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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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 determine 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

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

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^{232} (ppm)	U^{238} (ppm)	$A_{Th^{230}}$ (dpm/g)	$A_{Pa^{231}}$ (dpm/g)	$A_{Th^{230}} : A_{Pa^{231}}$
	Atlantic Ocean					
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
	Pacific Ocean					
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	(DWBDI) 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.)	(DWBD4) 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

correct for $A_{\mathrm{Th}^{227}}$ (if one assumes that $A_{\mathrm{Th}^{227}} = A_{\mathrm{Pa}^{231}}$) and to calculate $A_{\mathrm{Th}^{230}}$ and $A_{\mathrm{Th}^{230}}:A_{\mathrm{Pa}^{231}}$. Similarly,

$$A_{\text{total U}} = A_{\mathrm{U}^{238}} + A_{\mathrm{U}^{235}} + A_{\mathrm{U}^{234}} + A_{\mathrm{U}^{232}}.$$

Assuming $A_{\mathrm{U}^{235}} = 0.046\ A_{\mathrm{U}^{238}}$ and determining $A_{\mathrm{U}^{234}} : A_{\mathrm{U}^{238}}$ and $A_{\mathrm{U}^{232}} : A_{\mathrm{U}^{238}}$, one may calculate the individual activities. Precise activity ratios are obtained by use of this procedure, for it is unnecessary to know the efficiency of the two counting systems, providing that the total-alpha counter efficiency is the same for the uranium, thorium, and protactinium measurements. A small correction is usually necessary for the Ra^{224} and daughters that grow in during the first few hours while the thorium alpha activity is counted.

Duplicate determinations on 0.100-g portions of a counter-calibration sample (*6*), containing 0.5 percent uranium and equilibrium amounts of radioactive daughters, gave, for Pa^{231}, 16.1 and 16.9 dpm (disintegrations per minute); for Th^{230}, 351 and 355 dpm; average $\mathrm{Th}^{230} : \mathrm{Pa}^{231}$ ratio was 21.6. The uncertainty in these determinations due to counting variations was less than 2 percent. The 21.6 value compares favorably with the theoretical value of 21.8 derived from the half-lives and abundances of U^{238} and U^{235}.

The analyses are, with one exception for 1-g portions of homogenized material, of one-eighth to one-fourth sections of each nodule; the sections were approximately 1 cm thick. On the basis of a rate of 3 mm/10^6 years (*7*), this thickness represents deposition during about 10^7 years.

The predicted limits for the activity ratio $\mathrm{Th}^{230} : \mathrm{Pa}^{231}$ in samples such as I used are as follows:

1) The ratio is 10.8 if Th^{230} and Pa^{231} are being absorbed or precipitated, with no discrimination, as quickly as they are produced in sea water. This ratio would be observed if only very recently deposited material were sampled.

2) As a hypothetical outer layer became older and there was more deposition, the ratio would increase, with an apparent half-life of 56,500 years (21.6 at 56.5×10^3 years, 43.2 at 113×10^3 years, and so on). This regular increase would only continue as long as the unsupported activity was much greater than the activity supported by the uranium in the nodule. For completely supported activity the ratio would be 21.8. For samples such as I used, activity-ratio values between 10.8 and 21.8 would be predicted.

The data in Table 1 clearly show that for 6 of 11 nodules the homogenized samples have ratios of less than 10.8 (5.6 to 8.5). The surface portion of MN-9 has a ratio of 8.5 compared to 14.7 for the homogenized sample. Presumably the surfaces of the other nodules also would show a ratio lower than 10.8. These data indicate preferential deposition of Pa^{231} or rejection of Th^{230} during the formation of manganese nodules; the latter alternative would complement the finding by Ku of more Th^{230} in deep-sea aluminosilicate sediments that can be predicted from the radioactive decay of U^{234} in the overlying water column (*8*).

The uniformly low activity ratios for the Atlantic samples probably point to more-rapid formation relative to the Pacific nodules, because the random-sampling technique employed seemed to select in each instance a younger accumulation of the manganese.

Studies such as mine show that there has been differential precipitation of Th^{230} and Pa^{231} and postdepositional migration of U^{234}, Ra^{226}, and possibly Th^{230} (*8, 9*). Although these findings may in some instances invalidate some of the techniques for dating sediments, they may nevertheless help to study other geochemical phenomena such as the hypothetical migration of manganese from the reducing to the oxidizing layers of deep-sea sediments.

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References and Notes

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Deep Layer of Sediments in Alpine Lake in the Tropical Mid-Pacific

Abstract. *Sediments from a unique high-altitude lake on Hawaii indicate ash falls and other airborne and waterborne materials for a period estimated to extend into the Pleistocene.*

Lake Waiau (Fig. 1), lying within Waiau Cone (3970 m from sea level near the top of the inactive volcano Mauna Kea on Hawaii) appears to have been a natural trap for sedimentary materials since the lake was formed, probably in Pleistocene time (*1, 2*). More than 7.5 m of sediments were recently found on the bottom of this lake by probing it with a steel rod. Several coarse volcanic ash layers were evident, especially in the older deeper parts.

The first 2 m of the lake bottom have been sampled with a piston corer. The sediments were found to have a complex stratification, and to contain sufficient organic matter (for dating) among the volcanic ash layers. Thus these sediments contain evidence of the timing of some of the last ash eruptions in the area, and they may enable us to learn more about post-Pleistocene and Pleistocene weather conditions.

Two C^{14} analyses have been made on samples from the core (Fig. 2). At a depth of 1 m, the age of the organic matter was 2270 ± 500 years (sample W-1834), and at 2 m, 7160 ± 500 years (sample W-1833). The material was boiled in HCl to remove any carbonate present. The large error quoted is inherent in the method and the size of sample available.

The first coarse ash layer (4500 years old), containing particles as large as 1 mm in diameter, was located about 1.5 m below the surface. This layer is probably the result of a local eruption which formed one of the numerous nearby cones. Minor postglacial eruptions have been indicated on Mauna Kea (*3*). Extrapolation of the age-depth curve suggests 30,000 years as the maximum age of the deepest sediments. Such straight-line extrapolation is not entirely realistic, but until more data