bonate in apatite is still a much disputed question.

In conclusion, using the method presented in this report, it is possible to obtain a pure well-crystallized hydroxyapatite, with negligible quantities of extraneous ions in the crystals. The major disadvantage of the method is the small crop obtained from each hydrolysis because of the small capacity of the bombs used. Larger reaction vessels would minimize this objection.

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16 July 1956

## Beryllium-10 Produced by Cosmic Rays

The bombardment of the nitrogen and oxygen of the atmosphere by cosmic rays can produce four nuclides of useful life. Three of these, carbon-14, tritium, and beryllium-7, have been identified and used for studies of time scales of natural processes (*1*). This paper (*2*) reports the isolation and identification of the fourth, beryllium-10, a $\beta^-$ emitter of half-life $2.5 \times 10^6$ years (*3*).

The amount of $Be^{10}$ produced should be very small. Peters (*4*) predicts a production rate—equivalent in steady state to the decay rate—of 0.05 to $0.1/cm^2$ sec. My own prediction is about $0.04/cm^2$ sec, with a large uncertainty.

Beryllium-10 should have the same early history as $Be^7$, which is removed from the atmosphere chiefly by rain. That portion which falls on the ocean may or may not enter into true solution there, but, in any case, it should find its way into the bottom sediments. We have been led, therefore, to examine the deep-sea bottom sediments for $Be^{10}$. In particular, we have studied "red clay" sediments, which show the lowest sedimentation rates and thus probably the highest relative concentrations of $Be^{10}$.

Samples from two cores taken from the eastern Pacific have now been analyzed for $Be^{10}$. These cores were obtained by E. D. Goldberg of the Scripps Institution of Oceanography at approximately latitude 28°N, longitude 125°W at a depth of 2200 m. The cores were approximately 5 cm in diameter, with a total length of 120 cm. Each was divided into five sections, which were analyzed for $Be^{10}$.

The chemical problem of isolating milligram amounts of beryllium from hundreds of grams of clay proved quite difficult. The chemistry used in core G resulted in erratic yields. An improved procedure was used on core H, a brief account of which follows. The sample (wet clay) is treated with a mixture of 500 g of 48-percent HF and 500 g of $12N$ HCl in two 1-lit HH polythene beakers, after 10 ml of Be carrier (5.9 mg of BeO per milliliter) has been added. After the sample has been evaporated to dryness in a hot-air jet, 150 g of each acid is added, and the sample is again evaporated to dryness. Two further evaporations with 500 g of HCl serve to remove most of the fluoride. The sample is taken up in 1500 ml of $1N$ HCl, boiled, decanted, and centrifuged. The remaining solid is heated with $H_2SO_4$ until HF bubbles cease. The cake is taken up with water, the small amount of remaining solid being fused with $KHSO_4$. The final solid is discarded, and all solutions are combined. The precipitate is discarded.

Six hundred fifty grams of Versene (the commercial tetrasodium salt of EDTA) is added, and the solution is brought to *p*H 6 to 6.5. Twenty-five milliliters of 2,4-pentanedione is added, and after the solution has stood for 5 minutes, it is extracted with three 250-ml portions of reagent-grade benzene. These are combined and backwashed with acetate-buffered water at *p*H 5.5 to 6.

Table 1. Beryllium-10 activity of core samples.

| Sample | Depth in core (cm) | Chemical yield (%) | Observed count (count/min) | Activity per $cm^3$ of clay (disintegration/min) |
|---|---|---|---|---|
| G-2 | 25–50 | 37 | $0.310 \pm 0.020$ | $(7.6 \pm 0.5) \times 10^{-3}$ |
| G-4 | 75–100 | 36 | $0.184 \pm 0.023$ | $(4.5 \pm 0.6) \times 10^{-3}$ |
| H-1 | 0–25 | 34 | $0.257 \pm 0.037$ | $(7.1 \pm 1.0) \times 10^{-3}$ |
| H-2 | 25–50 | 56 | $0.228 \pm 0.040$ | $(4.4 \pm 0.8) \times 10^{-3}$ |
| H-3 | 50–75 | 9 | $0.063 \pm 0.037$ | $(6 \pm 3) \times 10^{-3}$ |
| H-4 | 75–100 | 35 | $0.143 \pm 0.049$ | $(3.8 \pm 1.3) \times 10^{-3}$ |
| H-5 | 100–117 | 41 | $0.142 \pm 0.036$ | $(4.9 \pm 1.3) \times 10^{-3}$ |

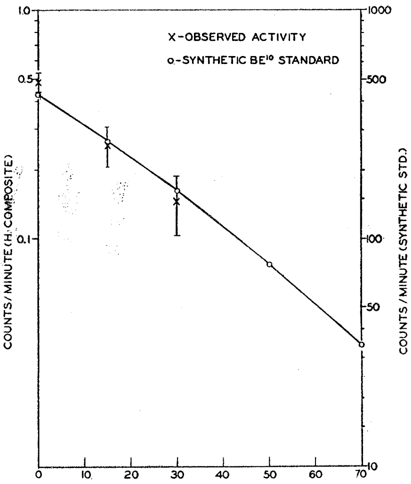

Fig. 1. Absorption curves of observed activity and of synthetic $Be^{10}$ standard in polyethylene in close cylindrical geometry.

The benzene layer is then extracted with two 150-ml portions of $6N$ HCl. Forty-five grams of disodium Versenate is added, and the HCl solution is brought to *p*H 6 to 6.5. Ten milliliters of 2,4-pentanedione is added, and, after the solution has stood, it is extracted with three 75-ml portions of benzene. The latter are combined, backwashed, and finally extracted with two 50-ml portions of $6N$ HCl. The acid solution is boiled down nearly to dryness, $HNO_3$ being added to destroy organic matter. Finally, 50 ml of water is added, the solution is made basic with ammonia, and the precipitate is filtered and ignited to BeO. This procedure seems to be entirely specific for beryllium. The reactions involved are discussed in the literature (*5*).

The samples were counted as BeO in close cylindrical geometry on two small thin-walled counters (*6*) inside rings of Geiger tubes in anticoincidence. The background was 0.25 to 0.5 count/min for a counter 6 cm long and 1.5 cm in diameter using a Q gas filling. The samples were not infinitely thin, and correction was made for self-absorption by the method of Libby (*7*), for geometry, and for chemical yield, in order to obtain the absolute disintegration rates. The activities are normalized to 1 $cm^3$ of clay, since this seems to be a more definite quantity than 1 g.

The results are shown in Table 1. The activity decreases somewhat with depth, but this tendency is neither marked nor regular. Core H was noted to be inhomogeneous with strong evidence of sorting at a depth of 35 cm. There is no reason to expect a regular decay with depth.

If the sedimentation rate is 1 mm/1000 yr, these cores have an equivalent depth of the order of $10^6$ yr. Our evidence suggests that the rate of sedimentation in our cores is not slower than this by a large factor. If we use this figure, averaging all results from both cores, we obtain an estimate of 0.03 disintegration/sec cm$^2$ contained in the sediment column. This is of the expected order of magnitude. No more can be said at present. Even this is not without interest from the point of view of the constancy of the cosmic-ray flux.

In addition to the data given here, other measurements were made to identify the observed activity. Samples G-2 and G-4 were combined, and a second complete cycle of purification was carried through. The original samples contained 0.92 ± 0.06 disintegration/min (assuming that the self-absorption correction of Be$^{10}$ applies). The recycled sample showed 0.68 ± 0.20 disintegration/min after correction for chemical yield. Seven months elapsed between the two measurements.

An absorption curve was run on a composite sample of H-1, H-2, H-4, and H-5, using polyethylene absorbers. The data are plotted in Fig. 1. A curve for a synthetic sample of Be$^{10}$ under the same conditions is shown for comparison. The absorption curve in close cylindrical geometry approaches an exponential (*7*). The half-thickness of the natural sample is $17 \pm 4$ mg/cm$^2$, while that of the synthetic sample is $21.2 \pm 0.3$ mg/cm$^2$ in the same region of the absorption curve. Using Libby's relation for half-thickness versus energy and mass number (*8*), we obtain $E = 0.52 \pm 0.08$ Mev, compared with 0.56 Mev for the known activity. A further check on the half-thickness is the self-absorption correction of the composite sample. The count rate of the composite sample was 0.65 ± 0.07 times the sum of the original samples, while the calculated value is 0.76. No gamma activity was found in any sample.

One set of data has been discarded—that obtained in my effort in Chicago to measure the absorption curve of the original G composite. The data indicate strongly that absorbers or other materials were contaminated.

Our intention is to use Be$^{10}$ if possible for radioactive age determination. Much work on the geochemistry of beryllium still must be done before this method can be safely used.

A final word should be said on measurement techniques. A counting method appears to be the most practical at the present time, although Peters (*4*) has suggested a photographic-plate technique. It is worth noting that, if the beryllium content of sediments is of the order of 1 ppm, the Be$^{10}$/Be$^9$ ratio is about $10^{-7}$. This does not seem to be permanently outside the range of solid-source mass spectrometry, although the difficulties would be extreme.

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2. I am indebted to many persons for assistance in this work. The cores were supplied by E. D. Goldberg. H. A. Al-Salih carried out the chemical extractions in the G series. E. F. X. Lyden assisted with those of the H series. T. T. Sugihara and E. A. Martell kindly made available their counting equipment and assisted in the counting. C. S. Wu kindly supplied the synthetic Be$^{10}$ sample. The work was supported by a contract with the Office of Ordnance Research, U.S. Army.
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29 June 1956

## Quantum Yields of Fluorescence of Plant Pigments

The fate of excitation energy in photosynthesis requires elucidation. Toward this end, we have determined the quantum yields of fluorescence of several photosynthetic pigments, *in vitro* and *in vivo* (*1*). The measurements were made with a specially constructed integrating sphere (*2*). The main results are shown in Tables 1 and 2.

Our values of the quantum yields of fluorescence $\phi$ of chlorophylls *a* and *b* are about 40 percent higher than those reported by Forster (*3*). We believe that this difference is the result of a more accurate determination in our experiments of the detector sensitivity as a function of wavelength, and a more reliable "sampling" of the incident light and fluorescence with the sphere. Both the ratio of the fluorescence yield of chlorophyll *b* to that of chlorophyll *a* and the strong effect of solvent on the former, reported by Forster, are confirmed.

As was anticipated by Duysens (*4*), $\phi$ of chlorophyll *in vivo* was found to be an order of magnitude higher than the value previously accepted on the basis of the measurements of Wassink *et al.* (*5*). The new data indicate that the actual lifetime of excitation of the first excited singlet state of chlorophyll *a in vivo* is of the order of $10^{-10}$ second, rather than $10^{-11}$ second, as has been previously assumed. This offers a correspondingly better chance for migration of excitation energy between chlorophyll molecules.

The quantum yield of chlorophyll fluorescence *in vivo* was previously known to change (usually to increase but sometimes to decrease) with increasing intensity of the exciting light at photosynthesis-saturating intensities (*6*). We found this yield to vary also with the exciting intensity when the latter was as low as 0.01 of that required for the compensation of respiration by photosynthesis (see Fig. 1). Recent measurements by Brugger (*7*) are consistent with the results shown in Fig. 1.

Franck's theory of "narcotization" of the chlorophyll complex, which could explain the intensity dependence of $\phi$ at

Table 1. Quantum yields of fluorescence of pigments in solution.

| Pigment and solvent | Wavelength of exciting light (mμ) | Quantum yield of fluorescence* ($\phi$) |
|---|---|---|
| Chlorophyll *a* | | |
| Ethyl ether | 436 | 0.33 |
| Methanol | 436 | 0.32 |
| Pyridine | 436 | 0.35 |
| Ethyl chlorophyllide *a* | | |
| Ethyl ether | 436 | 0.33 |
| Chlorophyll *b* | | |
| Ethyl ether | 436 | 0.16 |
| Methanol | 436 | 0.084 |
| Phycocyanin (from *Synechocystis* sp.) | | |
| Water (0.1*M* phosphate buffer, *p*H 6.2) | 546 | 0.53 |
| Phycoerythrin (from *Porphyridium cruentum*) | | |
| Water (0.1*M* phosphate buffer, *p*H 6.2) | 480 | 0.85 |
| Fluorescein | | |
| Aqueous NaOH | 436 | 0.91 |

* Corrected for self-absorption of fluorescence by extrapolation to zero concentration.

Table 2. Quantum yields of fluorescence of pigments in the living cell.

| Pigment and organism | Wavelength of exciting light (mμ) | Quantum yield of fluorescence* ($\phi$) |
|---|---|---|
| Chlorophyll *a* | | |
| *Chlorella pyrenoidosa* (green alga) | 436 | 0.027† |
| | 436 | 0.017–0.020‡ |
| *Navicula minima* (diatom) | 436 | 0.028† |
| *Synechocystis* sp. (blue-green alga) | 436 | ~ 0.015† |
| Phycocyanin | | |
| *Synechocystis* sp. | 546 | ~ 0.030–0.035 |

* Corrected for self-absorption of fluorescence by extrapolation to zero concentration.
† Excited with 50 erg/cm$^2$ sec.
‡ Extrapolated to very low intensities of exciting light.