NOTE

^{10}Be and $^{10}\text{Be}/^9\text{Be}$ in manganese nodules

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Depth profiles of ^{10}Be and ^9Be concentrations have been measured in five manganese nodules from widely varying locations of the Pacific Ocean. Mean accumulation rate of these manganese nodules ranges from 2.7 to 8.0 mm · m.y.⁻¹.

The variation of ^{10}Be and $^{10}\text{Be}/^9\text{Be}$ with depth or time is found to be less than ±30% for periods from 0.4–1.0 m.y. back to 6 m.y. B.P. Surface $^{10}\text{Be}/^9\text{Be}$ atomic ratio is found to be $(9\text{--}13) \times 10^{-8}$, that shows authigenic nature of manganese nodule accumulation by comparison with $(12\text{--}31) \times 10^{-8}$ for deep-sea water, $(2\text{--}7) \times 10^{-8}$ for clay sediments and $(7\text{--}9) \times 10^{-8}$ for fossil-rich sediments.

INTRODUCTION

Because of the ^{10}Be half-life being 1.5 m.y., ^{10}Be is a useful radionuclide for the study of marine system back to millions of years. ^{10}Be concentration in manganese nodules has been investigated by many workers (SOMAYAJULU, 1967; KRISHNASWAMI *et al.*, 1972; GUICHARD *et al.*, 1978; KU *et al.*, 1979, 1982; TUREKIAN *et al.*, 1979; KRISHNASWAMI *et al.*, 1982; SHARMA and SOMAYAJULU, 1982). In this study,

the depth profiles of ^{10}Be concentration and also of $^{10}\text{Be}/^9\text{Be}$ ratio in four manganese nodules from the Pacific have been investigated.

EXPERIMENTAL AND RESULTS

Investigated Pacific manganese nodules are listed in Table 1. ^{10}Be and ^9Be were determined by the method described in INOUE and TANAKA (1978). Beryllium was chemically separated from the nodule samples (2–6 g), and ^{10}Be

Table 1. Description of Mn-nodule samples

Sample (Station No)	Location	Size (cm)	Bottom topography	Water depth (m)	Associated sediment
1. KH68-3-16	162°39'E 37°07'N	15x13x~10	crest of north Shatsky rise	3700-2920	smooth thick sediment
2. KH74-4-16	150°27'E 29°26'N	14x11x10	summit of Markarov guyot	1378	brown clay
3. GDP11-TN-22	131°35'E 28°03'N	7.5x7 x~6	summit of Amami guyot	1630	globigerina ooze
4. GH72-2-07	153°34'E 16°02'N	8 x7 x7	eastern Mariana basin, south of Magellan seamount chain	5635	brown clay
5. G994	162°05'W 22°56'S	5 x5 x5	depression of southwestern Pacific basin	4848	brown clay

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was measured by a low-level needle counter with background count rates of 3 counts per day for 6 mm ϕ window (FUJITA *et al.*, 1975; TAKANO *et al.*, 1980).

To examine the contribution of authigenic component of the nodules, KH74-4-16 and G994, leaching experiments were carried out by acetylacetone aqueous solution. Layers of 3 mm depth were peeled off from the surface of both nodules. The samples were pulverized, and 5% acetylacetone aqueous solution was added to the powder. The solution was kept for 4 days at room temperature with occasional stirring. The supernatant was separated from the residue by centrifuging. ^{10}Be was determined in the same way as described previously. ^9Be was determined by atomic absorption spectrometry after beryllium extraction with

^7Be tracer added.

Table 2 presents the results of ^{10}Be measurements. The overall error in the specific activities was estimated on the basis of uncertainties (1σ) in chemical analysis of beryllium (3%), counting efficiency (5%) and counting statistics (4–30%). The concentration of ^9Be is twice as high as that in sediments given in TANAKA and INOUE (1978) and rather uniform with depth. The atomic ratio of $^{10}\text{Be}/^9\text{Be}$ is also tabulated in Table 1.

ACCUMULATION RATE OF MANGANESE NODULES

The depth profiles of ^{10}Be and $^{10}\text{Be}/^9\text{Be}$ in four manganese nodules are illustrated in Fig. 1. The solid lines have been drawn by least square fitting. The mean growth rates range between

Table 2 ^9Be concentration, specific activity of ^{10}Be and $^{10}\text{Be}/^9\text{Be}$ atomic ratio in Mn-nodules

Depth (mm)	^9Be concentration ($\mu\text{g/g}$)	^{10}Be SP. activity ($10^{-3}\text{ dpm cm}^{-3}$)	$^{10}\text{Be}/^9\text{Be}$ (10^{-8})
1. KH68-3-16			
*F = 6.5 ± 0.3 atoms $\text{cm}^{-2} \text{ s}^{-1}$			
0–2	4.1	51.0 ± 4.4	10.3 ± 0.8
2–5	3.6	23.6 ± 1.9	5.4 ± 0.4
5–8	3.3	20.6 ± 1.8	5.2 ± 0.4
8–11	3.7	17.3 ± 1.7	4.0 ± 0.4
11–13	3.7	10.7 ± 1.6	2.5 ± 0.2
13–16	3.2	10.3 ± 1.1	2.9 ± 0.3
16–18	3.7	4.25 ± 1.02	1.18 ± 0.30
18–19	3.8	5.13 ± 0.76	1.21 ± 0.17
19–22	3.8	2.47 ± 0.57	0.60 ± 0.14
22–24	3.9	3.20 ± 0.53	0.79 ± 0.13
24–26	3.7	4.04 ± 0.81	0.90 ± 0.17
2. KH74-4-16			
F = 13.2 ± 2 atoms $\text{cm}^{-2} \text{ s}^{-1}$			
0–3	3.8	47.0 ± 3.7	12.0 ± 0.9
3–6	4.1	40.8 ± 3.4	9.6 ± 0.7
6–10	4.0	31.5 ± 3.4	7.3 ± 0.7
10–14	3.6	15.1 ± 1.8	4.1 ± 0.5
14–18	3.1	23.5 ± 2.1	7.2 ± 0.6
3. GDP11-TN-22			
F = 9 ± 1 atoms $\text{cm}^{-2} \text{ s}^{-1}$			
0–5	4.7	29.9 ± 3.2	9.3 ± 0.9
5–10	4.8	30.5 ± 2.9	8.1 ± 0.5
10–15	5.4	5.85 ± 1.06	1.6 ± 0.2
15–22	6.3	10.6 ± 1.33	2.8 ± 0.3
22–30	8.3	8.65 ± 1.06	2.1 ± 0.3
4. GH72-2-07			
F = 5.5 ± 0.4 atoms $\text{cm}^{-2} \text{ s}^{-1}$			
0–2 (surface)	5.0	36.3 ± 5.4	9.5 ± 1.3
2–4	5.8	35.6 ± 4.3	8.1 ± 0.9
4–10	6.5	23.6 ± 2.6	4.7 ± 0.5
10–16	5.7	4.98 ± 0.92	1.13 ± 0.21
16–22	5.2	2.09 ± 1.05	0.66 ± 0.33
nucleus	2.2	ND	ND
6–12	5.1	3.80 ± 0.66	0.97 ± 0.17
0–6 (bottom)	4.5	3.01 ± 1.05	0.87 ± 0.28

* ^{10}Be flux, ND: Not detected

Fig. 1. Plot of $\log ^{10}\text{Be}$ versus depth in manganese nodules from the data of Table 2.

2.7 and $8.0 \text{ mm} \cdot \text{m.y.}^{-1}$. The rate derived from ^{10}Be is almost identical with that from $^{10}\text{Be}/^9\text{Be}$ for all nodules. Sample KH74-4-16 have been examined by HARADA and NISHIDA (1976) with biostratigraphic method. They reported a preliminary value of the growth rate which is consistent with our present result.

The ^{10}Be flux in Table 2 was calculated from ^{10}Be surface concentration and mean growth rate in Fig. 1. The flux of ^{10}Be in nodules is an order of magnitude lower than that for marine sediments. KRISHNASWAMI *et al.* (1979, 1982) also pointed out the deficiencies. The ^{10}Be in sediments is deposited by the precipitation process. On the other hand, in nodules,

radio-nuclides are supposed to be accumulated onto the surface from $2-4\pi$ direction only by adsorption mechanism. Recently, TUREKIAN *et al.* (1979) suggested that ^{10}Be flux onto the nodule surface seems to be roughly proportional to the nodule accumulation rate. Above relation seems to hold in most of data including ours, but some data fall rather far from the line in Fig. 5 of TUREKIAN *et al.* (1979). Deviation may be due to the difference of marine paleo-environments. Approximate proportionality between ^{10}Be flux and the sedimentation rate also can be seen in sediment cores (TANAKA *et al.*, 1982).

Comparison of $^{10}\text{Be}/^9\text{Be}$ ratio in manganese nodules, sediments, and sea water The comparison of $^{10}\text{Be}/^9\text{Be}$ ratio in deep-sea water, manganese nodules, and sediments will shed light on the accumulation process of manganese nodules. RAISBECK *et al.* (1980) and KRISHNASWAMI *et al.* (1982) have measured ^{10}Be concentrations in Pacific deep-sea water. These measured ^{10}Be concentrations give $^{10}\text{Be}/^9\text{Be}$ ratios of 12×10^{-8} and 31×10^{-8} , respectively, when we use ^9Be data from MEASURES and EDMOND (1982). The $^{10}\text{Be}/^9\text{Be}$ ratio in the top surface of the nodules measured in this study were found to be $(9-13) \times 10^{-8}$, which are similar to the data in KU *et al.* (1982), KRISHNASWAMI *et al.* (1982) and SHARMA and SOMAYAJULU (1982). The $^{10}\text{Be}/^9\text{Be}$ ratio in typical clay sediments has been measured by TANAKA and INOUE (1979) to be $(2-7) \times 10^{-8}$. These values are lower than that in deep-sea water. Higher values of $(7-9) \times 10^{-8}$ have been observed by INOUE and TANAKA (1979) and TANAKA *et al.* (1982) in sediments containing plenty of fossils of micro-organisms. Surface $^{10}\text{Be}/^9\text{Be}$ ratios observed in many nodules are similar to that in deep-sea water, suggesting that nodules reflect the components of sea water rather than sediment materials. To see the effect of detrital component, leaching experiments of beryllium from the surface samples (0–3 mm) of two manganese nodules (KH74-4-16

and G994) have been carried out with acetyl-acetone aqueous solution. The obtained $^{10}\text{Be}/^9\text{Be}$ ratios in the leached solution are $(17.4 \pm 1.2) \times 10^{-8}$ and $(16.1 \pm 1.2) \times 10^{-8}$, respectively. Both values are somewhat higher than those for unleached manganese nodules. The highest ratio in leached solution shows that ^{10}Be is leached more easily than ^9Be ; ^{10}Be and ^9Be are different in origin, and not completely equilibrated.

Differential accumulation history The micro-texture of GDP11-TN-22 and GH72-2-07 are investigated by powder X-ray diffraction analysis and reflection microscopic observation. GDP11-TN-22 have not clear boundary structure, and its microstructure is a mixture of $\delta\text{-MnO}_2$ and 10 Å manganite. The surface of GH72-2-07 is covered with 4 mm black crust of 10 Å manganite, and the inner layers are composed of $\delta\text{-MnO}_2$ with little 10 Å manganite. As shown in Table 3 and Fig. 2, the Ni and Cu contents of the surface crust are 0.18 and 0.10% respectively, significantly lower than 0.27 and 0.18% of the inner layers. Almost the same concentration of ^{10}Be at two points of the surface (Fig. 1) may suggest that the surface crust has grown faster than the inner layers.

On the cosmic-ray intensity and climatic changes in the past The ^{10}Be concentration and

Table 3 Chemical elements in Mn-nodules

Depth (mm)	Mn (%)	Fe (%)	Ni (%)	Co (%)	Cu (%)
GH72-2-07					
0–2 (surface)	16.5	18.3	0.18	0.40	0.093
2–4	14.5	21.0	0.15	0.37	0.10
4–10	16.8	16.8	0.27	0.42	0.17
10–16	16.6	13.9	0.26	0.38	0.18
16–22	13.9	11.8	0.26	0.28	0.18
nucleus	2.37	3.77	0.098	0.034	0.10
6–12	12.8	10.8	0.23	0.30	0.17
0–6 (bottom)	12.7	10.0	0.29	0.31	0.24
GDP11-TN-22					
0–5	25.7	13.0	0.67	0.24	0.10
5–10	18.5	12.4	0.66	0.23	0.13
10–15	20.6	14.4	0.49	0.29	0.11
15–22	14.5	13.6	0.37	0.20	0.10
22–30	16.3	13.3	0.37	0.20	0.10

Fig. 2. Plot of log (chemical element) versus depth in manganese nodules (GDP11-TN-22 and GH72-2-07) from the data of Table 3.

$^{10}\text{Be}/^9\text{Be}$ ratio show a monotonous decrease with depth; the limits of variation from the mean lines (solid line in Fig. 1) are $\pm 30\%$ for all nodules except for 10–15 mm point in GDP11-TN-22. A similar variation in both ^{10}Be and $^{10}\text{Be}/^9\text{Be}$ is caused by an approximate constancy of ^9Be with depth. The data for KH68-3-16 and KH72-2-07 can give the variation far back to 6 m.y.B.P. Thus it appears that the ^{10}Be accumulation rate and $^{10}\text{Be}/^9\text{Be}$ ratio for these nodules (therefore the intensity variation of cosmic rays) did not vary more than $\pm 30\%$ in the time scales of 0.4–1.0 m.y. during the past 6 m.y. Recently, KU *et al.* (1982) also reported the absence of large variation in ^{10}Be and $^{10}\text{Be}/^9\text{Be}$ in other nodules during the past 7 m.y.

A sharp drop on ^{10}Be concentration at around 3 m.y.B.P. has been found in two north Pacific sediment cores (KH70-2-7 and KH70-2-5) by TANAKA and INOUE (1980). Since the locations of these cores are separated by about 700 km from each other, a change of

marine environments in a considerable large scale has been suggested in these area of the Pacific at around 3 m.y.B.P. In the nodule of KH68-3-16, which is located about 3,000 km to the west of two sediment cores described above, no such drop has been observed at 3 m.y.B.P. Drastic changes in the ^{10}Be concentration observed in the two north Pacific cores may be attributed to a change of the local marine paleo-environments in the past.

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