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LAMONT GEOLOGICAL OBSERVATORY  
PALISADES, NEW YORK

SOME DATA AND OBSERVATIONS ABOUT AN INTERESTING DREDGE  
OF MANGANESE MODULES TAKEN IN THE "WESTERN ATLANTIC ABYSSAL-HILLS PROVINCE"

Prepared by: Mark Salkind

Technical Report No. CU-7-63 to the Atomic Energy Commission  
Contract AT(30-1)2663

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Lamont Geological Observatory

Some Data On and Observations About an Interesting Dredge of  
Manganese Nodules Taken in the "Western Atlantic Abyssal-Hills  
Province"

(Unpublished Technical Note)

Mark Salkind

INTRODUCTION

Several photographs, a core, and a bottom dredge were taken in the "Western Atlantic Abyssal-Hills Province" (Heezen, B.C. et.al. 1959) South-east of Bermuda by the Research Vessel "Robert D. Conrad", of Lamont Geological Observatory of Columbia University.

The area itself is of suspected volcanic origin. Not a well known region, it is characterized by discrete peaks of great topographic relief (as much as) 1000 meters) in depths to 5700 meters. (Heezen, B.C. et.al. 1959)

Photographs taken April 1 (Fig. 1) in 4575 meters at 32 26 N x 62 59 W show a bottom relatively clear of any debris.

Additional photographs taken in the same (Fig. 2) geologic province in 4700 meters on a peak top (Severdrup, Johnson, Fleming, 1955) at 26 35 N x 56 29 W showed a bottom thickly strewn with specimens having the appearance of volcanic debris and showing great variation in size.

A core of 549 centimeters length taken April 8, on the same peak had, to quote the shipboard description, "Manganese Nodules in soft red clay to 314 centimeters. Then an abrupt change to Foram Ooze. The bottom of the core contained volcanic debris mixed with Forams and one hard chunk of volcanic rock about 2 x 1 x  $\frac{1}{2}$  inches."

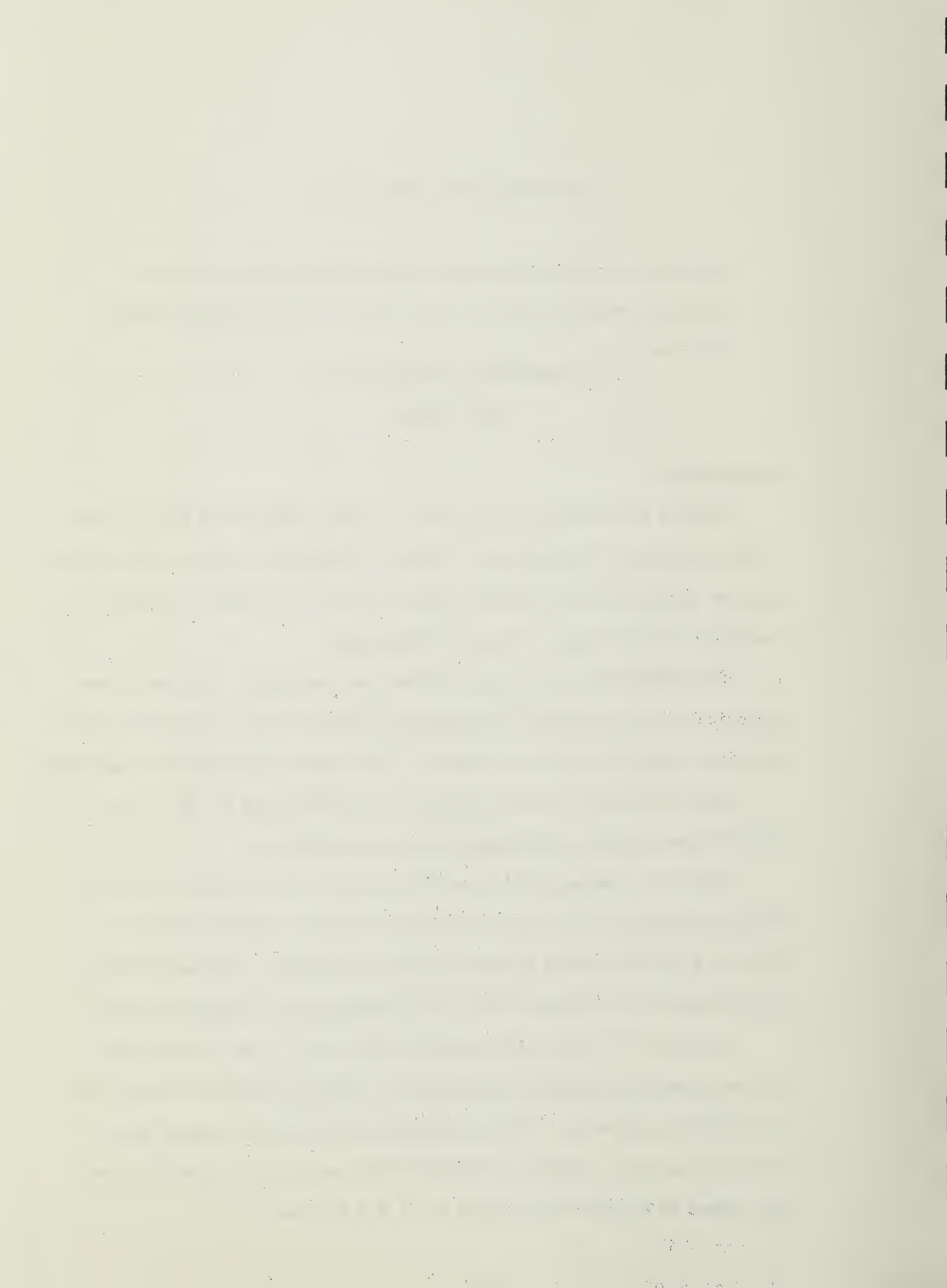






FIGURE 1



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FIGURE 2





## OBSERVATIONS

Five hundred pounds of the bottom debris was obtained by dredge on April 11, in 3935 meters at 21° 15' N x 56° 09' W (well within the "Western Atlantic Abyssal-Hills Province") on a peak top. (Fig. 3) This material was found to be chunks of clay covered evenly with a Manganese Oxide layer. The larger specimens (30 to 50 centimeters in diameter, 15 to 20 kilograms) had a flattened or tablet-like shape and a coating two to three centimeters in thickness. Smaller specimens tended to be more rounded having coatings one to two centimeters in thickness. (Fig. 4)

It was noted that the Manganese Oxide layer coated even the most strongly flattened tablets in a regular manner in spite of the fact that one side was exposed to sea water while the other lay in the sediment. (Fig. 5)

## RESULTS OF ANALYSIS

Separate analysis were made of the outer layer and inner clay body of a specimen of typical size and appearance.

The results obtained were as follows and are presented separately for Outer Shell and Inner Clay Body:

The room dried samples were completely dried to constant weight at 100 centigrade. The loss by weight of Interstitial water in the Outer Shell was 15.10 percent. The loss by weight for the Inner Clay Body was 9.7 percent.

Including the above percents; the Loss-on-Ignition for the Outer Shell was 31.18 percent and for the Inner Clay Body 23.78 percent.

The difference between the above of 16.08 percent in the Outer Shell and 14.1 percent in the Inner Clay Body is represented by chemically

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FIGURE 3 .









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50

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FIGURE 4





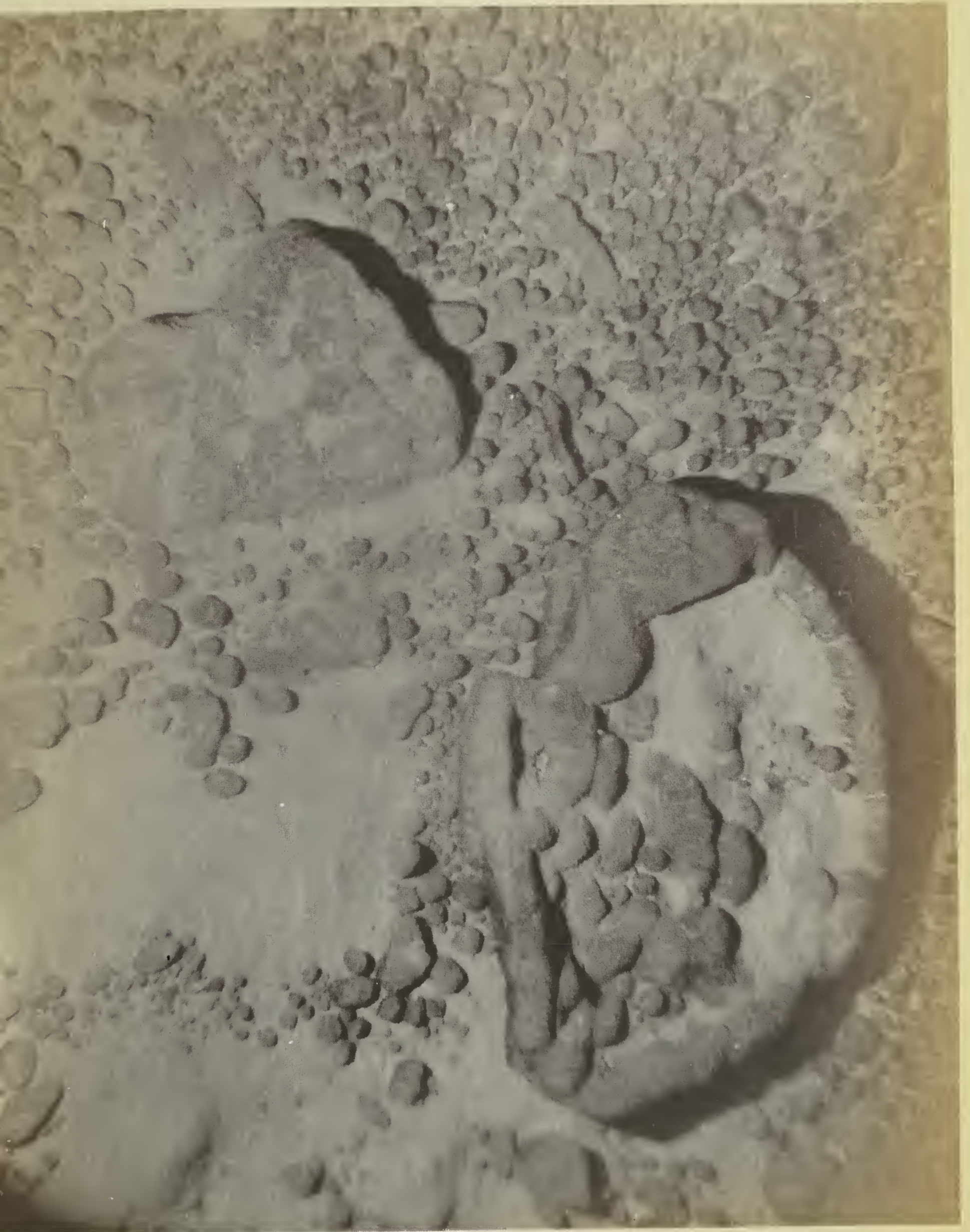


FIGURE 5





combined water, volatile carbonates, sulfates, and evaporated salts of sea water, primarily sodium and potassium which are readily oxidized and reported as  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$ .

Table I is the result of an Emission Spectrographic Analysis of the specimen. Its purpose, to identify the elements present in order that a complete and accurate Quantitative Analysis would be possible. The elements are arranged in order of considered importance.

Table II presents the result of the Quantitative Analysis of the material in a dry state.

#### CONCLUSIONS

Clearly, from Table II, the outer shell of this material is a Ferro-Manganese-Alumino-Silicate system containing large amounts of Titania compared to the Inner Clay Body.

Equally obvious from Table II is the rather surprising fact that there is less percent-by-weight content of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  and considerably more percent-by-weight of  $\text{TiO}_2$  (Titania),  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}_2$  than was contained in the inner clay body.

Table III (Goldberg, 1961) is a good standard to which we may compare this specimen's components.

A comparison of Tables III and IV demonstrates that the outer shell of this specimen is somewhat lower in manganese yet higher in iron and aluminum than the average nodules. In general the Outer Shell conforms to the composition of the manganese nodule type and may be considered as such.





TABLE I

Emission Spectrographic Analysis of the Dried and Ignited Material  
(Percent by Weight)

<u>Element</u>	<u>Outer Shell</u>	<u>Inner Clay Body</u>
Manganese	High	High
Iron	High	High
Aluminum	Medium-High	Medium-High
Silicon	High	High
Calcium	Medium	Medium
Magnesium	Medium	Medium
Sodium	Medium	Medium
Titanium	Medium	0.7
Boron	0.03	0.03
Barium	0.1	0.3
Cobalt	0.5	0.15
Chromium	0.005	0.005
Copper	0.10	0.03
Molybdenum	0.05	0.02
Nickel	0.6	0.2
Lead	0.01	0.03
Strontium	0.07	0.07
Vanadium	0.07	0.03
Zinc	0.05	0.05
Zirconium	0.07	0.03



TABLE II

Quantitative Analysis of the Dried Material (Percent by Weight)

<u>Component</u>	<u>Outer Shell</u>	<u>Inner Clay Body</u>
MnO <sub>2</sub>	21.68	10.76
Fe <sub>2</sub> O <sub>3</sub>	28.38	17.34
Al <sub>2</sub> O <sub>3</sub>	8.98	13.91
SiO <sub>2</sub>	11.68	31.22
CaO	3.29	2.54
MgO	4.99	4.33
Na <sub>2</sub> O	4.18	3.70
K <sub>2</sub> O	0.92	1.82
TiO <sub>2</sub>	1.45	0.72
B <sub>2</sub> O <sub>3</sub>	0.78	0.81
BaO	0.09	0.28
CoO	0.52	0.16
Cr <sub>2</sub> O <sub>3</sub>	0.006	0.006
CuO	0.11	0.03
MoO <sub>3</sub>	0.06	0.03
NiO	0.62	0.21
PbO	0.01	0.03
SrO	0.06	0.07
V <sub>2</sub> O <sub>5</sub>	0.10	0.04
ZnO	0.05	0.05
ZrO <sub>2</sub>	0.07	0.03



Table II(Cont.)

<u>Component</u>	<u>Outer Shell</u>	<u>Inner Clay Body</u>
$\text{Cl}^+$	3.06	2.72
$\text{CO}_2$	0.48	0.36
$\text{SO}_4$	0.99	0.75
Chemically Combined $\text{H}_2\text{O}$	12.27	11.48
$\text{P}_2\text{O}_5$	0.96	0.73





TABLE III

Average Composition of Manganese Nodules from the Pacific Ocean  
(Goldberg, 1961)

<u>Element</u>	<u>Percent by Weight</u>
Manganese	19
Iron	14
Aluminum	0.7
Titanium	0.8
Cobalt	0.3
Copper	0.5
Nickel	0.4
Lead	0.1
Phosphorous	0.5
Zinc	0.04
Zirconium	0.006



TABLE IV

Comparison Composition of Investigated Material  
(Percent by Weight)

<u>Element</u>	<u>Outer Shell</u>	<u>Inner Clay Body</u>
Manganese	13.7	6.8
Iron	20.8	12.7
Aluminum	4.8	7.4
Silicon	5.8	14.5
Titanium	0.9	.4
Cobalt	0.4	.1
Copper	0.1	.02
Nickel	0.5	.2
Lead	0.01	.03
Phosphorous	0.4	.3
Zinc	0.04	.04
Zirconium	0.05	.02



However, the Inner Clay Body does not conform to a manganese nodule composition. It contains too much aluminum. In addition, the amounts of manganese and titanium present are too low.

This proportioning of the above together with the chemically combined water present in the Inner Clay Body is reminiscent of a true clay structure.

A possible mechanism of formation of the "manganese oxide" shell on this sample that suggests itself is weathering of clay breccia on their surfaces resulting in a leaching of silica and alumina thereby enriching the surface in iron, manganese and the other metals present and typical of manganese nodules.

The typical metals manganese, iron, silicon and aluminum may possibly behave in the following manner during formation of the "manganese oxide" shell.

Manganese dioxide is extremely insoluble in a slightly basic solution such as sea water. Iron oxide too exhibits low solubility in such conditions.

Silica ( $\text{SiO}_2$ ) however is comparatively soluble in such conditions.

Alumina ( $\text{Al}_2\text{O}_3$ ) is only slightly soluble but its rate of solution may be increased by contact with carbon dioxide dissolved in water. In any case, it is expected that alumina would dissolve much more slowly than silica.

This is found to be the apparent case when comparing amounts





from the Inner Clay Body and the Outer Shell.

Possibly it is these properties that may result in a clayey material such as this sample weathering into a manganese-iron high, silica-alumina low, end product such as a manganese nodule.

Table V is an attempt to discover any obvious correlation between the abundance of elements in sea water and in the ferro-manganese coated sample.

Such a correlation does not seem obvious.

In order to prove the actual mechanism of change, X-ray diffraction, rational and further chemical analyses are needed.

These procedures are presently underway.



TABLE V

Relative Concentration of Elements in Sea Water and Dredge  
Specimens (Sea Water Information; Goldberg, 1961)

<u>Element</u>	<u>Sea Water</u>	<u>Outer Shell</u>	<u>Inner Clay Body</u>
Manganese	.2	24.8	13.7
Iron	1	37.4	25.6
Aluminum	1	8.6	12.6
Silicon	300	9.8	29.0
Calcium	40000	4.2	3.7
Magnesium	135000	5.4	5.2
Sodium	1,050,000	5.6	5.6
Titanium	.1	1.6	0.89
Cobalt	.05	0.72	0.24
Copper	.3	0.14	0.04
Nickel	.2	0.86	0.32
Lead	.003	0.018	0.006
Phosphorous	7	0.79	0.65
Zinc	1	0.072	0.08
Zirconium	-	0.086	0.04



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