subjective evaluation of the reinforcing stimulus may provide an independent measure of the reinforcing value of a verbal reinforcer.

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2. This study was supported by an undergraduate research grant from the Social Science Research Council and by a grant from the Center for International Studies, Massachusetts Institute of Technology.
3. We would like to thank Sherman Tatz for the use of the questionnaire which he developed for a similar study.

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Influence of "Aging" on the Characteristics of an Electrodeless Discharge

"Aging" of a freshly prepared discharge tube—that is, maintaining the discharge for a period of time—at a constant applied potential V, has been found to affect the discharge characteristics markedly. The influence of aging on the conductivity of a low-frequency electrodeless discharge in iodine vapor is reported here. The details of the experimental set up are similar to those reported earlier by Saxena and me (*2*).

Aging decreases the discharge current i and the "threshold potential" V_m, namely, the potential at which the discharge becomes self-maintained. The conductivity decreases (i) very rapidly during the first few minutes, (ii) less rapidly during the next few minutes, and (iii) slowly until it attains saturation. Figure 1 shows a typical plot of the discharge current i versus time t in minutes. The equation proposed by Saxena *et al.* (*3*) ($\delta i = kt^{1/m}$) for similar observations in water vapor and iodine vapor under ozonizer discharge seems to hold good only during the afore-mentioned period (ii).

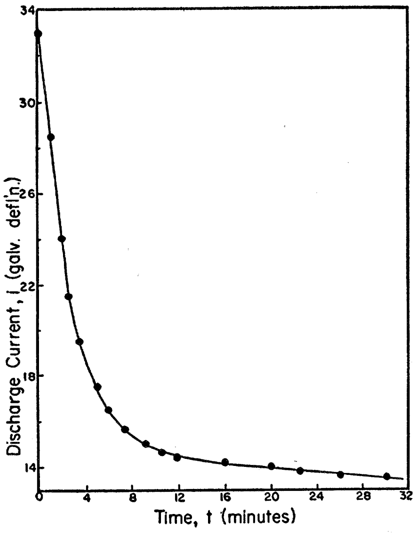

Fig. 1. Variation of discharge current with time.

The decrease of the threshold potential on aging was observed even in the presence of excess of solid iodine and therefore cannot be ascribed to the pressure drop caused by adsorption of the vapor on the walls of the vessel. Aging reduces the width of the period of the discharge which is not self-maintained. In a particular experiment, the potential in the period that was not self-maintained was between 0.79 and 1.33 kv before aging, while it was between 0.79 and 1.06 kv after aging. Furthermore, aging is effective only when it is carried out at $V > V_m$; aging at $V < V_m$ has no appreciable effect on the discharge characteristics.

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1. The work described was undertaken in the physicochemical laboratories of the Benares Hindu University, Benares, India. My thanks are due to S. S. Joshi for his kind interest in the work.
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1 August 1956

Preparation of Pure Hydroxyapatite Crystals

Naturally occurring hydroxyapatite exhibits a variable composition and contains impurities that have unknown effects on the structure and properties of the basic compound. A simple method for the production of pure, well-crystallized hydroxyapatite has long been needed. Methods of synthesis for this mineral have been reported in the past (*1*), but all of them produced impure and poorly crystallized products. This communication describes the preparation of pure hydroxyapatite suitable for x-ray diffraction, single-crystal studies.

The procedure is similar to an early preparation of hydroxyapatite by the hydrolysis of brushite ($CaHPO_4 \cdot 2H_2O$) (*2*). In the method outlined here, monetite ($CaHPO_4$), instead of brushite, is hydrolyzed to hydroxyapatite in a closed system. The reaction involved is probably one, or both, of the following.

$$10CaHPO_4 + 2H_2O \xrightarrow{300°C} Ca_{10}(PO_4)_6(OH)_2 + 4H^+ + 4H_2PO_4^- \quad (1)$$

$$14CaHPO_4 + 2H_2O \xrightarrow{300°C} Ca_{10}(PO_4)_6(OH)_2 + 4Ca^{++} + 8H_2PO_4^- \quad (2)$$

An orthophosphoric acid solution (1 vol of reagent-grade 85-percent H_3PO_4 to 5 vol of distilled water) was saturated at room temperature with reagent-grade tribasic calcium phosphate. Well-crystallized $CaHPO_4$ was precipitated from the clear saturated solution by heating the solution nearly to its boiling temperature. The $CaHPO_4$ was filtered from the hot solution, washed thoroughly with distilled water, rinsed with absolute alcohol, and finally dried at 105°C. From 0.5 to 1.0 g of $CaHPO_4$ may be obtained from 100 to 150 ml of the saturated solution.

Pure well-crystallized $Ca_{10}(PO_4)_6(OH)_2$ was prepared from the reaction of 0.1 g of the $CaHPO_4$ with 10 ml of distilled water in a platinum-lined, Morey-Ingerson type hydrothermal bomb (*3*) at 300°C for 10 days. During this time, the system had an internal pressure of about 1250 lb/in.^{2} owing to the vapor pressure of saturated steam at 300°C.

To obtain a complete reaction, it was necessary to use at least 10 ml of water for each 0.10 g of $CaHPO_4$. Less than this ratio of water to $CaHPO_4$ resulted in a mixed product of $Ca_{10}(PO_4)_6(OH)_2$ and $CaHPO_4$. Apparently the controlling factor for the hydrolysis is the final *p*H of the liquid. As long as this *p*H stays above 2.0 to 2.5, the reaction will proceed in the desired direction. Below a *p*H of about 2.0, the stable solid phase is $CaHPO_4$ for the reaction conditions used.

The presence of certain cation impurities can strongly influence the final product. During some preparations, the platinum lining developed cracks and Fe and Cr ions from the steel bomb were introduced into the water. When this happened, the final product contained a large proportion of well-crystallized whitlockite [β-$Ca_3(PO_4)_2$].

Under normal conditions, well-developed clear hexagonal dipyramidal crystals of hydroxyapatite, which range up to about 0.3 mm in length, are produced. A spectrographic analysis showed the following amounts of impurities: 0.01–0.1 percent = Cu, Fe, Na, Pb, Si, Sr; 0.001–0.01 percent = Al, Ba, Cr, Mg, Ni, Pt; 0.0001–0.001 percent = Ag, Mn.

A petrographic examination showed the crystals to be uniaxial negative with indices of refraction: $\varepsilon = 1.643 \pm 0.002$ and $\omega = 1.649 \pm 0.002$.

A method has been reported by Hayek, Lechtleitner, and Böhler (*4*) for obtaining well-crystallized hydroxyapatite by heating a finely divided hydroxyapatite with NaOH solution in a hydrothermal bomb. Although these investigators obtained well-formed crystals, the product was not as pure as might be desired, for these crystals contained at least 0.5 percent Na (*5*). Also, no attempt to remove the carbonate ion was made by Hayek and coworkers, and the influence of carbonate 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 β^- emitter of half-life 2.5×10^6 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/cm² sec. My own prediction is about 0.04/cm² 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 12*N* 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 1*N* 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 cm³ of clay (disintegration/min)
G-2	25–50	37	0.310 ± 0.020	$(7.6 \pm 0.5) \times 10^{-3}$
G-4	75–100	36	0.184 ± 0.023	$(4.5 \pm 0.6) \times 10^{-3}$
H-1	0–25	34	0.257 ± 0.037	$(7.1 \pm 1.0) \times 10^{-3}$
H-2	25–50	56	0.228 ± 0.040	$(4.4 \pm 0.8) \times 10^{-3}$
H-3	50–75	9	0.063 ± 0.037	$(6 \pm 3) \times 10^{-3}$
H-4	75–100	35	0.143 ± 0.049	$(3.8 \pm 1.3) \times 10^{-3}$
H-5	100–117	41	0.142 ± 0.036	$(4.9 \pm 1.3) \times 10^{-3}$

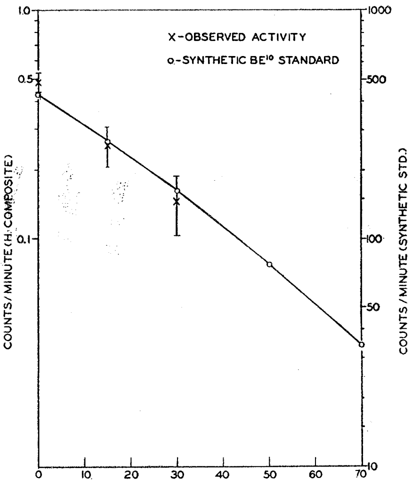

Fig. 1. Absorption curves of observed activity and of synthetic Be^{10} standard in polyethylene in close cylindrical geometry.

The benzene layer is then extracted with two 150-ml portions of 6*N* 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 6*N* 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 cm³ 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,