

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

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

Assuming  $A_{\text{U}^{235}} = 0.046 A_{\text{U}^{238}}$  and determining  $A_{\text{U}^{234}}:A_{\text{U}^{238}}$  and  $A_{\text{U}^{232}}:A_{\text{U}^{238}}$ , 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  $\text{Ra}^{224}$  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  $\text{Pa}^{231}$ , 16.1 and 16.9 dpm (disintegrations per minute); for  $\text{Th}^{230}$ , 351 and 355 dpm; average  $\text{Th}^{230}:\text{Pa}^{231}$  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  $\text{U}^{238}$  and  $\text{U}^{235}$ .

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<sup>6</sup> years (7), this thickness represents deposition during about 10<sup>7</sup> years.

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

1) The ratio is 10.8 if  $\text{Th}^{230}$  and  $\text{Pa}^{231}$  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  $56.5 \times 10^3$  years, 43.2 at  $113 \times 10^3$  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  $\text{Pa}^{231}$  or rejection of  $\text{Th}^{230}$  during the formation of manganese nodules; the latter alternative would complement the finding by Ku of more  $\text{Th}^{230}$  in deep-sea aluminosilicate sediments that can be predicted from the radioactive decay of  $\text{U}^{234}$  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  $\text{Th}^{230}$  and  $\text{Pa}^{231}$  and postdepositional migration of  $\text{U}^{234}$ ,  $\text{Ra}^{226}$ , and possibly  $\text{Th}^{230}$  (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.

WILLIAM M. SACKETT  
Chemistry Department, University  
of Tulsa, Tulsa, Oklahoma

#### References and Notes

- $A_{\text{Th}^{230}} = \frac{N_{\text{U}^{234}} \cdot \lambda_{\text{U}^{234}} [1 - \exp(-\lambda_{\text{Th}^{230}} t)]}{A_{\text{Pa}^{231}} = \frac{N_{\text{U}^{235}} \cdot \lambda_{\text{U}^{235}} [1 - \exp(-\lambda_{\text{Pa}^{231}} t)]}{= 10.8}$   
where  $t = 0$ ;  $N_{\text{U}^{234}} \cdot \lambda_{\text{U}^{234}} = 1.15 N_{\text{U}^{238}} \cdot \lambda_{\text{U}^{238}}$  [D. L. Thurber, *J. Geophys. Res.* **67**, 4518 (1962)];  $N_{\text{U}^{235}} \cdot \lambda_{\text{U}^{235}} = 0.0463 N_{\text{U}^{238}} \cdot \lambda_{\text{U}^{238}}$ ;  $t_{1/2}$ ,  $\text{Pa}^{231} = 32,480$  years; and  $t_{1/2}$ ,  $\text{Th}^{230} = 75,200$  years.
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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  $\text{C}^{14}$  analyses have been made on samples from the core (Fig. 2). At a depth of 1 m, the age of the organic matter was  $2270 \pm 500$  years (sample W-1834), and at 2 m,  $7160 \pm 500$  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

can be obtained it is the only procedure available. Piston core sampling to greater depths is planned in order to extend the age limits.

There is some evidence of annual layering, apparently caused in part by cycles in the production of the blue-green algae which covers the bottom of the lake with a thick mat. Gilmartin and Pasby have reported that the lake has a high standing crop of plankton but a low primary productivity (4). The amounts of plant life on the mountain at lake altitude are negligible (5).

Two relatively coarse layers of black ash make up about 5 percent of the sediments in the first 2-m core. More numerous finer gray ash layers comprise about 10 percent. The remaining sediments, in which the spicules and frustules from lake plankton are numerous, are various shades of red and olive green. The colors are largely pigments, soluble in acetone, benzene, and methanol. These colorful layers, constituting about 85 percent of the sediments, were found to be about 75 percent water, 5 percent combustible organic materials, and 20 percent clastic particles. The latter particles, which are very fine, have been blown into the lake or washed in from the slopes of the surrounding cone and flows. Identification of most of the clastic particles has not been attempted as yet, but they appear to be of local volcanic origin.

Gases arising from deep probings of the sediments have been trapped and analyzed, and have been found to be largely methane. The methane is thought to have come from decomposing algal material. This may explain, in part, the low organic content of the deeper sediments, despite the presence of the thick algal mat over the lake bottom. Bradley (6) reports sediments which are 89 percent organic under lake bottoms covered with algal mats.

Currently, the lake has a maximum depth of about 3 m when it overflows into Pohakuloa Gulch during the spring snow-melting periods. Most of the year the depth is less, and outflow appears to be through seepage and evaporation. The lake is heart-shaped (Fig. 1) with an area of about one hectare. Water temperatures are usually nearly isothermal and vary annually from about 0°C to 13°C. The temperature of the deeper sediments remains near 6°C all year. There is some thermal evidence of lateral flow of waters through ash aquifers in the area.

The local climate of the lake may be roughly characterized as cool and very dry. Freezing temperatures are reported at night during most of the year (2). The mean annual air temperature during 1965 and 1966, based upon daily maximum and minimum values (7), was 4.8°C. Mauna Kea, with an altitude of about 4200 m, extends well above

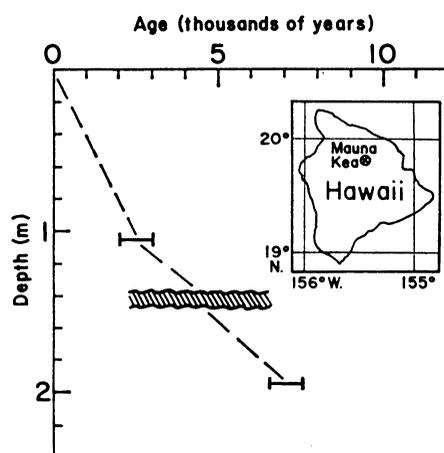


Fig. 2. Age-depth determination in Lake Waiau sediments. Age, measured to an accuracy of  $\pm 500$  years, is represented by the length of the symbols. Depth is somewhat uncertain due to the soft nature of the algal mats which constitute the top of the sediment. The hatched area at about 1.4 m represents the first coarse ash layer made up of several separate ash falls. At least five other coarse ash layers were detected at greater depths.



Fig. 1. Aerial view of alpine Lake Waiau, Hawaii, looking northeastward across the once glaciated summit region of Mauna Kea. The unique body of perched water is dwarfed by the laval flows and cinder cones of the great volcano. Colorful and complex bottom sediments of the lake, which is a natural trap for airborne and waterborne particles, reveal an age probably extending into the Pleistocene.

the northeast trade-wind inversion. This inversion is commonly near an altitude of 2500 m. The prevailing westerlies are a short distance above the mountain top.

At present, scientists at various laboratories are examining portions of several 2-m cores from the lake for quartz sands, pollens, and meteoric materials. It is planned to improve the  $C^{14}$  and perhaps other dating of the various layers in longer cores to be taken. Paleoclimatological and other studies may prove fruitful. Sections of these cores can be made available on request.

ALFRED H. WOODCOCK

Hawaii Institute of Geophysics,  
University of Hawaii, Honolulu

MEYER RUBIN

U.S. Geological Survey,  
Washington, D.C.

R. A. DUCE

Department of Chemistry,  
University of Hawaii, Honolulu

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