have been sought: Does a trend occur for each element and for paleotemperature for this core considered as a whole? If so, at what depth below top of core does first appearance of such a trend occur? The procedure for the application of the test is as follows: (i) determine the median value; (ii) assign a plus sign to those values above the median and a minus sign to those below it; (iii) consider as a run any sequence of one or more like signs preceded or followed by unlike signs; and (iv) calculate the total number of runs and determine from a table of previously calculated values whether the distribution is random or nonrandom [see Dixon and Massey (5)].

With regard to sequential analysis three alternatives present themselves, according to Dixon and Massey (5); accept the hypothesis of trend; reject it; or consider the data insufficient and continue sampling. There seems to be no reason why these criteria may not also apply to time series.

Table 1. Trend of elements and paleotemperature in core A 172-6. For both paleotemperature and the elements tested, distribution with depth was nonrandom. Paleotemperature data after Emiliani (2); $N_1 = N_2$, number of items above and below the median; and u, the critical value.

Paleotemperature and elements	$N_1 = N_2$	u .025*	u .975†	No. of runs
Paleotemperature	38	30	47	14
Iron + aluminum + silicon	47	38	59	22
Silicon	47	38	59	20
Aluminum	47	38	59	16
Iron	47	38	59	20
Titanium	46	37	56	30
Magnesium	47	38	59	30
Manganese	47	38	59	25
Calcium carbonate	47	38	59	26

* Lower critical percentile value at the 5 percent level of significance. † Upper critical percentile value at the 5 percent level of significance.

For all the elements under consideration, as well as for paleotemperature (Table 1), the number of runs is less than one might be led to expect by a purely random arrangement; it thus appears that a trend exists in every instance.

Hoel (6) states, "If a series possesses a long upward, or downward, trend, the total number of runs will tend to be small because of a few long runs at the beginning of the series and at the end of the series. If a series possesses a cycle that is fairly long in terms of the time between observations, the total number of runs will again tend to be small because most of the runs will be longer than expected under randomness. . . . Thus it appears that either a trend or cyclical movements will give rise to a small number of total runs."

The concept of first appearance of a trend below top of core in a deep-sea core has not, to my knowledge, previously appeared in the geologic literature. Determination of first appearance can be accomplished by calculating successive increments below top of core until a trend appears. Calculation is then continued throughout the remainder of the core to ensure that randomness does not reappear. The calculation is rather a tedious process, but it may have pertinence. This segment represents a sector of core that is statistically random with regard to the test under discussion. This may suggest that more detailed study should be undertaken with regard to this section of core. It may also suggest that in certain areas cores under a certain length may not be representative samples of the conditions of sedimentation. That is to say, for a given area is there a meaningful minimum length of core (7)?

The segment just prior to first appearance of trend in core A 172-6 for the major components under discussion ($CaCO_3$, iron, aluminum, silicon, and for paleotemperature) falls between 230 and 280 cm below top of core. If one accepts 3.70 cm per 1000 years as an average rate of sedimentation, then the stable part of this core represents a period of some 60,000 to 80,000 years before present (Table 2).

Table 2. Depth prior to first appearance of trend in core A 172-6. Paleotemperature data after Emiliani (2); $N_1 = N_2$, number of items above and below the median; u, the critical value.

Elements	Depth below top (cm)	$N_1 = N_2$	Median (%)	u .025*	No. of runs
Calcium carbonate	280	14	33.5	9	8
Silicon	230	12	20.35	7	6
Iron	270	14	2.35	9	8
Titanium	170	9	0.30	5	4
Magnesium	170	9	1.30	5	4
Aluminum	270	14	7.6	9	8
Manganese	140	7	0.13	3	2
Paleotemperature					
	250	13	23.65°C	8	7

* Lower critical percentile value at the 5 percent level of significance.

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8. I thank Dr. R. L. Miller, Dr. G. A. Rusnak, Mrs. Kay Weitz, and Miss Donna Meddaugh for their assistance during the course of this project.

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Apatite Crystallites: Effects of Carbonate on Morphology

Abstract. *Carbonate is a substituent in the apatite structure; when present, it limits the size of the growing apatite crystals and so influences their shape that they grow more equiaxed than needle-like. The tendency for carbonate apatites to be equiaxed is related to the nature of the chemical bonds formed in the crystal. The interference of carbonate with the good crystallization of apatite, and its weakening effect on the bonds in the structure, increase the dissolution rate and the solubility, thereby presumably contributing to the susceptibility to caries of dental apatites containing carbonate.*

The inorganic phase of teeth of vertebrates has been identified by x-ray diffraction as belonging to the apatites (1)—that is, crystalline basic calcium phosphates typified by hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$. Biologic apatites are modified by the presence of other constituents such as carbonate, magnesium, and sodium ions. These ions can be coprecipitated with the apatite, and no separate phase is detectable in the x-ray diffraction patterns. We now report the effects of coprecipitated carbonate ions on the physicochemical nature of apatites.

The role of carbonate in the structure of the mineralized tissues has been disputed for more than 30 years. In particular, it is yet to be decided whether the carbonate is adsorbed on the surface of the crystallite or is an integral part of the apatite structure; and, if it is part of the apatite structure, whether it substitutes for the phosphate or for the hydroxyl groups (*2*). We now present evidence that carbonate substitutes for the phosphate and explains how the presence of carbonate can contribute to the susceptibility of teeth to caries.

Synthetic apatites containing 0.4 to 22.5 percent CO_3 by weight were prepared by a precipitation method at 100°C (*3*); these precipitates give the x-ray diffraction patterns of well-crystallized apatite. Apatites prepared with increasing contents of carbonate exhibit proportional changes in dimensions of the *a*- and *c*-axes. As no phase other than apatite is detectable from the x-ray patterns, we conclude that the carbonate is a substituent within the structure of the apatite. Furthermore, when carbonate is included in the apatite structure, corresponding decrease in the amount of

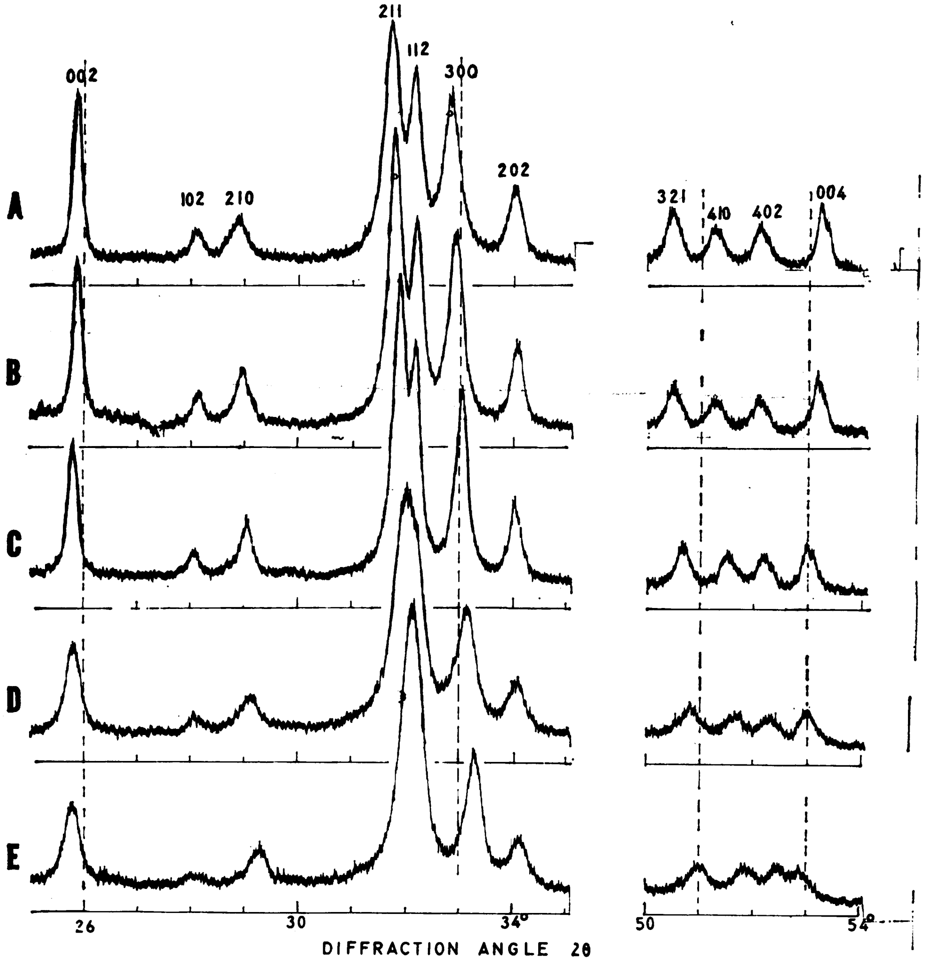

Fig. 1 (left). X-ray diffraction patterns of synthetic apatites, demonstrating shortening of the *a*-axis (as measured from the 300 reflection) with increase in carbonate content. Percentages of CO_3 by weight: (A) 0.5, (B) 5.0, (C) 10.0, (D) 15, (E) 20.

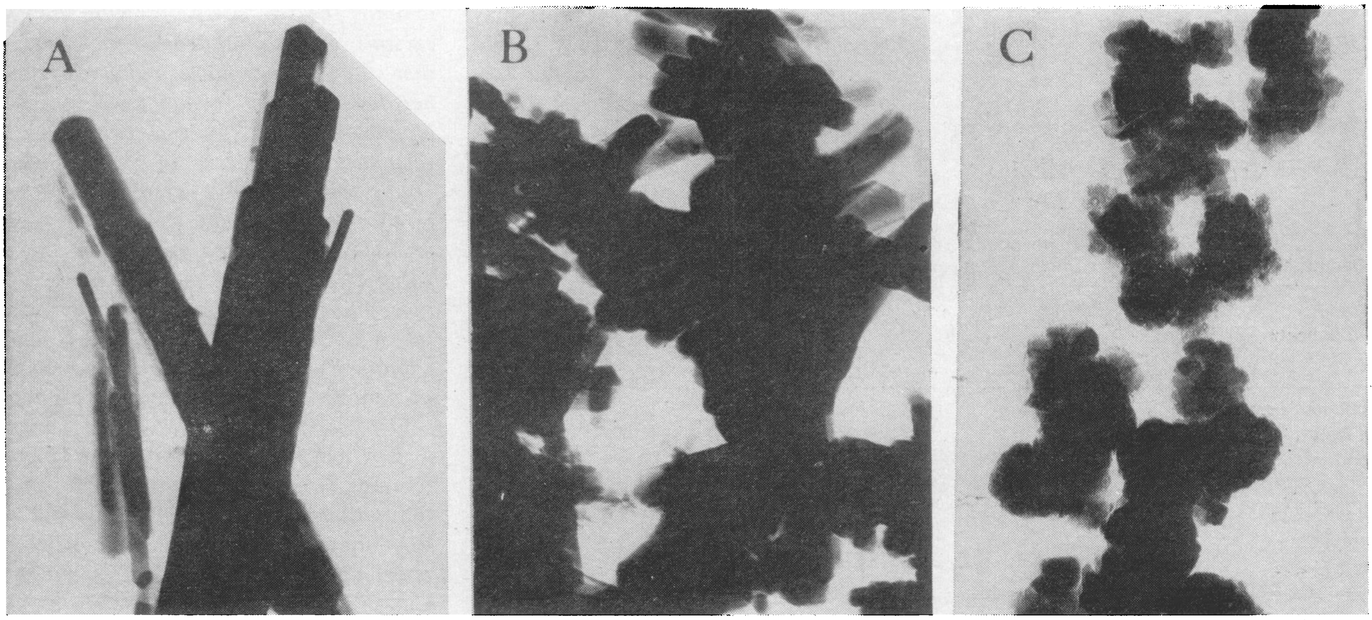

Fig. 2. Synthetic apatites showing the effect of carbonate on the size and shape of the apatite crystallites (× 125,000). Percentages of CO_3 by weight: (A) 0.5, (B) 5.0, (C) 15 to 22.

PO_4 is observed also when all OH^- has been replaced by F^- in synthetic apatites (*4*). Thus one may conclude that carbonate substitutes for phosphate and not for the hydroxyl groups.

The presence of carbonate in synthetic apatites, especially when precipitated at lower temperatures, disturbs the crystallization process (*5*) and increases their solubility (*6*). Carbonate content and susceptibility of teeth to caries have been correlated (*7*). Studies of x-ray diffraction line-broadening and with the electron microscope show that the presence of carbonate causes diminution in size and a change in shape of apatite crystallites. The increased solubility of carbonate-containing apatites thus reflects the increased surface area of the mass of apatite crystallites.

The synthetic apatites studied by us were prepared at 100°C by drop-by-drop addition of 250 ml of $Ca(Ac)_2$ ($0.02M$) solution to 750-ml portions of $0.016M$ Na_2HPO_4 solutions containing also various concentrations (0 to $0.54M$) of sodium carbonate; x-ray diffraction patterns of some of the precipitates appear in Fig. 1. The shift of the 300 and 410 reflections to higher angles demonstrates shortening of the *a*-axis dimensions from 9.43_5 to 9.29_9 Å; shift of the 002 and 004 reflections to lower angles indicates lengthening of the *c*-axis from 6.87_7 to 6.93_2 Å. With increasing carbonate content, the 211 and 112 reflections become superimposed (Fig. 1, D and E).

The breadth of the different peaks varies also (see Fig. 1, A and D or E). In general, increased x-ray diffraction line-broadening results from small crystallite size or from strain in the lattice, or from both. Assuming that the line-broadening in these synthetic apatites is chiefly due to small crystallite size, we determined (from the 002 and 300 reflections) the average crystal dimensions by use of the Debye-Scherer formula (*8*)

$$d_{hkl} = (K\lambda\ 57.3)/(\beta_{\frac{1}{2}} \cos \theta)$$

where the shape-constant K is 0.9, λ is 1.54 Å for $CuK\alpha$ radiation, θ is the diffraction angle, and $\beta\frac{1}{2}$ is line broadening in degrees. The broadening $\beta\frac{1}{2}$ equals the difference between the line breadth (at half-maximum intensity) observed with the samples and that obtained with the very well-crystallized Durango fluorapatite.

In the patterns of carbonate-free apatites we find a greater broadening of the 300 than of the 002 reflections, and therefore conclude that these crystallites must be thin needles elongated along the direction of the *c*-axis. When the apatites richer in carbonate are considered, broadening of the 002 peaks increases more than that of the 300 peaks, an indication that the crystallites have become more "spheroidal," with a length: thickness ratio approaching unity. Electron micrographs of the precipitated apatites confirm these results. Figure 2 shows needle-like crystals for materials very poor in carbonate, and clusters of equiaxed crystals for synthetic materials rich in carbonate.

A possible explanation of the changes in size and shape is that carbonate causes formation of weak bonds, and the growth of a crystal is less in the general direction of the formation of weak bonds than in the general direction of the formation of strong bonds (*9*). The carbonate's interference with the good crystallization of the apatite and its weakening effect on the bonds in the structure increase the rate of dissolution and the solubility. These increases make carbonate-containing dental apatites more susceptible to attack by the weak acids present in the mouth. Thus carbonate contributes to susceptibility to caries.

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X-Ray Diffraction Study of Some Fossil and Modern Resins

Abstract. *Samples of both fossil and modern resins have been investigated by x-ray diffraction techniques. Most fossil resins (ambers) yield only diffuse x-ray diffraction patterns, though some (settlingite, Highgate copalite, and guayaquillite) have relatively sharp patterns. Many modern resins, including those from species of* Pinus *and other conifers such as* Picea *and* Abies, *and many of those from* Protium *and* Bursera, *and* Styrax benzoin, *give sharp and distinctive patterns. Some crystalline constituents of the resins which yield the x-ray diffraction patterns have been identified. The similarity between the* Protium *and* Bursera *patterns and those of Highgate copalite and guayaquillite may indicate a possible genetic relationship between these modern and fossil resins.*

Fossil resins, to which the generic term amber usually is applied, have been highly prized and numerous investigations have been made of them. With a view to establishing a genetic relation between fossil and modern resin-producing trees, I have made x-ray diffraction studies of several hundred samples of both fossil resins and resins from modern coniferous and angiosperm trees (*1*). Small samples (approximately 150 mg) of the resins were powdered and spread on a glass slide or pressed into an aluminum holder, in preparation for study in a Norelco x-ray diffractometer. Filtered copper radiation was used.

Most of the fossil resins yielded only diffuse patterns. These patterns are very similar and are characterized by one broad band with its peak between 5.7 Å and 6.2 Å (2θ, 14.3° to 15.55°). Superimposed upon this band and at other positions in the x-ray diffraction spectrum there are minor and, in many cases, sharp peaks that indicate differences in the patterns of the various resins. Figure 1 shows some typical patterns obtained from Baltic Amber (succinite), Austrian copalite, and Mexican Amber from Chiapas. The *d*-spacings for these patterns are given in Table 1. On the basis of these diffuse x-ray patterns alone, it is not yet possible to postulate whether the differences and similarities are due to the botanical origin of the resins or to their various stages of oxidation and polymerization.

The sharp patterns, representing crys-