

iron, and is reprecipitated near the top of the sedimentary column (10). Present deep-sea sampling techniques such as dredging and coring provide areally scattered samples from surface layers of the ocean floor only; under such circumstances manganese minerals are sampled preferentially to iron minerals both in terms of area and depth.

While the present findings tend to support the volcanic theory on the origin of oceanic iron-manganese oxide minerals, there is also clear evidence in favor of similar minerals being formed elsewhere by other mechanisms, namely: (i) the slow chemical precipitation of iron and manganese derived from continental weathering, especially in areas close to land as on the Blake Plateau (11) or on banks off the California coast (12); and (ii) the diagenetic migration of dissolved manganese in buried reduced hemipelagic sediments and reprecipitation near the interface of water and sediment, as in the Guatemala basin (13) or in the Baltic Sea (14). One theory cannot be a general explanation for all occurrences of deep-sea iron-manganese oxide minerals; it is becoming increasingly clear that one or the other of the aforementioned mechanisms is dominant in different areas of the ocean floor.

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References and Notes

1. A. R. Miller *et al.*, *Geochim. Cosmochim. Acta* **30**, 341 (1966).
2. H. J. Rose, J. Adler, F. J. Flanagan, *Applied Spectros.* **17**, 81 (1963); R. L. O'Neil and N. H. Suhr, *ibid.* **14**, 45 (1960).
3. E. Bonatti, *Trans. N.Y. Acad. Sci.* **25**, 938 (1963); M. N. A. Peterson and J. J. Griffin, *J. Marine Res.* **22**, 13 (1964).
4. K. B. Krauskopf, *Int. Geol. Congr. 20th Rept., Mexico City* **119**, (1956); *Geochim. Cosmochim. Acta* **12**, 61 (1957).
5. E. Bonatti and Y. R. Nayudu, *Amer. J. Sci.* **263**, 17 (1965).
6. E. Bonatti, in preparation.
7. K. Boström, in preparation.
8. G. Arrhenius and E. Bonatti, in *Progress in Oceanography*, M. Sears, Ed. (Pergamon Press, London, 1965), vol. 3.
9. I. S. Skorniyakova, *Int. Geol. Rev.*, **7**, 2161 (1966); K. Boström and M. N. A. Peterson, in preparation.
10. D. C. Lynn and E. Bonatti, *Mar. Geol.* **3**, 457 (1965); K. Boström, in preparation.
11. R. M. Pratt and P. F. McFarlin, *Science* **151**, 1080 (1966).
12. R. S. Dietz, *J. Calif. Mines Geol.* **51**, 209 (1955).
13. D. C. Lynn and E. Bonatti, *Mar. Geol.* **3**, 457 (1965).
14. F. T. Manheim, *Narragansett Mar. Lab. Occas. Publ.* **3**, 217 (1965).
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Maya Blue: A Clay-Organic Pigment?

Abstract. *Maya Blue, a pigment used by the Mayas in Yucatan, is remarkably stable: the color is not destroyed by hot concentrated mineral acids or by heating to about 250°C. The principal constituent is the colorless mineral attapulgite. It is proposed that the pigment is an adsorption complex of attapulgite and natural indigo; a synthetic equivalent may be prepared from attapulgite and either indoxylester or indigo, or by applying the vat-dyeing technique, with reduced indigo. The low dye content of the pigment (less than 0.5 percent) indicates that the dye is absorbed only on the external surfaces of the attapulgite particles and not throughout the channels in their structures. The complex as such is not stable to acids, but the stability displayed by Maya Blue is achieved simply by heating the complex to from 75° to 150°C for several days. An analogous stable pigment can be prepared from sepiolite and indigo. No stable pigments could be prepared from clays with platelike structures or from zeolites.*

Maya Blue, a pigment used by the Mayas in Yucatan, most commonly during the late pre-Spanish period, is found in both pottery and murals; it is exceptionally stable against hot concentrated mineral acids, including aqua regia. The color cannot be extracted with acetone. Upon heating, the blue color persists to about 250°C before it becomes grayish. This exceptional stability caused Maya Blue to be thought an entirely inorganic pigment (1). Later the principal constituent proved to be the colorless mineral attapulgite, and it was proposed (2) that the pigment might be an attapulgite-organic complex. However, attempts to identify completely the organic material and to synthesize an attapulgite-dye complex having this remarkable chemical stability failed (1, 2).

Indigo being one of the most stable blue dyes available to the Mayas, I studied the formation of attapulgite-indigo complexes. Shepard (2) mentioned that traces of indigo had been identified in the pigment, but, since no stable attapulgite-indigo complex could be prepared, it was thought that indigo had been merely added to intensify the color.

The following observations were made in collaboration with C. T. Deeds. A blue attapulgite-indigo complex is easily obtained in this manner: When a slightly alkaline solution of synthetic indoxylacetate contacts attapulgite, the clay becomes blue; apparently, indoxyl is oxidized on the surfaces of the clay particles. The blue clay is filtered and washed with water. The resulting pigment is not stable to hot acids, and the color is extractable with acetone. The secret in achieving stability to acids is that the pigment must be heated at moderate temperatures—for example, for several days at 75°C or preferably at 105° to

150°C; the pigment is now stable to hot concentrated mineral acids, the dye cannot be extracted with acetone, and the color is not changed by heating to 250°C. In all these tests, the synthetic attapulgite-indigo complex thus behaves like Maya Blue. No tristimulus values have been obtained for the synthetic pigment, but to the eye the color matches Maya Blue.

Any excess of indigo in the reaction mixture can be removed by extraction with acetone or nitric acid. The dye content of the washed complex is very low (less than 0.5 percent), but nevertheless the color is rather intense.

Two alternative methods of preparing the indigo complex of attapulgite are:

1) Heat a mixture of indigo powder and attapulgite, and remove any excess of indigo by washing with acetone.

2) Reduce indigo with a solution of sodium hydrosulfite, contact attapulgite with this solution, and expose them to air; this procedure is the vat-dyeing technique. Heating is still required for stability to acids.

It seems reasonable to assume that Maya Blue is basically an attapulgite-indigo complex prepared according to one of these procedures or some modification thereof. Since natural indigo contains small quantities of other dyes, the color of the synthetic pigment may not be expected to match Maya Blue exactly.

A product quite analogous in behavior to the attapulgite-indigo complex is the sepiolite-indigo complex that can be prepared in the same way. Both attapulgite and sepiolite have crystal structures featuring parallel channels of molecular dimensions. The particle size of the attapulgite is rather critical: a fraction small as to particle size is required for achieving the intense coloring.

In order to determine whether other clay minerals yield comparable pigments, we have prepared indigo complexes from kaolinite, nontronite, Wyoming bentonite (all clays with platelike structures), and mordenite (a zeolite with a cage-type structure). All products were blue but none yielded stable pigments upon heating.

The channel structure seems to be essential for achieving acid stability of the complexes. The indigo molecules are undoubtedly too big to enter the channels of attapulgite or sepiolite, and the relatively small adsorption capacity of the minerals for indigo suggests that the dye is indeed adsorbed on only the external surfaces of the particles.

At the surface of the particles one finds grooves instead of channels. Upon heating, the longitudinal building blocks of the mineral may shift position and thus partly block the grooves and shield the dye molecules from acid attack. Such structural changes, which x-ray evidence shows occurring above about 350°C in the interior of the

crystallites concurrently with the loss of crystal water (3), may well occur at the surfaces at lower temperatures. It is interesting that prior heating of the clay to 200°C does not impair its ability to form a blue complex with indigo, but that subsequent heating of this complex does not induce acid stability. Yet the precise mechanism of the stabilization of the complexes by heating is not clear; if one assumes that the heated indigo-attapulgite complex is indeed the synthetic equivalent of Maya Blue, the solution of this puzzle has created a new one.

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References

1. R. J. Gettens, *Amer. Antiq.* **27**, 557 (1962).
2. A. O. Shepard and H. Gottlieb, "Maya Blue: alternative hypothesis," in *Notes from a Ceramic Laboratory* (Carnegie Inst. of Washington, Washington, D.C., July 1962).
3. A. Preisinger, *Clays and Clay Materials, Proc. 10th Nat. Conf.* (Pergamon, London, 1963), pp. 365-71.

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Manganese Nodules: Thorium-230: Protactinium-231 Ratios

Abstract. *The $Th^{230}:Pa^{231}$ activity ratio in 7 of 11 manganese nodules is less than 10.8, the theoretical production ratio of activities in the ocean. This finding indicates differential accumulation of these nuclides in authigenic deposits of manganese-iron oxide.*

The ratio of activities of Th^{230} and Pa^{231} ($A_{Th^{230}}:A_{Pa^{231}}$) produced in sea water by the radioactive decay of uranium in solution is 10.8 (1). These nuclides are precipitated rapidly from the ocean (2), and the change in ratio of these unsupported activities in deep-sea sediments has been used to deter-

mine sedimentation rates (3). The top sections of many cores do not have the predicted ratio of unsupported activities (10.8), but values as high as 35 (4), which finding cannot be entirely explained by mixing, because of recent C^{14} dates for the carbonate fraction. Upward migration of Th^{230} in the

cores or differential precipitation of Th^{230} and Pa^{231} are possible alternative explanations; the latter may be substantiated by the finding of a differential accumulation of Th^{230} and Pa^{231} in some other mineral phase of sediments—the authigenic manganese oxide phase. With this purpose in mind, I analyzed a suite of manganese nodules. While the work was in progress, Broecker and Ku (5) informed me that one nodule analyzed by them had an anomalous ratio < 10.8 , indicating either relatively less precipitation of Th^{230} or more of Pa^{231} .

The analytical procedures for carrier-free separation of uranium, thorium, and protactinium from manganese nodules make use of U^{232} , Th^{234} , and Pa^{233} tracers to monitor yield, diisobutyl carbinol extraction of protactinium, and anion- and cation-exchange techniques for separation of uranium and thorium. All separations end with extraction into thenoyltrifluoroacetone benzene solutions that are evaporated on stainless-steel plates. Yields, as measured by the activities of the samples and portions of the tracers, mounted and counted in the same manner, are usually greater than 50 percent.

The alpha activities of protactinium and thorium are counted, soon after separation in a gas-flow proportional counter, with about 50-percent efficiency. As Pa^{231} is the only naturally occurring alpha emitter of protactinium, the total alpha activity is a measure of Pa^{231} . Total thorium activity

$$A_{total\ Th} = A_{Th^{232}} + A_{Th^{230}} + A_{Th^{228}} + A_{Th^{227}}.$$

By use of an alpha analyzer the ratios $A_{Th^{230}}:A_{Th^{232}}$ and $A_{Th^{228}}:A_{Th^{232}}$ are determined. Total $A_{Pa^{231}}$ is used to

Table 1. Uranium, thorium and protactinium analyses of selected manganese nodules; dpm, disintegrations per minute. Indicated uncertainties are the expected standard deviations for the numbers of counts recorded.

Sample (No.)	Source; water depth (m)	Th^{230} (ppm)	U^{238} (ppm)	$A_{Th^{230}}$ (dpm/g)	$A_{Pa^{231}}$ (dpm/g)	$A_{Th^{230}}:A_{Pa^{231}}$
<i>Atlantic Ocean</i>						
MN-1	Western Atlantic Hills Province, 21°15'N, 56°09'W, from top of hill; 3935	60 ± 3	4.0 ± 0.5	24.6 ± 1.3	4.1 ± 0.1	6.0 ± 0.4
MN-4	Blake Plateau, 30°53.5'N, 78°47'W; 792	27 ± 2		6.6 ± 0.4	0.87 ± .04	7.6 ± .6
MN-6	Blake Plateau, 31°29.0'N, 77°20'W; 1029	35 ± 2		6.4 ± .3	0.91 ± .03	7.0 ± .4
MN-7	Caryn Seamount, 36°45'N, 67°55'W; about 3000	63 ± 3		8.9 ± .5	1.56 ± .05	5.7 ± .4
<i>Pacific Ocean</i>						
MN-2	NW of Tuamotu Archipelago, 14°18'S, 149°32'W; about 3000	4 ± 1	7.4 ± 0.7	22.5 ± 1.2	3.4 ± .1	6.6 ± .4
MN-8	(DWDI) Baja Calif. Seamount Province, 21°27'N, 126°43'W; 4300	24 ± 1		4.9 ± 0.2	0.33 ± .02	14.9 ± 1.1
MN-9 (surf.)	(DWD4) E side of peak on edge of Tuamotu Escarpment, W of Fakarava	6 ± 1		20.1 ± .6	2.35 ± .12	8.5 ± 0.5
MN-9	E side of peak on edge of Tuamotu Escarpment, W of Fakarava	8 ± 1		13.8 ± .7	0.94 ± .04	14.7 ± 1.0
MN-10	(DWD 47) 41°59'S, 102°01'W; 4260	9 ± 1		5.9 ± .3	0.56 ± .03	10.5 ± 0.7
MN-11	(FAN BD 20) S side Mendocino Escarpment, 40°15'N, 128°28'W; 4500	26 ± 1		15.0 ± .5	1.24 ± .04	12.1 ± .5
MN-12	(MP 25, F-2) Horizon Guyot, 19°07'N, 169°44'W; 1740	16 ± 1		14.0 ± .4	2.46 ± .07	5.7 ± .3
MN-13	(MP26, A-3) 19°03'N, 171°00'W; 1372	8 ± 1		12.0 ± .8	0.96 ± .06	12.5 ± 1.1