25)	Gray ooze* (JEDS-10)
Larger than 177		0.134	7.50	6.21
177 ~ 125	52	0.298	3.14	2.20
125 ~ 74	51	0.254	3.32	5.55
74 ~ 46	28	0.456	1.68	11.19
46 ~ 20	26	2.855	10.01	38.04
Smaller than 20 (size in micron)	20	96.003	74.35	36.81

* Gray ooze; obtained at the location, off the Torishima Island, (30°08'N, 139°08'E) at a depth of 1820 m.

The size distributions of red clay and globigerina ooze agree with Sverdrup's data²²⁾. And then, in each size group nickel, iron and manganese contents are determined. The results are given in Table 5, 6 and 7.

The weights of nickel, iron and manganese components, which are contained in 100 grams of each samples, are calculated in respective size groups. The

Table 5. Nickel content in six size groups of red clay, globigerina ooze and gray ooze.

Size group	Size interval	Red clay (St-17)	Globigerina ooze (St-25)	Gray ooze (JEDS-10)
Larger than 177		147	43	55
177 ~ 125	52	170	44	51
125 ~ 74	51	189	40	41
74 ~ 46	28	301	47	35
46 ~ 20	26	399	41	33
Smaller than 20 (size in micron)	20	229	81	66

(ppm by weight)

Table 6. Iron content in six size groups of red clay, globigerina ooze and gray ooze.

Size group	Size interval	Red clay (St-17)	Globigerina ooze (St-25)	Gray ooze (JEDS-10)
Larger than 177		3.81	0.126	3.81
177 ~ 125	52	3.69	0.139	4.54
125 ~ 74	51	3.17	0.119	4.57
74 ~ 46	28	3.29	0.159	4.27
46 ~ 20	26	3.41	0.123	3.95
Smaller than 20 (size in mibron)	20	6.29	1.53	3.28

(percent by weight)

Table 7. Manganese content in six size groups of red clay, globigerina ooze and gray ooze.

Size group	Size interval	Red clay (St-17)	Globigerina ooze (St-25)	Gray ooze (JEDS-10)
Larger than 177		0.275	0.008	0.053
177 ~ 125	52	0.510	0.017	0.240
125 ~ 74	51	1.219	0.015	0.223
74 ~ 46	28	2.13	0.037	0.169
46 ~ 20	26	2.62	0.017	0.193
Smaller than 20 (size in micron)	20	0.698	0.045	0.302

(percent by weight)

Table 8. Calculated weights of nickel in six size groups per 100 grams of red clay, globigerina ooze and gray ooze.

Size group	Size interval	Red clay (St-17)	Globigerina (St-25)	Gray ooze (JEDS-10)
Larger than 177		0.020	0.323	0.342
177 ~ 125	52	0.051	0.138	0.112
125 ~ 74	51	0.048	0.133	0.228
74 ~ 46	28	0.137	0.079	0.588
46 ~ 20	26	1.139	0.410	1.255
Smaller than 20 (size in micron)	20	21.985	6.022	2.429

(mg per 100 grams of the sample)

results are given in Table 8, 9 and 10.

The calculated data of Table 8, 9 and 10 are plotted in Figs. 5, 6 and 7. In these Figures the average size D_0 is defined with the following formulation; the average volume, V_{av} , is given by $V_{av} = \pi/6 \cdot D_0^3$ assuming spherical forms. And $V_{av}(D_2 - D_1) = \int_{D_1}^{D_2} D^3 dD$, thus from these relation the average size

$$D_0 = \frac{1}{2} \sqrt[3]{2(D_1 + D_2)(D_1^2 + D_2^2)}.$$

Table 9. The calculated weights of iron in six size groups per 100 grams of red clay, globigerina ooze and gray ooze.

Size group	Size interval	Red clay (St-17)	Globigerina ooze (St-25)	Gray ooze (JEDS-10)
Larger than 177		5.10	9.45	236.6
177 ~ 125	52	10.10	4.37	99.9
125 ~ 74	51	8.05	3.95	253.6
74 ~ 46	28	15.00	2.67	477.8
46 ~ 20	26	100.77	12.31	1502.6
Smaller than 20 (size in micron)	20	6038.6	1137.6	1207.4

(mg per 100 grams of the sample)

Table 10. The calculated weights of manganese in six size groups per 100 grams of red clay, globigerina ooze and gray ooze.

Size group	Size interval	Red clay (St-17)	Globigerina ooze (St-25)	Gray ooze (JEDS-10)
Larger than 177		0.37	0.60	3.29
177 ~ 125	52	1.52	0.53	5.28
125 ~ 74	51	3.10	0.50	12.38
74 ~ 46	28	9.71	0.62	18.91
46 ~ 20	26	74.80	1.70	73.42
Smaller than 20 (size in micron)	20	656.7	33.46	111.2

(mg per 100 grams of the sample)

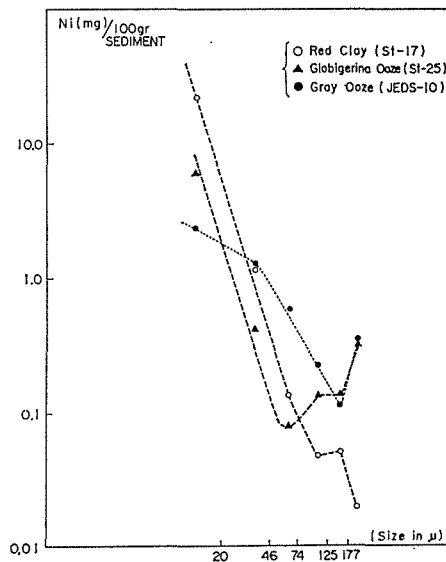


Fig. 5. The calculated weights of nickel in six size group per 100 grams of red clay, globigerina ooze and gray ooze. (The average size D_0 in a size region ($D_1 \sim D_2$) is obtained from a calculation; $D_0 = 1/2 \sqrt[3]{2(D_1 + D_2)(D_1^2 + D_2^2)}$).

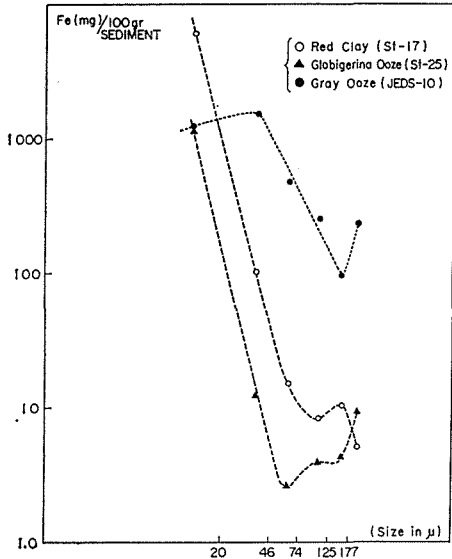


Fig. 6. The calculated weights of iron in six size groups per 100 grams of red clay, globigerina ooze and gray ooze.

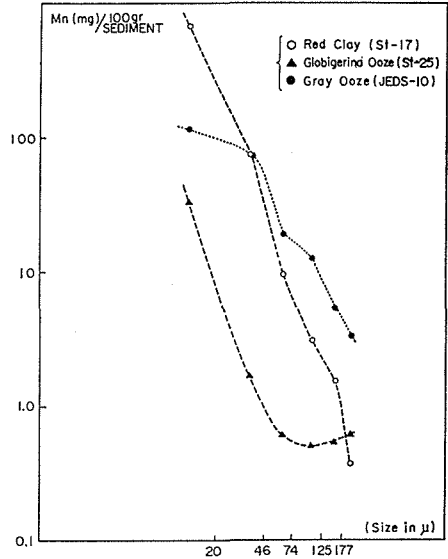


Fig. 7. The calculated weights of manganese in six size groups per 100 grams of red clay, globigerina ooze and gray ooze.

The curves in Globigerina ooze seem to be similar to the curves of Red Clay in smaller size region and quite different from the curves of Gray ooze, off the Torishima Island. Anomalous features in Globigerina ooze in larger size region may be caused by growing up of grains by calcification.

Excluding the different size intervals, the total weight of nickel component is quite different in each size groups. Therefore in the pelagic deep-sea sediments the nickel component supplied from the grains, which satisfy the relation $NV = \text{constant}$, is not so high.

Next the ratios of nickel to iron and manganese fractions in each size group are calculated and shown in Table 11.

Table 11. The calculated ratios of nickel to iron and manganese weights contained in six size groups in red clay, globigerina ooze and gray ooze.

Size Group	Red clay (St-17)		Globigerina (St-25)		Gray ooze (JEDS-10)	
	(Ni/Mn)	(Ni/Fe)	(Ni/Mn)	(Ni/Fe)	(Ni/Mn)	(Ni/Fe)
Larger than 177	0.054	0.0039	0.538	0.034	0.104	0.0014
177 ~ 125	0.034	0.0051	0.259	0.032	0.021	0.0011
125 ~ 74	0.016	0.0060	0.267	0.034	0.018	0.00089
74 ~ 46	0.014	0.0092	0.127	0.030	0.021	0.00082
46 ~ 20	0.015	0.0117	0.241	0.033	0.017	0.00084
Smaller than 20 (size in micron)	0.033	0.0037	0.180	0.005	0.022	0.0020

In three samples the (Ni/Mn) ratio is slightly higher in the largest size group than in other size groups, while the (Ni/Fe) ratio patterns are different each other in three samples. It is thought in the all size groups except the smallest one that the constituents are supplied with grains or supplied with clay-minerals and ferromanganese nodules grown in deep-sea sediments. In red clay the amount of clay-mineral and ferromanganese nodules supply, however, is probably not so high, because in the middle size groups the ratios of (Ni/Mn) and (Ni/Fe) are different from the ratios of (Ni/Mn) and (Ni/Fe) are different from the ratios in the smallest size group, in which group they are grown up.

The ratios (Ni/Mn) and (Ni/Fe) for average igneous rocks are 0.1 and 0.002 and then for average sea water are 0.02 and 0.05 respectively. The content of Ni, Mn and Fe and the ratios (Ni/Mn) and (Ni/Fe) for gray ooze in the largest size group are close to the values of average igneous rocks. The content of Ni and Mn for red clay in the largest size group, however, are ten times of those of average igneous rocks. On the other hand in globigerina ooze the ratios of (Ni/Mn) and (Ni/Fe) are quite higher than those in red clay and gray ooze, because the manganese and iron contents in globigerina ooze are quite lower than those of other samples. These facts suggest the supply of materials of relatively high nickel content to globigerina ooze. No definite, quantitative conclusion can be drawn from the three examinations mentioned above, except that ionic supply of nickel overcomes grain supply to the deep-sea sediments.

The total amounts of grain and ionic supply (including colloidal supply) of nickel fraction to deep-sea sediments are estimated with a simple model calculation;

$$\frac{a+bx}{\rho x}=c,$$

where x =sedimentation rate of deep-sea deposit, ρ =density of deep-sea deposit, c =nickel content of deep-sea deposit, a =grain sedimentation rate of nickel fraction and bx =ionic sedimentation rate of nickel fraction, in whose term it is expressed, that the ionic sedimentation is related to x .

Here the two cases are considered, in red clay we have $c=200$ ppm, $\rho=1.5$ and $x=0.05$ mm/10³ yr and in gray ooze $c=50$ ppm, $\rho=1.4$ and $x=5$ mm/10³ yr. So we have $a=12.8 \times 10^{-6}$ (gr/cm², 10³ yr) and in red clay $bx=2.2 \times 10^{-6}$ (gr/cm², 10³ yr), in gray ooze $bx=2.2 \times 10^{-6}$ (gr/cm², 10 yr). Hence the ratio of the amounts of grain and ionic supply of nickel is $r=a/bx=5.8$ in red clay and $r=0.58$ in gray ooze. Here the supplied grains are not only derived from extraterrestrial sources, but from continental and/or volcanic sources. It is thought, however, the grains of continental and volcanic sources have not so high nickel content.³⁾

The estimation of grain and ionic supply of nickel fractions is a interesting problem. Hence determinations of the sedimentation rate and the nickel content in deep-sea sediments at various locations of deep-sea bottom surfaces and also determinations at various depths in core samples are necessary for studies of this problem.

4. Discussions of nickel supply to deep-sea sediment by cosmic materials

It is thought, a large amount of cosmic dust accumulates on Earth's surface and the accretion rate of cosmic dust are estimated to be the values between 10³ to 10⁸ tons per year.^{23,24)} Among the cosmic materials meteorites are often

recovered on Earth's surface, but the total amounts of fallen meteorites do not exceed 200 kg per year on the earth.

"Cosmic Spherules" are thought to be of cosmic origin, which are discovered in deep-sea sediments or polar ice layers. In author's laboratory a number of metallic, silicate and glassy spherules were picked up also from deep-sea sediments.

During the cruise of H. M. S. Challenger John Murray discovered metallic and silicate spherules in deep-sea sediments and deduced in 1876 their extraterrestrial origin.¹⁾ After that discovery the "cosmic spherules" found in marine sediments has been studied by many investigators.^{1,25-36)} These spherules, however, are not yet recognized as of cosmic origin. In order to discuss the origin of the "cosmic spherules", the detection of cosmic ray produced nuclides are necessary. In author's group the detection of cosmic ray produced radio-nuclides is in progress.

The nickel, iron and manganese contents of metallic and silicate spherules are reported by Yamakoshi and Tazawa.³⁷⁾ And the results are shown in Table 12. It is noteworthy, that the nickel contents in metallic and silicate spherules are quite lower than the average value in meteorites.³⁸⁾

Table 12. The nickel, iron and manganese contents of metallic and silicate spherules.³⁷⁾

	[Ni]	[Fe]	[Mn]
Metallic spherules*	0.14	82.6	0.50
Silicate spherules*	0.014	0.96	0.04

(percent by weight)

Here the nickel fraction supplied from cosmic materials in deep-sea sediments is calculated as follows;

$$\frac{MC}{S\rho R} = [\text{Ni}],$$

where M =the accretion rate of cosmic dust, S =the total area of the earth's surface, ρ =density of deep-sea deposit, R =sedimentation rate of deep-sea deposit and C =nickel content of cosmic dust. Using the following numerical values, $M=5 \times 10^{11}$ grams/yr, $S=5.1 \times 10^{18}$ cm², $\rho=1.5$ and $R=1$ mm/10³yr, the expression becomes

$$[\text{Ni}] = 0.67 \times 10^{-2}C.$$

If we use the numerical values of nickel content in metallic and silicate spherules, we have Ni=1 ppm and 0.1 ppm respectively. And the average nickel content of 3.5 % in meteorites³⁸⁾ gives Ni=23 ppm in deep-sea sediments. High nickel content in materials of unknown source is thought to be one of the effective indicators of extra-terrestrial origin. In deep-sea sediments, however, the nickel fraction supplied from extraterrestrial materials is probably not so high as compared with the terrestrial nickel fraction.

The most essential criterion of extra-terrestrial origin is the detection of Nickel-59 and Manganese-53 in deep-sea sediments, which are produced by

* Samples were obtained at the location (17°18.2'N, 175°12.3'W), St-40 (KH-67-5).

bombardments of iron component in cosmic dust by cosmic proton and alpha particles in the solar system.³⁹⁾ If the nickel fraction in deep-sea sediments supplied from extraterrestrial sources is brought through ionic sedimentation, the Ni⁵⁹ (half life= 7.5×10^4 years) will be never detected, because the residence time of nickel component in the sea water is about 2.4×10^5 years.⁴⁰⁾

ACKNOWLEDGEMENTS

The author wishes to express his thanks to Dr. Y. Tazawa of Kyoto University for his fruitful discussions. The author is indebted to Professor N. Nasu, director of the deep-sea expedition with the Hakuho-Maru, for the samples used in this study. The author is also grateful to Japan Analytical Chemistry Research Institute for chemical analyses of the samples. Part of this work was supported financially by the Nishina Memorial Foundation.

REFERENCES

- 1) J. Murray and A. F. Renard, "Deep-Sea Deposits," Rep. Challenger Exp., 4 (1891).
- 2) H. Pettersson and H. Rotschi, "Nickel Content of Deep-Sea Deposits," *Nature*, 166, 308 (1950).
- 3) H. Pettersson and H. Rotschi, "The Nickel Content of Deep-Sea Deposits," *Geochim. Cosmochim. Acta*, 2, 81 (1952).
- 4) A. A. Smales and J. D. H. Wiseman, "Origin of Nickel in Deep-Sea Sediments," *Nature*, 175, 464 (1955).
- 5) T. Laevastu and O. Mellis, "Extraterrestrial Material in Deep-Sea Deposits," *Amer. Geophys. Union*, 36, 385 (1955).
- 6) E. J. Oepik, "Cosmic Sources of Deep-Sea Deposits," *Nature*, 176, 926 (1955).
- 7) A. A. Smales, D. Mapper and A. J. Wood, "The Determination, by Radioactivation, of Small Quantities of Nickel, Cobalt and Copper in Rocks, Marine Sediments and Meteorites," *Analyst*, 82, 75 (1957).
- 8) H. Pettersson, "Manganese and Nickel on the Ocean Floor," *Geochim. Cosmochim. Acta*, 17, 209 (1959).
- 9) S. Amano, A. Okada and M. Shima, "Vertical Distribution of Nickel Content in a Long Deep-Sea Core," *Bull. Nat. Mus. Tokyo*, 10, 471 (1967).
- 10) E. D. Goldberg, "Marine Geochemistry; I. Chemical Scavengers of the Sea," *J. Geol.*, 62, 249 (1954).
- 11) D. F. Schutz and K. K. Turekian, "The Distribution of Cobalt, Nickel and Silver in Ocean Water Profiles Around Pacific Antarctica," *J. Geophys. Res.*, 70, 5519 (1965).
- 12) J. P. Willis and L. H. Ahrens, "Some Investigations on the Composition of Manganese Nodules, with Particular Reference to Certain Trace Elements," *Geochim. Cosmochim. Acta*, 26, 751 (1962).
- 13) D. S. Cronan and J. S. Tooms, "Geochemistry of Manganese Nodules from the N. W. Indian Ocean," *Deep-Sea Res.*, 14, 239 (1967).
- 14) M. Tatsumoto, "Chemical Studies of Deep-Sea Sediments" (in Japanese), *Nihon Kagaku Zasshi*, 77, 1637 (1956).
- 15) E. E. Angino, "Geochemistry of Antarctic Pelagic Sediments," *Geochim. Cosmochim. Acta*, 30, 939 (1966).
- 16) E. D. Goldberg and G. O. S. Arrhenius, "Chemistry of Pacific Pelagic Sediments," *Geochim. Cosmochim. Acta*, 13, 153 (1958).
- 17) K. H. Wedepohl, "Spurenanalytische Untersuchungen an Tiefseetonen aus dem Atlantik," *Geochim. Cosmochim. Acta*, 18, 200 (1960).
- 18) H. Hamaguchi, M. Osawa and N. Onuma, "The Vertical Distributions of Trace Elements in Sedimental Core Samples of Japan Trench" (in Japanese), *Nihon Kagaku*

- Zassi, 82, 691 (1961).
- 19) J. L. Mero, "Ocean-Floor Manganese Nodules," *Econ. Geol.*, 57, 747 (1962).
 - 20) N. S. Skorniyakova, "Manganese Concentrations in Sediments of the North-Eastern Pacific Ocean," *Dokl. Acad. Nauk*, 130, 653 (1960).
 - 21) T. Laevastu and O. Mellis, "Size and Mass Distribution of Cosmic Dust," *J. Geophys. Res.*, 66, 2507 (1961).
 - 22) H. U. Sverdrup, M. W. Johnson and R. H. Fleming, "The Oceans, Their Physics, Chemistry and General Biology," Prentice Hall Inc. (1942).
 - 23) R. A. Schmidt, "A. Survey of Data on Microscopic Extraterrestrial Particles," NASA TN-D-2710 (1965).
 - 24) D. W. Parkin and D. Tilles, "Influx Measurements of Extra-Terrestrial Particles." *Science*, 159, 936 (1968).
 - 25) K. Fredriksson, "Cosmic Spherules in Deep-Sea Sediments," *Nature*, 177, 32 (1956).
 - 26) H. Pettersson and K. Fredriksson, "Magnetic Spherules in Deep-Sea Deposits," *Pacific Sci.*, XII, 71 (1958).
 - 27) W. Hunter and D. W. Parkin, "Cosmic Dust in Recent Deep-Sea Sediments," *Proc. Roy. Soc.*, 255A, 382 (1959).
 - 28) W. D. Crozier, "Black, Magnetic Spherules in Sediments," *J. Geophys. Res.*, 65, 2971 (1960).
 - 29) K. Fredriksson and L. R. Martin, "The Origin of Black Spherules Found in Pacific Island, Deep Sea Sediments and Antarctic Ice," *Geochim. Cosmochim. Acta*, 27, 245 (1963).
 - 30) C. C. Langway Jr. and U. B. Marvin, "Some Characteristics of Black Spherules," *Ann. New York Acad. Sci.*, 119, 205 (1964).
 - 31) H. Fechting and K. Utech, "On the Presence or Absence of Nickel in Dark Magnetic Cosmic Spherules and Their Mechanics of Origin," *Ann. New York Acad. Sci.*, 119, 243 (1964).
 - 32) F. R. Park and A. M. Reid, "A Comparative Study of Some Metallic Spherules," *Ann. New York Acad. Sci.*, 119, 250 (1964).
 - 33) R. R. Larson, E. L. Dwornik and I. Adler, "Electronprobe Analysis of 'Cosmic' Particles," *Ann. New York Acad. Sci.*, 119, 282 (1964).
 - 34) P. W. Hodge and F. W. Wright, "Studies of Particles for Extraterrestrial Origin," *J. Geophys. Res.*, 69, 2449 (1964).
 - 35) R. A. Schmidt and K. Keil, "Electron Microprobe Study of Spherules from Atlantic Ocean Sediments," *Geochim. Cosmochim. Acta*, 30, 471 (1966).
 - 36) W. A. Cassidy, "Nondestructive Neutron Activation Analysis of Small Particles," *Ann. New York Acad. Sci.*, 119, 318 (1964).
 - 37) K. Yamakoshi and Y. Tazawa, "Chemical Composition of "Cosmic Spherules" in Marine Sediments," *Memoir of Fac. Science, Kyoto Univ.*, 33-II, 161 (1970).
 - 38) H. Brown, "A Table of Relative Abundances of Nuclear Species," *Rev. Mod. Phys.*, 21, 635 (1949).
 - 38) H. Hasegawa, K. Yamakoshi, M. Noma and T. Maihara, "Cosmic-Ray Produced ^{59}Ni and its Astrophysical and Geophysical Implications," *Can. J. Phys.*, 46, S930 (1968).
 - 40) E. D Goldberg, "The Oceans as a Chemical System," "The Sea" volume II (1963) edited by M. N. Hill (Interscience Publishers).