

## TECHNO ENCRUSTATION II. - STRUCTURAL AND CHEMICAL STUDY

C. LALOU (\*), E. BRICHET (\*), C. JEHANNO (\*)

**ABSTRACT.** - Using as a starting point the results giving "traditional" growth rates as determined by the decrease of radioelements (part I) and the hypothesis of rapid formation, the different mineralogical, structural and chemical characteristics of the sample have been studied to try to understand the possible mode of formation of this encrustation. A rapid formation would account for: i) the very peculiar structure of the sample composed of oriented botryoids and the bundle-like structure of the outermost oxide layer; ii) the fact that this sample represents a substitution of a preexisting hyaloclastite; iii) the different chemical gradients, mainly iron, thorium and uranium; iv) the fact that this sample which cannot have been maintained at the sediment-water interface by bioturbation is not covered by a great thickness of sediments. On the other hand, an unsolved problem remains: Why different radionuclides used for dating give growth rates of the same order of magnitude and different "exposition ages".

**RÉSUMÉ.** - Partant des résultats obtenus pour la vitesse de croissance « traditionnelle » par la décroissance des radionuclides (première partie) et d'une hypothèse de formation rapide, on cherche les différentes caractéristiques, minéralogiques, structurales ou chimiques, pouvant venir à l'appui de l'une ou l'autre théorie. Une formation rapide permettrait d'expliquer à la fois la structure très particulière en botryoïdes orientés ou en faisceaux, le fait que cet échantillon soit une substitution d'une hyaloclastite préexistante, les différents gradients chimiques observés, essentiellement ceux du fer, du thorium et de l'uranium, et le fait que cet échantillon qui n'a pu être maintenu en surface par bioturbation ne soit pas enfoui par la sédimentation. Elle ne permet toutefois pas d'expliquer pourquoi les différents radionuclides utilisés pour la datation donnent des vitesses de croissance du même ordre de grandeur et des « âges d'exposition » différents.

### I. - INTRODUCTION

In the first part of this paper, we have seen that slow growth rates may be calculated from radiochemical data and then that this sample may be considered as a "normal sample", but we have also seen that some of those radiometric measurements require explanation if the slow growth rates are to be accepted.

In this second part, we will try, in the light of the structure and of some chemical characteristics of this encrustation, to discuss the possible ways of formation.

### II. - STRUCTURE

The overall structure of the sample is a well stratified hyaloclastite which has been deeply altered into montmorillonite and in which subsequently the glass fragments have been replaced by Fe-Mn oxides, while some silica had reprecipitated in the form of opal (G. Marinelli pers. comm). This well oriented structure is shown in Figure 2 Part I. This figure is a reflection microphotograph of a polished section of the whole sample.

Only the lower layer, layer A, may be considered as essentially of sedimentary origin.

A detailed study has been done, essentially by S.E.M. examination of broken fragments in the 5 different layers.

- *Layer A* shows no well marked structures, and seems characteristic of a sedimentary layer, including numerous nanofossils. Figure 1 shows an association of coccoliths among which, *Coccolithus pelagicus*, a solution resistant species, has been tentatively identified. Unfortunately, this species has an age range from Eocene to present and can therefore only provide a maximum age of  $50 \times 10^6$  years. As a general rule, the walls of the microorganisms are composed of Si, K, Ca, Na and Al, and the filling is made of Fe, Ti, Mn, Cu.

After HF attack, the more resistant minerals remaining are rutile, chromite and zircon, as identified by their X-ray diffraction pattern.

- *Layer B* consistently exhibits a confused structure but shows a tendency towards a better organization towards layer C. Some features as the one presented Figure 2, may be considered as the beginning of botryoids. The spherical feature is composed of Fe, Si, Al, K and a little Ti, and can be differentiated from the surrounding material in which, in addition to those elements, Ti is much more abundant and Ca and Mn are present. Heavily altered microorganisms are also

(\*) Centre des Faibles Radioactivités Laboratoire mixte CNRS - CEA, 91190 - Gif sur Yvette, France.

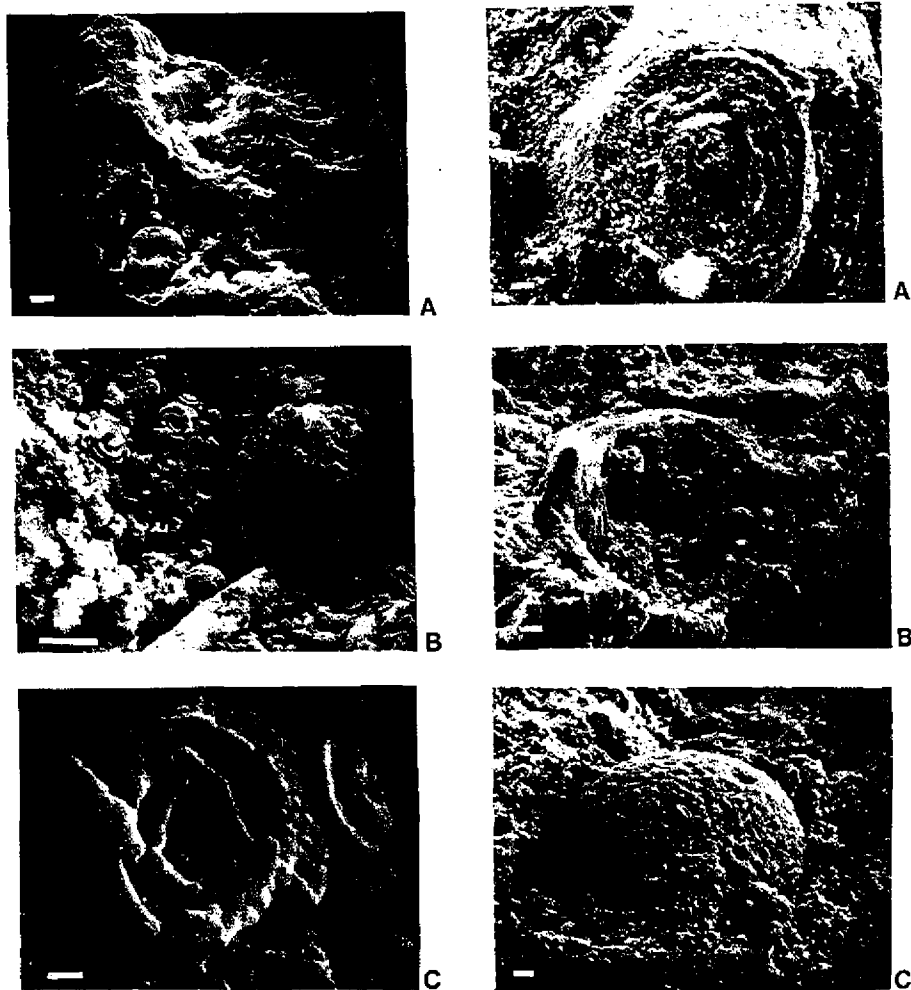


FIG. 1. - S.E.M. picture of a fracture from zone A: A) General view showing numerous microorganisms made of Fe, Ti, Mn, Cu. The bar is 10 microns; B) Enlargement of upper right part of A showing coccoliths. The bar is 10 microns; C) Enlargement of coccoliths showing the dissolution. The bar is 1 micron.

present and are composed of Fe, Si, Al and K, even the coccoliths.

- In layer C, the botryoidal appearance of the sample becomes evident, with botryoids crowded one against the other. Numerous organisms consisting mainly in Si and Fe are present inbetween the botryoids. An accumulation of small spheres has been found (Figure 3) with Mn as their principal constituent

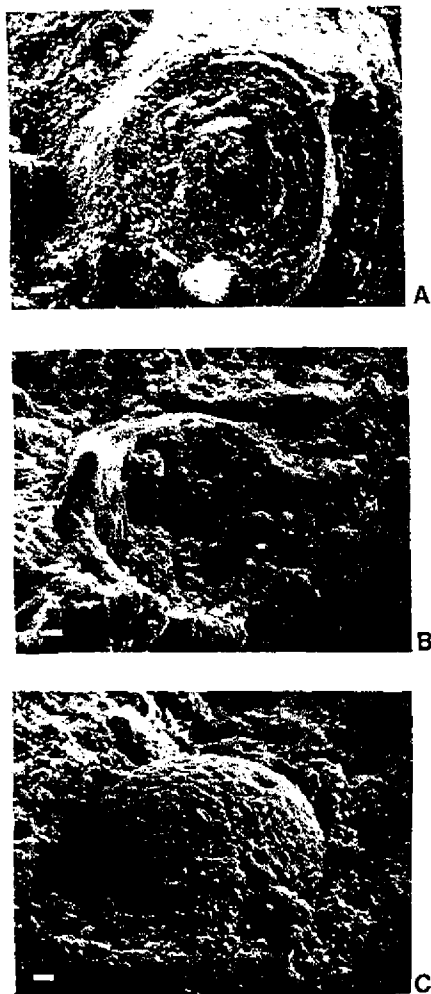


FIG. 2. - S.E.M. picture of a fracture from zone B: A and B) departures of botryoids; C) Sphere made with Fe + Si + Al + K and a few Ti in a mixture of Fe + Si + Al + K + Mn and important Ti. The bar is 10 microns.

but also very enriched in nickel. The appearance of these spheres suggests that they may be composed of birnesite.

In Figure 2 (Part I) the regular organization of the botryoids is well illustrated. This layer is dark black in color, in contrast to the two surrounding layers (layer B and layer D) which are brownish.

- Layer D is brown in color, but S.E.M. study of

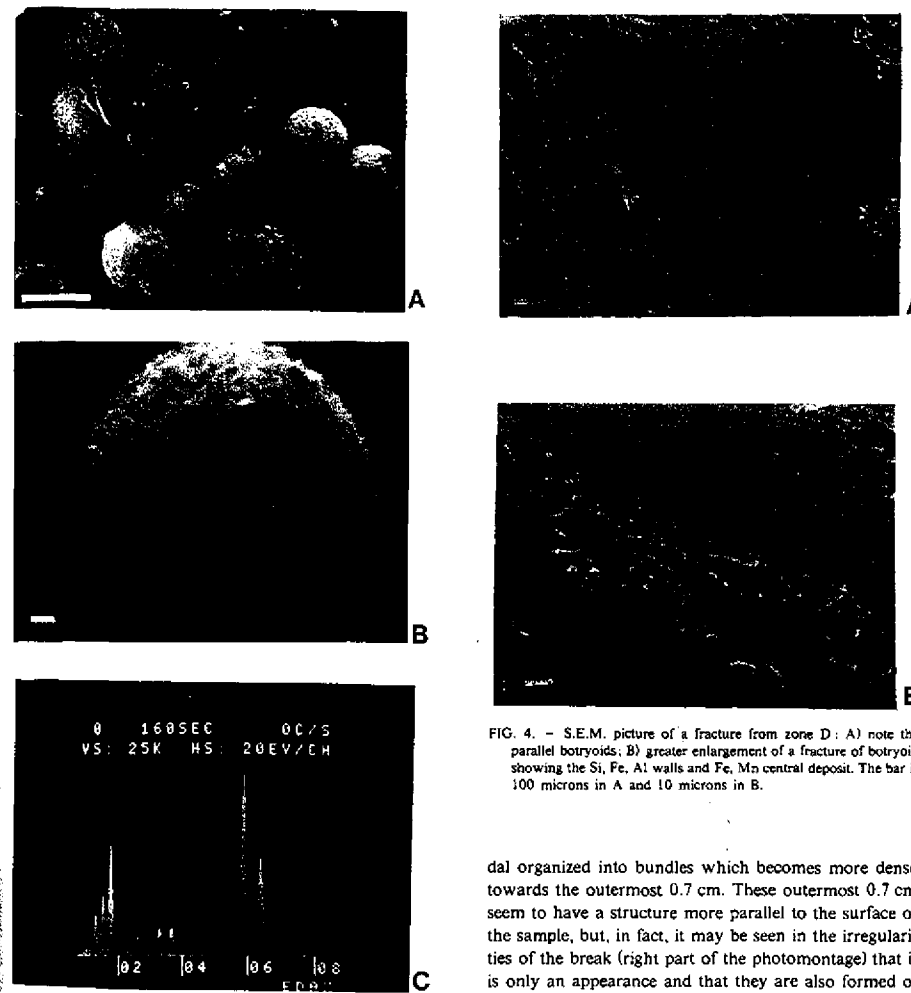


FIG. 3. - S.E.M. picture of a fracture from zone C showing an accumulation of spheres and their E.D.A.X. spectrum. The bar is 10 microns for A and 1 micron for B.

dal organized into bundles which becomes more dense towards the outermost 0.7 cm. These outermost 0.7 cm seem to have a structure more parallel to the surface of the sample, but, in fact, it may be seen in the irregularities of the break (right part of the photomontage) that it is only an appearance and that they are also formed of botryoids crowded one against the other.

At greater enlargement (Figure 6), the botryoids appear covered with tiny craters. They are formed with concentric sublayers which can be easily separated one from the other.

the fracture shows that it is composed of a somewhat columnar Mn oxide (Figure 4), completely surrounded by particles of Al, Si, Fe, partly made up of organisms.

- Layer E is the layer on which the radiochemical study of part 1 was performed. Figure 5 is a photomontage of a break across the entire layer.

From the contact with layer D towards the outermost surface of the sample, one may see that from 2 cm depth until about 0.7 cm, the structure is purely botryoi-

### III. - CHEMICAL STUDY

#### 1) EDAX STUDY OF THE BOTRYOIDS

From the 5 zones, we have separated botryoids, imbedded and polished them for quantitative analysis

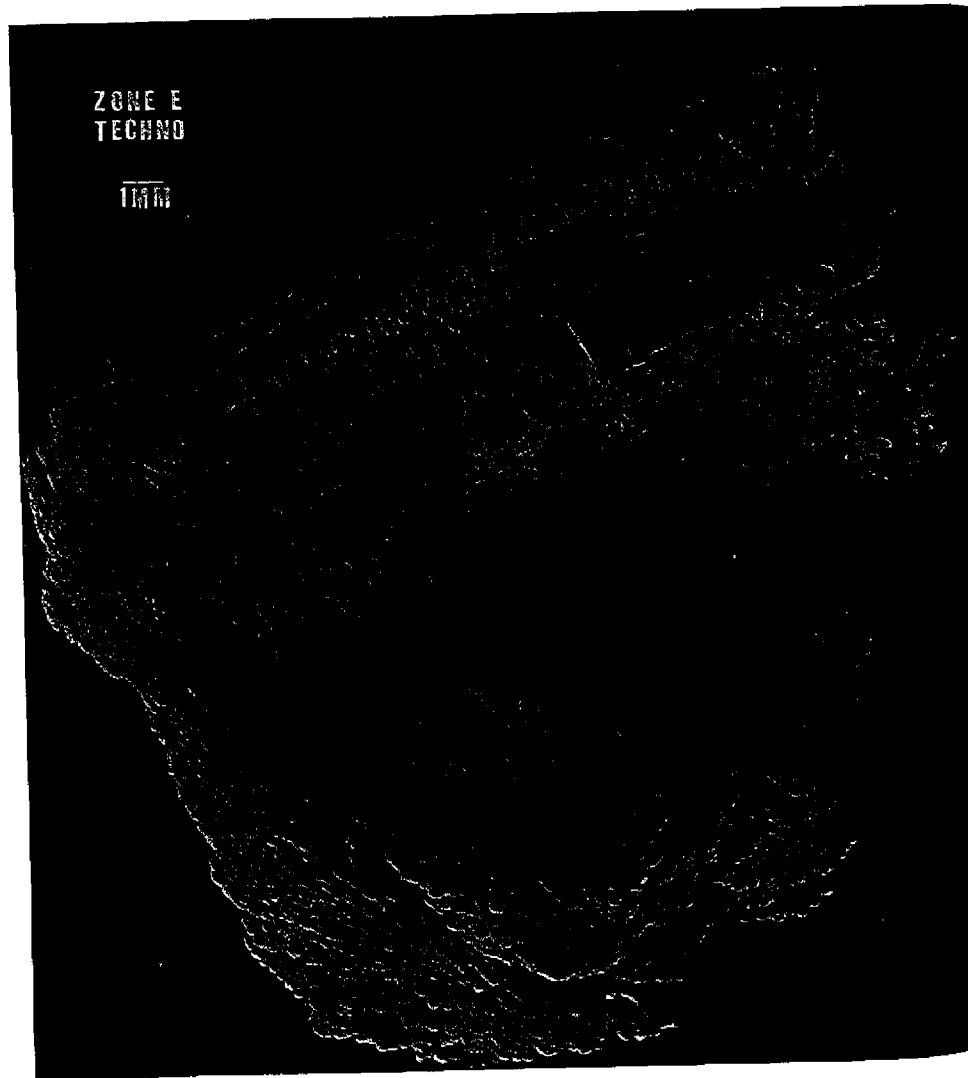


FIG. 5. - Photomontage of S.E.M. pictures of a fracture from the whole layer E.

with X ray dispersive analysis system (EDAX). The X ray spectrums are given in Figure 7, and the elemental composition in Table 1.

The different tendencies are :

Na and Mg are quite constant, Al, Si, Ti decrease towards the exterior of the sample, as always, Fe and Mn are negatively correlated, Fe

being dominant until layer C, and Mn in layers D and E.

#### 2) NEUTRON ACTIVATION ANALYSIS AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

On five microlayers in layer E, from 0 to 1.1 mm

TABLE 1  
EDAX analysis of botryoids  
from different layers of TECHNO

Element (%)	Layer A	Layer B	Layer C	Layer D	Layer E
Na.....	2.6	1.3	2.3	1.9	1.6
Mg.....	1.4	1.5	1.0	1.2	1.3
Al.....	1.6	1.6	1.3	0.5	0.8
Si.....	5.2	3.3	3.6	2.0	2.4
K.....	0.1	0.1	0.1	0.2	0.4
Ca.....	1.4	2.1	1.7	3.0	2.6
Ti.....	3	0.5	0.4	0.4	1.4
Mn.....	13.5	21.8	18.5	34	36
Fe.....	32.7	30.4	33.3	19.8	18.2
(O <sub>2</sub> ,H <sub>2</sub> )...	38.5	37.4	37.8	37	35.3

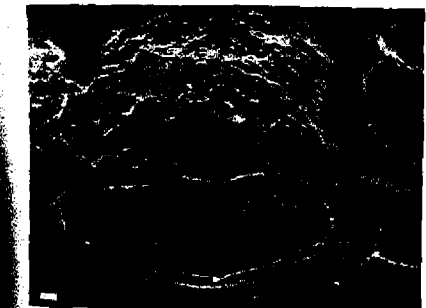
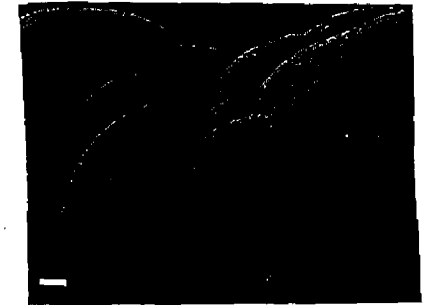


FIG. 6. - Details of figure 5 : A) Botryoids of the upper part of layer E showing the concentric sublayers; B) Botryoids of the lower part of layer E, showing the tiny craters; C) Lower part of botryoids (right upper part of Figure 5). The bars are 10 microns in the three photos.

depth, Na, Fe, Co, La, Ce, Nd, Sm, Eu, Yb, Lu and Th have been measured by neutron activation, while Ni, Cu and Pb have been measured by atomic absorption spectrophotometry.

Moreover, some of those elements have been measured in bulk samples of other zones.

Results are given Table 2.

In the 5 microlayers, Na, Fe, Pb, Nd, Sm and Lu are

quite constant, Co, Ni and Th, as shown also by radiochemistry for this last element, show a tendency to decrease while Cu, La, Ce, Eu, Yb show a tendency to increase.

Zone A', the lowest part of zone A, is characterized by a greater abundance of microorganisms and a higher content in Cu ( $\approx 0.2\%$ ) possibly due to those microorganisms.

The rare earth element patterns for the elements measured by neutron activation, La, Ce, Nd, Sm, Eu, Tb, Yb and Lu are shown Figure 8. The values are normalized to shales (Haskin and Haskin, 1966) and show only a slight tendency towards a positive anomaly of cerium, which is generally lower than those shown by Piper (1974).

#### IV. - DISCUSSION

The structure of this sample certainly reflects its origin. We have to take into account that, at least until layer E, the oxide is a refilling of a preexisting structure and certainly not a simple precipitation. For layer E which is made of a purer deposit, in which foreign material is scarcer, it may possibly be considered as the result of a true precipitation without preexisting frame, but its structure has been evidently predetermined by the underlying structure. Effectively, in layer D (Figure 2 part 1) it may be seen that the same bundles of botryoids exist, but separated by patches of Fe-Si material.

This structure may be of some help in choosing between the two radically different growth rates hypothesized. Two origins for the elements must be considered to render into account these two different possible growth rates :

If the slow growth rates are to be kept, sea water is the origin of the elements (hydrogeneous origin in Bo-

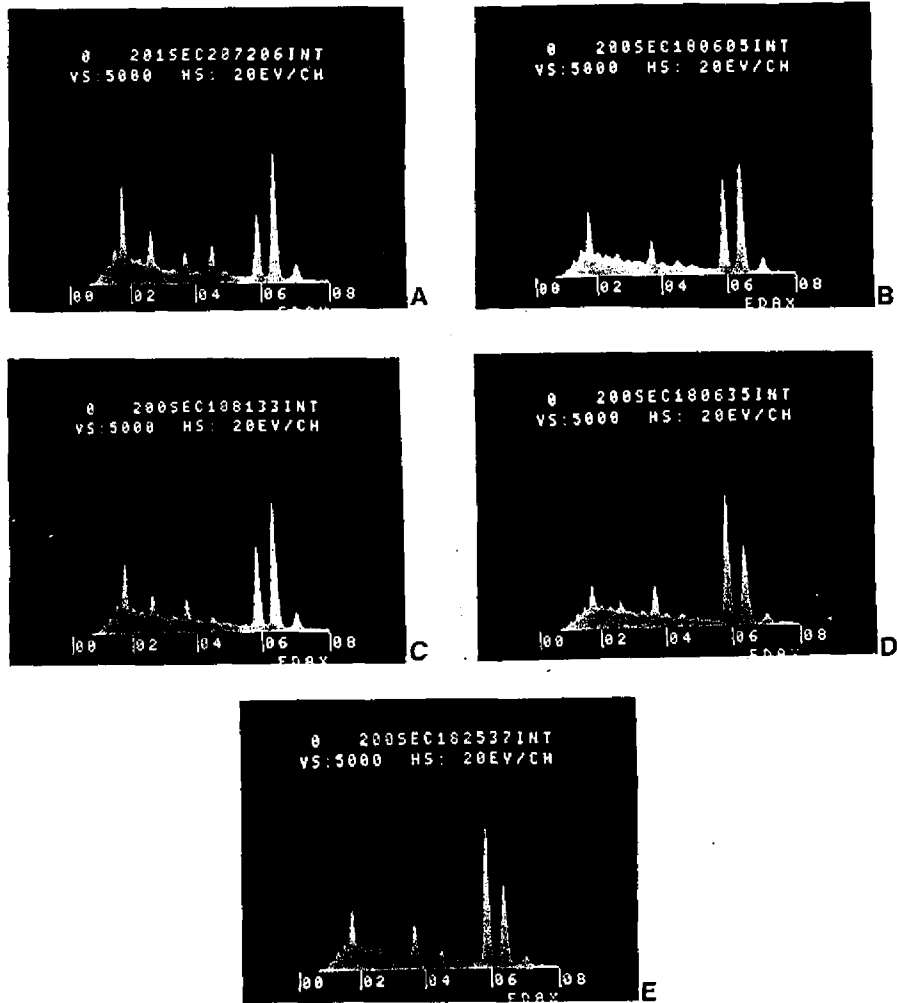


FIG. 7. - E.D.A.X spectrum of botryoids for layers A,B,C,D and E respectively.

natti's classification, 1972). This implies a preferential direction for the introduction of the oxides, from outside to inside. As at least the 8 deepest centimeters are formed of a preexisting body, this requires a regular precipitation first in the deeper parts and gradually towards the surface. It seems difficult to think that such a slow precipitation is no longer effective as soon as it reaches the surface of the preexisting block, forming an impermeable layer at the boarder of the sample which does not allow further oxide penetration in the structure

on a large scale. In such a case, numerous patches of preexisting hyaloclastite would remain without filling, as it is the case in ordinary nodules formed around a more or less altered fragment of rock or indurated sediment. In such cores, manganese and iron oxides penetrate, but only following preferential paths.

The same restriction may be applied if we consider a diagenetic origin. In this case, we have to reverse the path of introduction of the elements. But, even if diagenetic origin may introduce manganese (it is sometimes

TABLE 2

Sample	Depth interval (mm)	Na %	Fe %	Co ppm	Ni ppm	Cu ppm	Pb ppm	La ppm	Ce ppm	Nd ppm	Sm ppm	Eu ppm	Yb ppm	Lu ppm	Th ppm
Layer E															
(1)	0 -0.23	1.54	21.5	8260	3220	826	947	264	663	297	56	7.8	19.0	3.7	39.7
(2)	0.23-0.47	1.58	21.7	8400	3580	895	989	278	679		58		20.6		38.6
(3)	0.47-0.69	1.54	19.3	8140	3455	949	969	263	676	253	58	10.8	21.0	3.3	36.6
(4)	0.69-0.90	1.54	20.8	7440	3091	1033	948	277	677		60		24.3		
(5)	0.90-1.11	1.58	21.3	6990	2927	1075	928	288	736	297	62	11.1	24.2	3.8	32.4
Layer E mean value		1.55	20.9	7846	3254	955	956	274	686	282	59	9.9	21.8	3.6	
Layer D				2750	1720	642									
Layer C		1.23	33.7	2060	1950	1540	1270	309	701	361	56	9.3	25.1	3.5	7.9
Layer A						640	133								
Layer A'						1900	575								

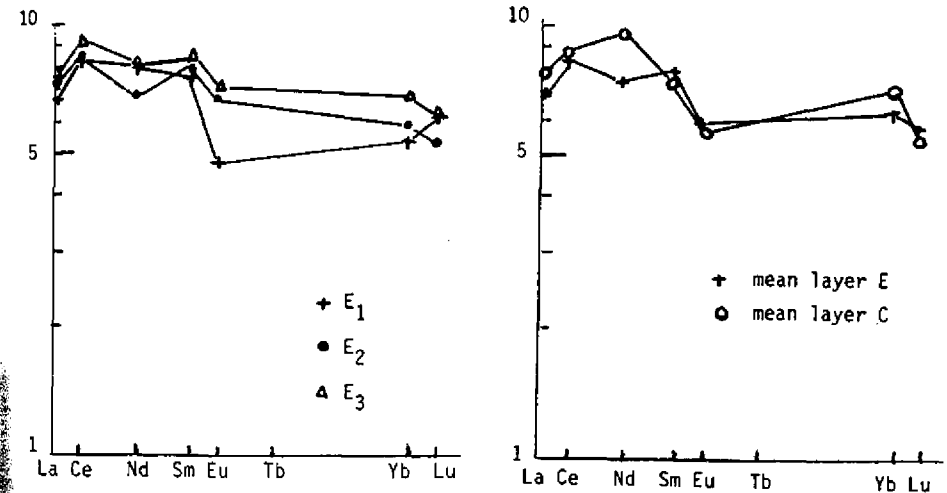


FIG. 8. - Rare earth elements patterns normalized to shales for 3 microlayers in layer E and for mean samples in layers E and C.

invoked to render into account pure Mn deposits in some nodules at the contact between lower face and sediment, Krishnaswami and Cochran, 1978) it is relatively difficult to introduce iron by such a process.

Anyway, a slow regular precipitation cannot explain why oxide botryoids are richer in iron at depth.

In the case of a rapid formation, another source than sea water or interstitial waters is implied for the metallic constituents, and a volcanic, halmolytic or hydrothermal origin must be considered. In this case, a super-saturated solution may percolate through the hyaloclastite. Such a mechanism can explain some of the characteristics of this sample:

i) *the gradient of iron in the botryoids*: iron being deposited at a lower pH than manganese, as seen in present day hydrothermal deposits (Hoffert et al. 1978); and/or during the alteration of highly unstable basaltic glass fragments of the hyaloclastite, Fe is left behind, and then is relatively enriched in the less altered part of the hyaloclastite (Bonatti, 1975).

ii) *the gradient of silica in the botryoids*: as silica precipitates as soon as the solution cools.

iii) *the exclusion from the botryoids in layers B to D of the Si and Fe impurities which are then relocated around those botryoids.*

iiii) *the characteristic precipitation of layer E, which*

could be formed from a supersaturated solution percolating through the hyaloclastite and precipitating when debouching into sea water. There, the kinetics of precipitation may be of the same order as those leading to the formation of oolitic iron ores or to the formation of speleothems, in caves, which have, on a different scale the same appearance as layer D. According to Rozentsvit and Epshteyn (1965) the development of minerals from complex gels determines the extensive occurrence of globular, concentrically layered, reticulate botryoidal and other colloform textures and structures.

As the solution becomes less concentrated by mixing with sea water, or the gel less dense, the individual botryoids become less developed and finally become coalescent, giving rise to the denser outermost layer. This layer, in fact, seems to close the system, being a fossil boarder and not a growing one.

Another particular characteristic of layer E must be emphasized: the cratered surfaces of botryoids which appear to be the result of passing of microbubbles throughout the botryoidal material. This could perhaps occur in the case of rapid formation due to a volcanic event during which gases, as for example  $^3\text{He}$  (Clark et al. 1969, Craig et al. 1975, Lupton and Craig, 1975; Jenkins et al. 1978) or  $\text{CO}_2$  (Bostrom, 1974) are emitted, but is difficult to explain in the case of a slow, quiet formation from sea water.

iiii) the gradients found for the elements other than the radionuclides used for the measurements of growth rates and which, in case of radionuclides cannot be interpreted in term of radioactive decrease, i.e. principally  $^{235}\text{Th}$  and  $^{238}\text{U}$ . Those gradient, as well as the one of iron, would be due to a modification of physico-chemical conditions during precipitation.

From an environmental point of view, the presence of hyaloclastites over a wide region of the South Pacific, due to the thermal shattering of the lava has already been established by Bonatti (1967) who indicates that they are often intimately associated with deposits of ferromanganese oxides. In fact, one of the samples studied by this author comes from very near TECHNO. Challenger 276 dredge station (13°28'S, 149°30'W, 4,300 m depth) is described as small fragments of porphyritic basalt, hyaloclastites associated with Mn oxides.

"The transformation of the comminuted fragments of hyaloclastite into montmorillonite is a rapid phenomenon, lasting less than hours for lavas starting from temperatures close to 1000°C (Bonatti, 1967). Moreover, a recent example of this is the Capelino hyaloclastite formation which occurred in 1959 at Fayal Island and which, after only 20 years is completely palagonitized. Consequently, the palagonitization observed in the frame of TECHNO does not imply a great age. As processes of migration and segregation of the metallic elements take place during the high temperature interaction of lava and water (Bonatti and Nayudu, 1965) this process may explain the gradient of iron in TECHNO and the purest final oxide deposit of layer E, and supply

the supersaturated gel needed to have the botryoidal formation of layer E.

In the same region, some other nodules have been studied (Lalou et al. in press):

DO 23 F and DIV A (16°28'S, 146°34'W, 1000 m depth); DO 111 (17°13'S, 145°44'W, 1140 m depth); TA 02 12c, TA 02 12d 1 and 2 (13°50'S, 151°W, 4500 m depth). All those nodules present apparent slow growth rates when studied for  $^{230}\text{Th}$  decrease (some mm/10<sup>4</sup> years), but present, as well as TECHNO, characteristics which do not fit well with such slow growth rates:

DO 23 F presents in the central part of the core, carbonate precipitation in which  $^{14}\text{C}$  activity is measurable (Lalou et al, 1973)

DIV A presents, inbetween oxide and core a postglacial fauna presenting also  $^{14}\text{C}$  activity.

DO 111 presents an important excess of  $^{230}\text{Th}$  in the core (Lalou et al. in press)

For those three nodules, another point must be noted, the initial carbonaceous core is completely or partly epigenized into fluorapatite which needs substantial source of fluorine.

For the other nodules, having a phillipsite core,  $^{234}\text{U}/^{238}\text{U}$  ratios as low as 0.6 have been found in the core.

If we take into account the  $^{230}\text{Th}/\text{cm}^2$  as an "exposition age", for those nodules, we found: DO 23 F = 6.8 10<sup>3</sup> years; TA 02 12 C = 3.1 10<sup>3</sup> years; TA 02 12 d2 = 3.1 10<sup>3</sup> years. For TECHNO, this "exposition age" is, with  $^{230}\text{Th}$ , 8 10<sup>3</sup> years.

In the "volcanic" theory, this implies a very recent volcanic activity in this area, this is not in contradiction with the observations of Hoffert et al. (1978) who indicate that the two peaks on both sides of station 23 are probably structures which are forming nowadays and that neighbouring subactual sediments contain fresh volcanic glasses.

Finally, in the two hypothesis of growth rates, different problems persist:

In the case of slow rate:

i) the excess of  $^{230}\text{Th}$  in deep layers, or the too rapid decrease of  $^{10}\text{Be}$  activity.

ii) the different chemical gradients, mainly iron,  $^{235}\text{Th}$  and  $^{238}\text{U}$ .

iii) the absence of sedimentation for 43 to 120 10<sup>4</sup> years (12 cm of oxide thickness and growth rates of 2.8 mm/10<sup>4</sup> years given by  $^{10}\text{Be}$ , or, 1 mm/10<sup>4</sup> years given by alpha tracks decrease).

iiii) Complete filling of the preexisting body and structure of layer E

v) microcraters on the surface of botryoids in layer E.

For the case of a rapid growth rate, all the aforementioned points may be resolved, but we are still faced with the unsolved question:

Why different nuclides present different profiles, leading to somewhat identical apparent growth rates for

$^{10}\text{Be}$ ,  $^{230}\text{Th}$  and  $^{231}\text{Pa}$ , and why the different nuclides give somewhat different "exposition ages"?

To clarify this point, we need probably a more precise knowledge of the geochemical budget of the isotopes in sea water, and then, of their actual flux on the bottom. Moreover, this implies also that nodules are not chemical closed systems, which has yet been evidenced at least for radium 226 by the measurements of Krishnaswami and Cochran (1978), allowing the penetration (or departure) of elements. In this view, some experiments of Brichet and Lalou are being developed at present which show the possibility of obtaining in the laboratory profiles similar to those occurring in nature.

To conclude, the best way is to quote Nayudu's conclusion (1964): "If some of the results presented here seem to rebel against conformity, it is not the writer's fault; it is because they are of nature's and not of man's conception".

#### ACKNOWLEDGMENTS

We want to thank Professor G. Marinelli for the fruitful discussions, D' J. Labeyrie, D' J.C. Duplessy and L. Labeyrie for their criticisms and D' Walter Dudley who helped to give its form to this manuscript.

Part of this study has been supported by CNEXO and DGRST Grants.

#### REFERENCES

- BONATTI E. (1967). - Mechanisms of deep sea volcanism in the South Pacific. In: *Res. in Geochemistry. P.H. Abelson ed. J. Wiley and sons, vol. 2.* 453-491.
- BONATTI E. (1975). - Metallogenesis at oceanic spreading centers. *Ann. Rev. Earth and Planet. Sci.* 3: 401-431.
- BONATTI E., KRAEMER T., RYDELL H. (1972). - Classification and genesis of submarine iron and manganese deposits. In: *Horn ed: Ferromanganese deposits on the ocean floor. Papers from a conference held at Lamont Doherty Geological Observatory, IDOE-NSF 149-166.*
- BONATTI E., NAYUDU Y.R. (1965). - The origin of manganese nodules on the ocean floor. *Amer. Journ. Sci.* 263, 17-39.
- BOSTROM K. (1974). - The origin and fate of ferromanganese active ridge sediments. *Stockholm contr. Geol.* 27: 149-243.
- CLARKE W.B., BEG M.A., CRAIG H. (1969). - Excess  $^3\text{He}$  in the sea: evidence from terrestrial primordial helium. *Earth Planet. Sci. Lett.* 6: 213-217.
- CRAIG H., CLARKE W.B., BEG M.A. (1975). - Excess  $^3\text{He}$  in deep water of the East Pacific ridge. *Earth Planet. Sci. Lett.* 26: 125-132.
- GUICHARD F., REYSS J.L., YOKOYAMA Y. (1978). - Growth rates of manganese nodules measured with  $^{10}\text{Be}$  and  $^{26}\text{Al}$ . *Nature*, 272, 155-156.

- HASKIN M.A., HASKIN L.A. (1966). - Rare earth in European shales: a re-determination. *Science*, 154, 507-509.
- HOFFERT M., KARPOFF A.M., CLAUER N., SCHAAF A., COURTOIS C., PAUTOT G. (1978). - Néoformations et altérations dans trois faciès volcanosédimentaires du Pacifique sud. *Oceanologica Acta*, 1, 2, 187-202.
- HOFFERT M., PERSEIL A., HEKINIAN R., CHOUKROUNE P., NEEDHAM H.D., FRANCHETEAU J., LE PICHON X. (1978). - Hydrothermal deposits sampled by diving saucer in transform fault "A" near 37°N on the Mid Atlantic Ridge. FAMOUS area. *Oceanologica Acta*, 1, 1, 73-86.
- JENKINS W.J., EDMOND J.M., CORLISS J.B. (1978). - Excess  $^3\text{He}$  and  $^4\text{He}$  in Galapagos submarine hydrothermal waters. *Nature*, 272, 156-158.
- KRISHNASWAMI S., COCHRAN J.K. (1978). - Uranium and thorium series nuclides in oriented ferromanganese nodules: growth rates, turnover times and nuclides behavior. *Earth Planet. Sci. Lett.* 40, 45-62.
- LALOU C., BRICHET E., BONTE P. (in press). - Some new data on the genesis of manganese nodules. In: *IAGOD monograph on the Geology and Geochemistry of Manganese ore deposits. Hungarian Academy of Science.*
- LALOU C., DELIBRIAS G., BRICHET E., LABEYRIE J. (1973). - Existence de carbone 14 au centre de deux nodules de manganèse du Pacifique, âges  $^{14}\text{C}$  et  $^{230}\text{Th}$  de ces deux nodules. *C.R. Acad. Sc. Paris*, 276, 3013-3015.
- LUPTON J.E., CRAIG H. (1975). - Excess  $^3\text{He}$  in oceanic basalts: evidence for terrestrial primordial helium. *Earth Planet. Sci. Lett.* 26, 133-139.
- NAYUDU Y.R. (1964). - Palagonite tufts (hyaloclastites) and the products of post-eruptive processes. *Bull. Volcanologique*, 27, 391-410.
- PIPER D.Z. (1974). - Rare earth elements in ferromanganese nodules and other marine phases. *Geochim. Cosmochim. Acta*, 38, 1007-1022.
- ROZENTSUIT A.O., EPSHTEYN G.Y. (1965). - Some features of minerals developing from gels of complex composition. *Trans. Intern. Geology Rev.* 9, 7, 939-946.

#### DISCUSSION

D. HEYE: In your last two figures, which are not in the paper, there was shown that  $^{231}\text{Pa}$  and  $^{10}\text{Be}$  were contacted to nodule material in a solution. During about 20 days only these elements moved in the material up to 3-5 mm depth. I am sorry but these results argue against your own model concerning "exposure times" of several thousand years. If these elements can move so far within a few days, then these elements would move all over the nodule during an exposure time of several thousand years. In such a case the radioactive elements Pa and Be must be distributed constant all over the nodule. The consequence can only be that something is wrong here.

C. LALOU: I don't think that these first experiments can argue for one of the other hypothesis as they are far from the natural phenomenon, specially concerning the way of introduction. In nature, the radionuclides are added continuously and not at once as in our experiments.

These experiments of "diffusion" of radionuclides have been conducted essentially to show that nodules are not closed systems and that artifacts may exist.

L. LABEYRIE: The radiotracer penetration experiments would show, by the very rapid increase at depth of the  $^{231}\text{Pa}$  and  $^{10}\text{Be}$ , an

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  $^{230}\text{Th}$  and  $^{231}\text{Pa}$ .

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  $\text{FeOOH} \cdot x\text{H}_2\text{O}$ . 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, anisotropy, 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 ( $\text{MnO}_2$ ). 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

P. SHARMA (\*) and B.L.K. SOMAYAJULU (\*)

ABSTRACT. —  $^{10}\text{Be}$ , U and Th isotopes, Ra,  $^{210}\text{Pb}$ , 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  $^{10}\text{Be}$  deduced growth rates (2.3 and 3.3  $\text{mm}/10^6$  years) are in good agreement with those reported in literature for other nodules using independent techniques. The order of magnitude discrepancy between the integrated  $^{10}\text{Be}$  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  $^{10}\text{Be}$ , les isotopes de U et Th, le Ra, le  $^{210}\text{Pb}$ , 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  $^{10}\text{Be}$  (2.3 et 3.3  $\text{mm}/10^6$  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  $^{10}\text{Be}$  (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 de 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 all these theories can be had from Goldberg (1954); Arrhenius (1967); Ku (1977) and Lalou et al. (1977). An up-to-date account on all aspects of the ferromanganese

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 (Crevelius et al. 1971), cosmogenic  $^{10}\text{Be}$  (Bhat et al., 1970; Krishnaswami et al., 1972) and  $^{26}\text{Al}$  (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  $\text{mm}/10^6$  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  $^{230}\text{Th}$ ,  $^{234}\text{U}$  are doubted especially in nodules where anomalous behaviour of these nuclides was found (Lalou and Bricquet, 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  $^{230}\text{Th}$  values that show the nodules to be growing at rates  $\text{mm}/10^6$  yrs (Lalou et al., 1977). Arrhenius (1967) sus-

(\*) Physical Research Laboratory, Ahmedabad 380009, India.