adsorption effect on the walls of some holes and cracks opened to the outside area. These elements would then give an idea of the changes of specific area of the nodule with depth, and of the area existing as potential sink for sea water ^{230}Th and ^{231}Pa.

J. FOCT : Let us remark that what we call "diffusion" is in fact the sum of transport phenomena including the influence of porosity, of solid state diffusion and of chemical reactivity. Then, it may be difficult to say what will the diffusion profile be. Moreover, the structure at the lattice cell or better at the atomic scale is different at the surface and in the depth of nodules, so a diffusion profile may be a "structure variation" profile.

C. LALOU : I agree, we always incorrectly speak of "diffusion" the term penetration would be better.

P. HALBACH : If Fe and Mn are precipitated out of ionic solutions we can expect that Fe is deposited at lower pH values than Mn. But, in the case of formation of ferromanganese nodules, we have to take into account that Fe and Mn migrate in the near-bottom seawater in a colloidal state. Therefore, the rules of colloid chemistry are valid. In pseudosolutions Fe, especially if it is complexed with organic compounds, is much more stable than Mn in colloidal solutions, that means that colloidal Mn oxide hydrates may be deposited out of the near-bottom sea water before FeOOH xH$_2$O. This is proved by the fact that iron content is sometimes higher than the Mn content in the near-bottom sea water (results of VA - 13-11).

C. LALOU : If we admit that "normal oceanic conditions" prevail for the formation of Mn nodules, you are right, but if we accept the concept of rapid formation, in which hydrothermal conditions are implied as shown in different "official" hydrothermal deposits (i.e.

Famous) iron precipitates first and an enrichment in iron is often seen at the contact between the core and the oxide deposit.

M. HOFFERT : Le cœur de l'encroûtement étudié par Lalou et al. présente beaucoup d'analogies avec le cœur d'un autre encroûtement ainsi qu'avec un niveau induré prélevé à proximité (Hoffert et al., 1978). Il s'agit dans les trois cas de niveaux volcano-sédimentaires indurés. Or nous avons constaté le comportement minéralogique et géochimique différent du niveau induré au contact de l'eau de mer par rapport à celui du nodule. Le niveau induré est le siège d'échanges importants avec l'eau de mer alors que le cœur de l'encroûtement semble avoir été rapidement isolé du milieu par un encroûtement de Fe-Mn. Cela ne nous donne pas d'indications sur la vitesse de croissance de ce revêtement de Fe-Mn, mais cela indique que la première précipitation de Fe-Mn a été d'épaisseur suffisante pour isoler le cœur du futur nodule et a dû se faire rapidement.

R.K. SOREM : What oxides minerals have been identified ? If no identification, what kind of patterns were obtained. What method was used ?
    Were any polished sections of high quality made and studied with the ore microscope ? If so, were different optically distinct materials (opaque) observed ? What were their properties (reflectivity, aniso-tropy, etc.)

C. LALOU : X-ray diffraction patterns show that the principal manganese oxide present is badly crystallized, with two large rays at 7 Å and 10 Å (δMnO$_2$). Polished sections as the one shown Figure 2 (part I) have been examined with the ore microscope, but only to study the structure and not the mineralogical characteristics as we are not specialists in mineralogy.

GROWTH RATES AND COMPOSITION OF TWO FERROMANGANESE NODULES FROM THE CENTRAL NORTH PACIFIC

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ABSTRACT. - ^{10}Be, U and Th isotopes, Ra, ^{210}Pb, Mn, Fe and several trace elements are measured in the hydroxylamine hydrochloride leachates and residues of two ferro-manganese nodules collected from the Central North Pacific. The two nodules which are from the same location are about identical in composition. The ^{10}Be deduced growth rates (2.3 and 3.3 mm/10^6 years) are in good agreement with those reported in literature for other nodules using independent techniques. The order of magnitude discrepancy between the integrated ^{10}Be activity (in the nodules) with its production rate confirms the earlier explanations put forward by Bhat et al (1970). Additionally it is possible that nodule formation results from only a few hundred meters of the overlying waters. Hydroxylamine hydrochloride appears to be an ideal leachant for the authigenic components in the nodules - the leach can conveniently be used for most of the analyses.

RÉSUMÉ. - Le ^{10}Be, les isotopes de U et Th, le Ra, le ^{210}Pb, le Mn, le Fe et plusieurs éléments trace ont été mesurés dans la solution de léchage par chlorhydrate d'hydroxylamine et dans les résidus de léchage de deux nodules de manganèse provenant du Pacifique central nord. Les deux nodules proviennent du même endroit et ont à peu près la même composition, les taux de croissances déduits du ^{10}Be (2,3 et 3,3 mm/10^6 ans) sont en bon accord avec ceux donnés dans la littérature et obtenus par d'autres techniques pour d'autres nodules. L'ordre de grandeur du désaccord entre l'activité intégrée du ^{10}Be (dans les nodules) et son taux de production confirme les explications données antérieurement. De plus, il est possible que les nodules ne se forment qu'à partir des quelques centaines de mètres d'eau susjacente. Le chlorhydrate d'hydroxylamine semble être une solution de léchage idéale pour les composants authigènes des nodules. La solution de léchage peut être facilement utilisée pour la plupart des analyses.

INTRODUCTION

Ferromanganese minerals on the ocean floor continue to interest geochemists all over the world both due to their future resource value as well as due to the mystery surrounding their origin. With the employment of different techniques to study various properties of these deposits and with the involvement of more and more scientists a stage is reached when a good look at the data available is taken and future strategies planned. From this point of view this colloquium is timely.
    Three main theories exist concerning the origin of this most abundant mineral on the ocean floor, some of which were proposed at about the time it was discovered (Murray and Renard, 1891). The first is the slow, authigenic precipitation of hydrous oxides of Mn and Fe which in turn scavenge a host of trace elements and radioactivities to the depositional sites. The second theory postulates a rapid growth of the nodules due to submarine volcanism playing an important role whereas the third theory concerns the biological origin which depends on the association of organisms and organic matter with manganese nodules. A detailed account of these theories can be had from Goldberg (1954); Arrhenius (1967); Ku (1977) and Lalou et al. (1977). An update account on all aspects of the ferromanganese

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deposits can be had in Glasby (1977). Radiometric studies using U-Th decay series isotopes (Bender et al., 1966; Barnes and Dymond, 1967; Ku and Broecker, 1969; Krishnaswami and Cochran, 1978), fission track studies (Heye, 1975; Anderson and MacDougall, 1977), and magnetic reversals (Crecelius et al. 1971), cosmogenic ^{10}Be (Bhat et al., 1970; Krishnaswami et al., 1972) and ^{26}Al (Reyss and Yokoyama, 1976; Guichard et al., 1978) measurements performed on the Mn crusts have all confirmed the slow-growth hypothesis as do the techniques like K-Ar dating (Barnes and Dymond, 1967) and racemization of amino acids (Bada, 1972) performed on the nodule nuclei. All these studies yield nodule accumulation rates in the region of mm/10^6 yrs. Recently Greenslate (1978) based on material balance (non-radiochemical) considerations concluded that manganese nodules must not be growing rapidly. For nodules from the open deep oceans, on which all radiometric and other techniques can satisfactorily be employed, only methods employed on the Mn crust are more accurate and even amongst these, radiometric techniques involving isotopes of short half lives like ^{230}Th, ^{234}U are doubted especially in nodules where anomalous behaviour of these nuclides was found (Lalou and Brichet, 1972). It is argued that the surface topography of nodules is such that sampling of the top sections in the range of a few hundred microns would always yield ^{230}Th values that show the nodules to be growing at rates mm/10^6 yrs (Lalou et al., 1977). Arrhenius (1967) sus-

pected that diffusion of ^{230}Th and U upto a depth of a few millimeters would yield patterns similar to their decay patterns. These criticisms cannot be held against the cosmogenic ^{10}Be ($E_{max}\bar{\beta}$ = 0.555 MeV; half life = 1.5×10^6 yr – Yiou and Raisbeck, 1972). ^{10}Be measurements can be made upto depths of a few cms in the nodule compared to U decay series nuclides which are measurable only upto a millimeter or two. The only problem that exists now is the lack of many ^{10}Be data on nodules. So far only three nodules have been dated out of which two of them were based on two point decay lines which are not what one would really like to have to satisfactorily prove the slow growth hypothesis.

Though not as abundant as the smaller nodules the larger ones (surface area >30 cm^2) are available in sufficient numbers for dating using the ^{10}Be technique.

This paper is a beginning towards that end. We report the ^{10}Be measurements and the composition of two manganese nodules.

EXPERIMENTAL TECHNIQUES AND RESULTS

The two manganese nodules analysed in this study were collected during the Aries expedition of the Scripps

Institution of Oceanography to the central north Pacific. Aries 12D is a trapezium shaped almost flat nodule with a surface area of ~56 cm^2 and total thickness of about 4.5 cm out of which the manganese crust occupied 2.5 cm. The rest 2 cm at the bottom is an altered basalt which has a few patches of Mn here and there (Fig. 1). Three sections from the top 0-1.9 cm have been sampled. The second nodule Aries 15D comes from about the same location and has an area of about 125 cm^2 with a 2.2 cm thick Mn crust. This nodules looks like a right-angle-triangle with almost no basaltic cover at the bottom. Only a few spots of clay can be seen (Fig. 1). Five sections were sampled from the entire Mn crust out of which three are analysed so far. The relevant details of the nodules are given in Table 1.

SAMPLING

Nodule sections were sampled by chipping with a small, clean stainless steel chistle and hammer as well as a dental drill. Thickness was directly measured as well as ascertained from the area of the nodule before and after chipping and the total weight chipped and assuming a specific gravity of 2.5 g/cm^3 for the nodules. The thicknesses obtained by both the methods are in

FIG. 1. – Photographs of the nodule studied. Upper pictures are the top views and lower ones show the bottom views.

TABLE 1
Sample and dissolution details

Sample (Location)	Mean water depth (m)	Sample depth (mm)	Weight taken for analysis (g)	Residue left after NH$_2$OHHCl leach (g)	Insolubles (%)
ARIES 12 D (20°45.1'N 173°26.4'E)	1623	0-3.8 3.8-7.5 7.5-19.1	44.1 55.4 193.6	5.6 10.6 36.7	12.8 19.1 19.0
ARIES 15 D (20°47.3'N 173°20.4'E)	1278	0-3.1 3.1-5.5 7.9-14.5	66.5 60.2 197.1	15.0 (7.1) 7.0 22.9	22.5 11.6 11.6

Number in parenthesis is the weight of residue left after leaching the 15 g residue with 6M HCl. See text for details.

agreement within ± 20 %. The nodule samples were powdered using an agate mortar and pestle, dried at 110° C overnight and used for analysis.

LEACHING AGENT

Although manganese nodules are supposed to be primarily authigenic, they do contain acid-insoluble material amounting to 10 %. Somayajulu (1967) in his first experiments, dissolved a manganese nodule in 6M HCl + H$_2$O$_2$ for ^{10}Be measurements. Subsequently Bhat et al. (1970) avoided the HCl leaching technique by using a 40 % aqueous solution of EDTA (ammonium salt), about 10 ml per gram of the nodule material. While this method was faster since Be could be recovered by TTA extraction avoiding other procedures (Amin et al., 1966), it has the disadvantage that if one tries to analyse other cosmogenic activities like ^{26}Al, ^{53}Mn and ^{59}Ni since the EDTA complexes of these elements are very stable (Fairhall, 1960). Now that ^{26}Al was also detected in manganese nodules (Reyss and Yokoyama, 1976) it was felt necessary to look for a new leaching agent which could only dissolve the authigenic part leaving the clay and other detrital components unattacked. Our choice fell on hydroxylamine hydrochloride (NH$_2$OHHCl) which was in fact used by Kharkar et al. (1963) in an attempt to leach the authigenic ^{10}Be in sediments. While a good amount of Mn was leached out only a very small amount of ^{10}Be came along with it. Even if one assumes that Be goes along with Mn, the result is not surprising since the Mn content of sediments is only of the order of 1 %. Arrhenius (1963) used a 1M solution of hydroxylamine hydrochloride for leaching manganese nodules, and found that Mn, Cu, Ni and Sr are almost quantitatively leached out of Mn nodules by this reducing reagent. All these observations prompted us to use NH$_2$OHHCl.

CHEMISTRY

Each sample was boiled in a solution of 10 % NH$_2$OHHCl (about 15 ml per gram nodule) for about

1 hr. After cooling and centrifuging the leachate, the residue was subjected to two more leachings with NH$_2$OHHCl. The amount of residue left after the leaching ranged from 11.6 to 22.5 %. The leach was further acidified with concentrated HCl to pH 1 and 10 % of it was set aside for other analyses.

For ^{10}Be and ^{26}Al studies 90 % of the leach was taken and stable Be carrier (equivalent to 73.2 mg BeO) was added in the form of beryllium sulphate. The hydroxides were precipitated with NH$_4$OH. Al and Be were separated from the rest by NaOH. Since the Al content of nodules is small no Gooch Haven separation is necessary for separating it from Be. Both Al + Be hydroxides were taken through all the purification steps followed by Amin et al. (1966). Be was then separated from Al by cation exchange method using Dowex-50 and was purified by TTA extraction (Amin et al., 1966). The overall chemical efficiency varied between 51 to 76 % averaging 66 %. Radiochemically pure Be was deposited on a lucite holder of 4.08 cm^2 area and was assayed for beta activity in a flow gas 2 π beta counter. In the case of Aries 15D surface sample the residue left after NH$_2$OHHCl leaching, was further leached by boiling three times each with 200 ml of 6M HCl. This leach was also processed for ^{10}Be to see the efficiency of NH$_2$OHHCl in dissolving ^{10}Be from the nodule.

PURITY CHECKS

All samples were counted at regular intervals for about a month until the beta activity reached a constant level (immediately after deposition there usually will be a little short lived activity which decays off within a week or so) and absorption measurements were made using mylar absorbers. The half thickness of the beta radiation which is indicative of the beta energy for all samples, ranged from 18-20 mg cm^{-2} in mylar compared to 20.2 mg cm^{-2} measured for synthetic ^{10}Be (Amin et al., 1966). Results of the beryllium-10 measurements are given in Table 2.

TABLE 2
^{10}Be measurements of the two manganese nodules

Nodule	Depth (mm)	Net ^{10}Be* (cph)	^{10}Be concentration (dpm/kg dry nodule)
ARIES 12 D	0-3.8	9.4 ± 0.5	24.0 ± 1.3
	3.8-7.5	6.7 ± 0.7	15.3 ± 1.5
	7.5-19.1	7.5 ± 0.7	5.1 ± 0.5
ARIES 15 D	0-3.1	16.5 ± 0.9	30.6 ± 1.7
	3.1-5.5	7.5 ± 0.7	15.3 ± 1.3
	7.9-14.5	5.4 ± 0.9	4.0 ± 0.7

* Samples from ARIES 12 D were counted in a β-γ system in the beta mode with a 34 % efficiency for ^{40}K betas and 2-3 cph background (Bhandari, 1969) whereas ARIES 15 D samples were counted in a conventional 2 π beta system (Lal and Schink, 1960) with the same efficiency as above, but with 6-7 cph background.
Errors indicated are due to 1 σ counting statistics only.

MEASUREMENT OF U-Th SERIES ISOTOPES

About 5 % of the total solution was used for determining ^{210}Pb, ^{226}Ra, ^{230,232}Th and ^{234,238}U. Ra was measured by the Rn technique (Bhat, 1970) and the rest according to the procedures described by Krishnaswami and Sarin (1976). Results of these measurements are given in Table 3.

DETERMINATION OF COMPOSITION

The concentrations of Mn, Fe, Ca, Mg, Co, Al, Ni, Sr, Ba, Cu, Zn and Cr in the leaches and residues of the

surface sections of the two nodules were determined using a Model 305 A Perkin Elmer Atomic Absorption Spectrophotometer. A reagent blank was also measured to estimate the blank levels for various elements. Results of the radioactive and stable elemental concentrations are given in Tables 4 and 5.

DISCUSSION

Before discussing the growth rates, it is relevant to go into the compositional details of the nodules and the leaching procedures adopted.

COMPOSITION

As has been mentioned in the experimental section, both the NH$_2$OHHCl leach and residue were analysed for major and trace elements in Aries 12D. In the case of Aries 15D the residue left after NH$_2$OHHCl leaching, was further leached with 6M HCl and the final residue was also brought into solution and all the three fractions were analysed. Tables 4 and 5 give all the data from which the following conclusions can be drawn :
i) The elemental composition of the nodules is very similar.
This would be expected since both nodules come from about the same location (Table 1).
ii) Hydroxylamine hydrochloride is a good leachant for most of the elements. It is clear from Tables 4 and 5 that Mn, Ca, Mg, Co, Ni, Sr, Ba, Cu and Zn are leached with efficiencies exceeding 90 % — in fact Mn is leached out quantitatively. It only proves that all these

TABLE 3
U, Th, Ra and ^{210}Pb concentrations in the two manganese nodules studied

Sample	Depth (mm)	^{238}U* (dpm/g)	^{226}Ra* (dpm/g)	^{210}Pb* (dpm/g)	^{210}Pb/^{226}Ra* (A.R)	^{234}U/^{238}U* (A.R)	^{230}Th$_{exc}$/^{232}Th** (A.R)
ARIES 12 D	0-3.8	10.6 ± 0.1	44.7 ± 0.9	33.7 ± 1.1	0.75 ± 0.02	1.01 ± 0.04	3.9 ± 0.1
	3.8-7.5	9.0 ± 0.7	9.3 ± 0.3	11.2 ± 0.4	1.2 ± 0.5	1.07 ± 0.07	–
	7.5-19.1	10.0 ± 0.4	1.0 ± 0.1 (1.1 ± 0.1)	7.3 ± 0.2	7.3 ± 0.2	0.93 ± 0.03	–
	Core	3.4 ± 0.2*	6.9 ± 0.2*	8.3 ± 0.6*	1.2 ± 0.1*	0.99 ± 0.05*	6.9 ± 1.0*
ARIES 15 D	0-3.1	6.8 ± 0.6	49.5 ± 0.8	59.0 ± 0.9	1.19 ± 0.03	1.09 ± 0.14	5.2 ± 0.2
	5.5-7.9	10.0 ± 0.4	25.3 ± 0.5	17.5 ± 0.5	0.78 ± 0.03	0.99 ± 0.03	–
	7.9-14.5	4.3 ± 0.3	5.1 ± 0.1	8.9 ± 0.2	1.75 ± 0.05	1.00 ± 0.07	–

* Measurements on NH$_2$OHHCl leachate only.
** Measurements on HCl leachate of the residue.
* Core was completely dissolved for the analyses.
A.R : Activity Ratio.
Errors indicated are due to 1 σ counting statistics only.

TABLE 4
Radioctive and stable elemental composition of ARIES 12D (0-3.8 mm)

Element/Isotope	Total concentration* (Wt.%)	Fractional Concentration	
		In NH$_2$OHHCl leach (%)	In residue (%)
Mn	21.75	99.9	0.1
Fe	15.2	95.7	4.3
Ca	2.5	99.0	1.0
Mg	1.0	98.4	1.6
Co	0.69	99.99	0.01
Al	0.78	47.6	52.4
Ni	0.39	99.9	0.1
Sr	0.14	99.7	0.3
Ba	0.14	98.3	1.7
Cu	0.042	99.3	0.7
Zn	0.05	98.5	1.5
Cr	0.002	45.7	54.3
^{210}Pb dpm/g	30.5 ± 0.8	98.5	1.5
^{226}Ra dpm/g	40.4 ± 0.8	98.0	2.0
^{230}Th dpm/g	31.9 ± 0.4	1.0	99.0
^{232}Th ppm	22.3 ± 0.7	2.0	98.0
^{238}U ppm	13.9 ± 0.1	90.0	10.0

* Total concentration is based on that in NH$_2$OHHCl leach and residue.

TABLE 5
Radioctive and stable elemental composition of ARIES 15D (0-3.1 mm)

Element, Isotope	Total concentration* (Wt. %)	Fractional Concentration		
		In NH$_2$OHHCl leach (%)	In HCl leach of residue (%)	In the remainder (%)
Mn	20.8	99.9	0.1	0
Fe	14.8	81.1	18.8	0.1
Ca	2.1	98.6	0.6	0.8
Mg	0.89	94.1	4.5	1.4
Co	0.86	99.9	0.1	0
Al	0.72	35.4	25.4	39.2
Ni	0.38	99.3	0.7	0
Sr	0.13	99.4	0.1	0.5
Ba	0.11	94.6	3.2	2.2
Cu	0.03	97.0	2.8	0.2
Zn	0.04	92.6	7.2	0.2
Cr	0.002	11.0	81.7	17.3
^{210}Pb dpm/g	46.9 ± 0.7	97.4	nm	2.6
^{226}Ra dpm/g	39.5 ± 0.6	97.0	3.0	nm
^{230}Th dpm/g	59.1 ± 0.6	0.7	99.3	nm
^{232}Th ppm	40.4 ± 1.1	0.7	99.3	nm
^{238}U ppm	10.0 ± 0.7	70.0	30.0	nm
^{10}Be dpm/kg	33.4 ± 1.8	72.0	28.0*	nm

* Total concentration is based on the three fractions indicated.
+ This sample has to be recounted for better statistics and constancy check.
n.m. : Not Measured.

elements are primary authigenic. To check on this point we have leached standard W1, basalt by NH$_2$OHHCl as in the case of nodule samples. Only 4 % of the total Mn (1350 ppm for W1) and 6.8 % of the total Fe (W1 has 7.8 % Fe by weight) could be effectively leached by NH$_2$OHHCl. Arrhenius (1963) was the first to do this type of leaching with 1M NH$_2$OHHCl. Barring Mg, Ca, Al and Zn he measured all the elements we have done plus some others we have not. His results on Mn, Cu, Ni and Sr are in good agreement with ours. However, he finds Ba enriched in residue left after both NH$_2$OHHCl and HCl leaches. This residue is most probably barite. Nodules from productive areas will indeed have large amounts of Ba in the form of insoluble BaSO$_4$. Cobalt is the only element where his NH$_2$OHHCl leaching efficiency varied anywhere between 14 to 99 %. One needs to analyze more nodules from different regions to check on this element.

iii) Fe is leached with 95 % in the case of Aries 12D and with 81 % for Aries 15D by NH$_2$OHHCl. Where the leaching was poor most of the Fe remained behind in the residue insoluble in HCl. Arrhenius (1963) also found the same behaviour for Fe in the nodules; the leaching efficiency of NH$_2$OHHCl varied from 30-90 %. Aluminium is another element which could be leached only with 35-47 % efficiency. The remainder is probably present as insoluble alumino-silicates and could only be removed by HCl and HF treatments. The Al leached by hydroxylamine hydrochloride most probably represents the authigenic part and should be more useful for measuring ^{26}Al in nodules. The HCl leachates dissolve some of the detrital aluminosilicates thereby diluting the ^{26}Al activity in the Al fractions.

iv) Cr is not leached efficiently by NH$_2$OHHCl since most of it is detrital. It is also known that Cr accumulates about 40 times more in sediments compared to nodules (Somayajulu et al., 1971).

v) Of the U-Th decay series isotopes studied only Ra content of the two nodules is identical. Also ^{226}Ra and ^{210}Pb are leached efficiently by NH$_2$OHHCl. U in Aries 15D appears to be more concentrated in the residue (Table 5).

vi) The most striking example is Th. Both ^{230}Th and ^{232}Th are not leached by NH$_2$OHHCl. Either they are mostly attached to clays which could no be leached by the weakly acidic (pH 3) reducing reagent or that the Th isotopes being very reactive adsorbed back on to the clays even during leaching. Further experiments are in progress to understand the Th isotope behaviour.

vii) Finally, the ^{10}Be : There appears to be about 28 % of this activity in the residue. Unlike most other samples the radioactivity from the residue has yet to be repurified and subjected to constancy checks, before a final inference can be made. The ^{10}Be activity in units of dpm/gMn appears to be same in both the nodules studied here as well as in the NH$_2$OHHCl leaches of marine sediments. The value is 0.2 dpm/g Mn. In this comparison we have used the data of Amin et al. (1966)

on core MSN 96 which has Mn concentration far in excess of the detrital contribution (Krishnaswami, 1976). It, thus, appears that Mn scavenges Be effectively.

GROWTH RATES

Only the ^{10}Be method is used for determining the growth rates. The ^{10}Be activity measured in the NH$_2$OHHCl leach of the individual sections of each of the nodules is plotted as a function of depth (Fig. 2) from which the rates of accumulation are determined to be 3.3 and 2.3 mm/10^{6}yrs respectively for Aries 12D and 15D. These rates are in good agreement with those determined using ^{10}Be and ^{26}Al on other nodules (Bhat et al., 1970; Guichard et al., 1978) as well as with the ones determined by the U-Th decay series nuclides (Ku, 1977).
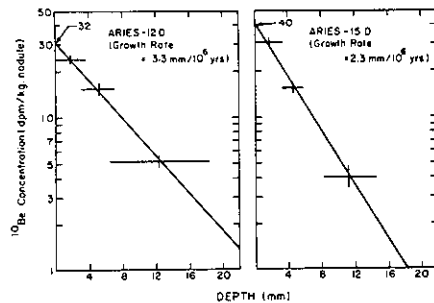

FIG. 2. – ^{10}Be versus depth plots in the two nodules. The extrapolated surface activities are also indicated for each nodule.

The integrated ^{10}Be activity in the two nodules is 0.06 and 0.05 dpm/cm^2 which is about 20 times smaller than its production rate. Three possible explanations for this discrepancy have already been put forward for nodules using ^{10}Be and ^{230}Th studies (Bhat et al., 1970; Krishnaswami et al., 1972). These are : (i) that nodules grow for < 10 % of their life time on the sediment surface, (ii) that there is a continuous growth and erosion of their surface such that the net growth is only < 10 % and (ii) that nodules do not effectively scavenge Be isotopes. Explanations (i) and (ii) are equally likely. Photographic evidence of organisms cleaning nodule surfaces covered with sediments, was presented by Paul (1976) which lends support to the first explanation. As far as (iii) is concerned, it is likely that the precipitation of hydrous oxides of Mn and Fe might be taking place from within a few hundred meters of the water column above the site of formation. Most of the ^{10}Be might have been scavenged by clays and whatever ^{10}Be reaches within this water column will only be scavenged by the nodule material.

LATITUDINAL VARIATION OF ^{10}Be IN NODULES.

Based on the ^{10}Be concentrations of Arctic sediments and those of Amin et al. (1975), Finkel et al. (1977) observed that the pattern of variation of ^{10}Be production rate resembles the fallout pattern of ^{90}Sr in the northern hemisphere. Such a resemblance is due to the fact that the oceanic residence time of ^{10}Be is very small. We have tried to see if there is a latitudinal ^{10}Be variation in manganese nodules. The integrated ^{10}Be activity (Σdpm/cm^2) in all nodules so far studied have been calculated and the data is presented in Table 6. It is clearly seen

TABLE 6
*Integrated ^{10}Be activity in manganese nodules
from different locations in the Pacific*

Nodule	Location Latitude	Longitude	Water depth (m)	^{10}Be activity at surface extrapolated (dpm/g)	Growth rate (cm/10^{6}y)	Integrated* ^{10}Be activity (Σdpm/cm^2)	Référence
ZETES 3D	40°16'N	170°20'E	3000	0.130	0.13	0.10	Bhat et al. (1970)
ARIES 15D ...	20°47.3'N	173°20'E	1278	0.040	0.23	0.05	This work
ARIES 12D ...	20°45.1'N	173°26.4'E	1623	0.032	0.33	0.06	This work
TRIPOD 2D ...	20°45'N	112°47'W	3000	0.035	0.66	0.12	Bhat et al. (1970)
DODO 15-1 ...	19°23'N	162°20'W	4160	0.02	0.33	0.04	Somayajulu (1967)
TECHNO 1 ...	15°S	145°W	4020	0.027	0.28	0.04	Guichard et al. (1978)

* Σdpm/cm^2 = K.ρ.N$_o$ X, where K is geometrical factor (= 1 for flat nodules), ρ = density (assumed to be 2.5 g/cm^3), N$_o$ = extrapolated activity at surface and X the depth at which the activity = N$_o$/e = s/λ, where s = accumulation rate and λ = ^{10}Be decay constant = 4.62 × 10^{-7}yr^{-1} (Yiou and Raisbeck, 1972).
Two other nodules A47-61-3 (9°2.3'N, 151°11.4'W) and C57-58-2 (15°19.5'N, 125°54.4'W) recently analysed for ^{10}Be have dpm/cm^2 values of 0.03 and 0.04 respectively (Krishnaswami – personal communication).

that there is no ^{10}Be variation in nodules covering a latitude range 15°S-40°N. Four nodules analyzed are obtained from 20°N out of which three have values, 0.04-0.06 dpm/cm^2. Since the integrated ^{10}Be activity of the nodules is < 10 % of its production and the growth rates are sporadic as well as a 1000 times lower than those of sediments, variations, if any, would more or less even out.

Th AND U DECAY SERIES ISOTOPES

These measurements on NH$_2$OH.HCl leachates (Table 3) are made mostly to see whether there is any strange behaviour of these nuclides especially in the inner sections of the nodule. Ra in both nodules shows a steep decrease with depth by an order of magnitude. U in Aries 12 D is constant with depth, but varies from 4.3 to 10 dpm/g in Aries 15 D. The high Ra in the surface sections should be due to ^{230}Th exc. The ^{234}U/^{238}U activity ratio is close to unity as expected. The most glaring disequilibrium is the factor of 2-8 enhancement of ^{210}Pb over its parent Ra. In Aries 12 D Ra is grossly depleted with respect to U whereas in Aries 15 D it is in equilibrium with U.

We analyzed the core material (bottom surface) of the nodule Aries 12 D (by total dissolution of the sample) and found that ^{210}Pb and Ra are in equilibrium. Also the U content of the core is significantly lower (3.4 dpm/g) compared to the crust material. The residues of the surface sections of the two nodules after NH$_2$OH.HCl leaching and the core material of Aries 12 D were analyzed for Th isotopes; all three samples show excess ^{230}Th (Table 3). Since nodule is flat (Fig. 1) the core is open and hence the excess ^{230}Th presence is not unexpected.

The problem of ^{210}Pb excess over Ra in the bottom sections of the crust is being investigated further.

FUTURE WORK

Doubts cast on the ^{230}Th methods, due to the irregular surface features of the nodules, diffusion, etc. can be eliminated by resorting to the ^{10}Be method of dating. Even then Frazer and Arrhenius (1972) contend that large nodules such as the ones used for ^{10}Be are atypical. Now there is scope to clear this doubt too by extending ^{10}Be measurements to small nodules as well. With the development of a sensitive technique for the determination of ^{10}Be/^{9}Be ratios using accelerators (Raisbeck et al., 1978) it is possible to measure ^{10}Be/^{9}Be atom ratios as low as 10^{-11} at the extreme. It must also be noted that the naturally encountered ^{10}Be/^{9}Be ratios in nodules will be 10^{-7} to 10^{-8} if no ^{9}Be carrier is added. For a clean separation of Be from the rest of the material even if a few mg Be carrier is added, the ^{10}Be/^{9}Be ratios will not fall below 10^{-11}.

CONCLUSIONS

i) Hydroxylamine hydrochloride leaching of manganese nodules provides a very effective method of sampling the authigenic elements from this mineral.

ii) The ^{10}Be measurements carried out on such leachates (which constitutes at least 72 % of the total ^{10}Be in the nodule) yield accumulation rates that are in the common range determined during several other independent techniques.

iii) The three explanations earlier put forward by Bhat et al. (1970) and Krishnaswami et al. (1972) for the order of magnitude discrepancy between the Σdpm ^{10}Be/cm^2 in nodules and the ^{10}Be production rate still hold. Another possibility is that nodule formation may be taking place from the bottom few hundred meters of the water column above the depositional site.

iv) The composition and growth rates of the two nodules from the same location are very similar.

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DISCUSSION

K. BOSTROM : You state that the nodules only incorporate 10 % of the ^{10}Be produced. However, how do you know that they should receive more ; after all, isn't much depositing along the margins of the oceans where we have most of the biological productivity ?

B.L.K. SOMAYAJULU : Abyssal, sediments have about the same Σ^{10}Be as expected. Nodules have only less than 10 % because they either grow for less than 10 % of the time, due to sediment depositing, or they hate beryllium. We have given other explanations in the text.

L. LABEYRIE : Have you any idea how ^{10}Be and ^{230}Th are incorporated within the nodule. The difference between the integrated fluxes of Be and Th, have to be explained chemically.

B.L.K. SOMAYAJULU : Chemically ^{10}Be and ^{230}Th should behave rather similarly. The reason why they have only less that 10 % has something to do with the growth of nodules. Possible explanation are given in the text.

K. COCHRAN : For the samples with anomalously ^{226}Ra, it would be interesting to dertermine the ^{226}Ra content of the residue.

B.L.K. SOMAYAJULU : Certainly, we will do it soon.
I think it would be very worthwhile to form a group and select some nodules with definitive mineralogical and chemical composition. All radiometric and other studies should then be performed on them. As it is different people who are making measurements on different nodules without any idea of what the others are doing.

G. ARRHENIUS : The U.S. National Science Foundation has a project, extending over many years, aiming at a comprehensive investigation of manganese nodule genesis. This program (MANOP) maintains a collection of nodules from which, in principle, samples could be obtained.

RADIOACTIVE DISEQUILIBRIUM IN FISSURE-FILLING MATERIAL AND ITS IMPLICATION IN DATING OF MANGANESE NODULES

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ABSTRACT. – Study has been made of the uranium-series nuclides distribution in the interior of manganese nodules – in regions deeper than the outermost 3-4 mm where U-unsupported ^{230}Th and ^{231}Pa are normally found. Within experimental error, radioactive equilibrium among ^{238}U-^{234}U-^{230}Th prevails in most of the inner layers examined. The disequilibrium observed in a few cases is shown to results from infiltration of "young" sedimentary material (e.g. clay and carbonate) along diagenetically formed cracks or fissures. The extent of the disequilibrium indicates that the fissure-filling process initiated at least 300,000 years ago. This age should constitute a lower limit for the age of the nodules. The observed logarithmic decrease of radioactivity with depth in nodules can be the combined effect of decay and mixing process such as migration of material through fissures observed here. In this case, the accretion rates of nodules must be slower than those estimates obtained by assuming the logarithmic decrease as being solely due to radioactive decay.

RÉSUMÉ. – Une étude de la répartition des nuclides de la famille de l'uranium a été faite à l'intérieur de nodules de manganèse – dans les couches plus profondes que les 3 à 4 mm supérieurs où l'on trouve normalement des excès de thorium 230 et de protactinium 231. Dans la limite des erreurs expérimentales, l'équilibre radioactif entre ^{238}U- ^{234}U- ^{230}Th est réalisé dans la plupart des nodules étudiés. Les déséquilibres observés dans quelques cas résultent de l'infiltration de matériel sédimentaire « jeune » (par exemple argiles et carbonates) le long de fractures ou fissures formées au cours de la diagenèse. L'importance des déséquilibres indique que le processus de remplissage des fissures a commencé il y a au moins 300.000 ans. Cet âge peut constituer une limite inférieure pour l'âge des nodules. La décroissance logarithmique de la radioactivité que l'on observe en fonction de la profondeur dans les nodules peut être due à l'effet combiné de la décroissance radioactive et de processus de mélanges tel que la migration dans les fissures d'un matériau tel que celui que l'on a observé ici. Dans ce cas, les taux d'accrétion des nodules doivent être plus lents que ceux que l'on obtient en supposant que la décroissance logarithmique est due seulement à la décroissance radioactive.

INTRODUCTION

Measurements of ^{231}Pa and ^{230}Th in sediment substrates directly beneath manganese nodules (Ku, 1966 ; Somayajulu et al., 1971 ; Lalou et al., 1978) have highlighted the observation that nodules commonly occur on or in deep-sea sediments of late Quaternary age. That this contrasts with the great antiquity of the nodules, accreting at rates of mm's/10^{6}yr (Ku, 1977), has often been viewed as being paradoxical. The majority of nodule dating results are based on the analyses of U-series isotopes in outermost rinds of a few millimeters thick. Thus it has been suggested that the reported radiochemical profiles result from processes such as surface adsorption and/or mixing, rather than radioactive decay (Bonatti and Nayudu, 1965 ; Arrhenius, 1967 ; Lalou and Brichet, 1972). If so, manganese nodules could form rapidly and their ages could be thousands (instead of millions) of years old (Cherdyntsev et al., 1971 ; Lalou et al., 1978). Such possibility can be dismissed on the basis of concordant age estimates from a variety of methods (Ku, 1977). However, the reported ^{230}Th-^{234}U and ^{231}Pa-^{235}U disequilibria in inner layers (Cherdyntsev et al., 1971 ; Nakanishi et al., 1977 ; Lalou et al., 1978) do merit further investigation, as they have been used as evidence for the rapid formation of nodules.

This paper reports the results of a study in extending measurement of the U-series isotopes from surface to deeper layers (> 4 mm deep) in five nodule specimens. It will show that within experimental error, secular equilibrium between ^{230}Th and ^{234}U is found in most of the deeper layers examined. In case where disequilibrium is observed, it can be explained by the presence of "young" contaminant material contained in the cracks or fissures occurring in the nodules (Ku et al., 1975).

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