melting point mixed with an authentic sample, 111°–112°C).

Thus petroleum-type hydrocarbons are produced relatively rapidly by the reaction of cholesterol and farnesol with sulfur at temperatures no more than 50°C above those prevailing in some sediments which are commonly regarded as source beds of petroleum. The reaction at a temperature near 100°C would take place very slowly but over a long time period may be expected to produce the same or similar hydrocarbons. Our experiments do not conform with the geological conditions in other respects. These include dilute solutions of the components, an aqueous reducing environment, and the presence of acid clays. With regard to the latter Kawai and Kobayshi (*4*) report that squalene and cholesterol give petroleum-like mixtures of hydrocarbons when heated with acid clays.

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Carbonate in Hydroxylapatite

Abstract. *Unit cell dimensions of hydroxylapatite synthesized hydrothermally are* $a_0 = 9.42_6$ *Å and* $c_0 = 6.88_5$ *Å, whereas carbonate apatite (2.29* CO_2*) gave* $a_0 = 9.43_6$ *Å and* $c_0 = 6.88_5$ *Å. A deficiency of both calcium and phosphorus in the carbonate apatite suggests a coupled substitution of hydronium and carbonate ions in the structure.*

Table 1. Analyses of apatite. The product after heating to 1460°C in each case was apatite, and the Ca : P ratios were 1.760 for the carbonate and 1.665 for the hydroxylapatite (Calcd. 1.667).

Item	Carbonate (64-AP-2)		Hydroxyl (64-Ap-4)		Calcd. for $Ca_{10}(OH)_2(PO_4)_6$ (%)
	Weight (%)	Molecular proportions	Weight (%)	Molecular proportions	
CO_2	2.29	0.0520	0.00		
CaO	53.87	.9620	55.22	0.9860	55.78
P_2O_5	38.74	.2728	41.97	.2955	42.43
H_2O					1.79
Total weight loss after drying at 130°C, cumulative values					
~ 800°C, 12 hr	0.9		0.0		
~ 1120°C, 3 hr	2.0		0.0		
~ 1460°C, ½ hr	3.1		1.5		

Chemical analyses of dental enamel, bone, phosphorite rock, and even single crystals of apatite commonly show carbon dioxide. However, the manner of its occurrence has been a subject of controversy for many years. Some investigators suppose that carbon dioxide is present as an absorbed layer on the crystallites of teeth and bone. Others suppose that the carbonate is a separate phase, presumably calcite or aragonite; however, if such a separate phase exists, it cannot be detected by any experimental method that has been applied. Still other investigators are aware of the solid solution of carbonate ions in calcium phosphate minerals and dental enamel, and they believe that such solid solution is also possible in crystallites of dentin and bone. The purpose of this study is to determine precise values for the unit cell dimensions of apatite, with and without substitution of carbonate ions, and the effect on the omega index of refraction.

Many periodicities for hydroxylapatite are recorded in the literature (McConnell has reviewed the problem, *1*). The differences probably result from x-ray analysis of nonstoichiometric materials. Most analyses were made on precipitates that were very fine-grained; only rarely was hydrothermal synthesis used. Reported periodicities for hydroxylapatite represent a range of nearly 0.1 Å for both c_0 and a_0.

McConnell (*2*) and Altschuler *et al.* (*3*) found that carbonate fluorapatite from Staffel, Germany, has a significantly smaller a_0 dimension and a slightly larger c_0 dimension than does fluorapatite from Durango, Mexico.

To establish the effect of the carbonate ion on the unit cell dimensions of apatite, control of the purity and stoichiometric composition of the material is essential. Carbonate apatite was prepared from reagent grade dibasic calcium phosphate ($CaHPO_4$) having a Ca : P ratio of 1.03 and low-alkali calcium carbonate. These two solids were well mixed. This mixture, with a calcium-to-phosphorus ratio of 1.67, was then sealed in a gold tube. No water was added to the mixture prior to sealing because the dibasic calcium phosphate contained sufficient water for the formation of apatite. Carbonate-free hydroxylapatite was prepared after heating the same reagents to a temperature in excess of 900°C. Dibasic calcium phosphate was heated to form β-calcium pyrophosphate. The pyrophosphate and low-alkali calcium carbonate were mixed to yield a calcium-to-phosphate ratio of 1.67, and the mixture was then heated to 900°C for 8 hours to eliminate the CO_2 from the system. The resulting mixture of lime and β-calcium pyrophosphate was packed in a closed-end gold tube and then reheated for 4 hours. It was reheated until the sample attained a constant weight. A slight amount of water was added to this sample and the tube was immediately closed by welding to prevent the absorption of CO_2.

The sealed gold capsules containing the carbonate hydroxylapatite mix and and the carbonate-free hydroxylapatite mix were then placed in a "cold-seal"

Table 2. Lattice dimensions of apatite (values in angstroms).

Reference	a_0	c_0
	Carbonate apatite	
*	9.43_6	6.88_3
	Hydroxylapatite	
*	9.42_6	6.88_5
	Fluorapatite†	
*	9.39_8	6.89_9
(*2*)	9.39_5	6.88_2
(*3*)	9.38_6	6.87_8
	Hydroxylapatite	
(*5*)	9.418 ± .003	6.883 ± .003
(*6*)	9.420 ± .001	6.885 ± .001
(*7*)	9.421 ± .003	6.881 ± .003
(*8*)	9.416 ± .002	6.883 ± .002
	Dahllite	
(*6*)	9.454 ± .004	6.892 ± .0025

* This work. † Durango, Mexico.

reaction vessel and heat treated at 400°C and 1 kb total pressure for a period of over 20 days. During this period both mixtures reacted completely to form apatite. On microscopic examination no other phases were found.

The synthesized apatite was anhedral and had an average crystal dimension about 0.001 mm. Under the microscope the larger crystals, almost 0.003 mm, show faint birefringence. The carbon dioxide contents were determined by dissolving the samples in hydrochloric acid and collecting the liberated carbon dioxide in a weighing tube containing ascarite-magnesium perchlorate. By this method, the carbonate hydroxylapatite was found to contain 2.29 percent of carbon dioxide (by weight), and carbon dioxide was not detected in the carbonate-free hydroxylapatite. Apatite from Durango, Mexico, was analyzed and found to contain 0.05 percent carbon dioxide.

Analyses of the two samples and weight loss data are given in Table 1. The carbonate apatite is characterized by a deficiency in both phosphorus and calcium compared to hydroxylapatite. Substitution of the carbonate ions for phosphate ions coupled with the substitution of hydronium ions for calcium ions could easily explain these differences. The carbonate apatite lost several percent of volatile substances on heating to 1120°C; whereas the hydroxylapatite lost no weight. Heating to 1460°C results in a weight loss for both samples, although the *heated product is still apatite, and the heated carbonate apatite still effervesced in acid, indicating that some carbon dioxide is still contained in the material.* As a result, the analyses in Table 1 plus the total weight loss with heating to 1460°C do not and should not total 100 percent. Glass was not found by microscopic examination of the heated material.

Dimensions of the unit cell of the synthesized apatite was determined by x-ray powder diffraction. The average value was obtained from (300), (310), and (410) for a_0 and (002) was used for c_0 (see Table 2 where they are compared with apatite from Cerro de Mercado, Durango, Mexico).

There is no significant difference in c_0 between pure hydroxylapatite and a carbonate-bearing hydroxylapatite. The a_0 dimension, however, shows a slight increase for the substitution of carbonate containing hydroxylapatite. Such an increase, although slight, is opposite to that reported by McConnell (*2*) and by Altschuler *et al.* (*3*) for natural fluorapatite and carbonate fluorapatite. Possibly there are chemical differences other than the carbonate contents of the natural materials.

Omega index of the synthesized carbonate apatite is 1.637 ± .002, and that of the hydroxylapatite is 1.642 ± .002. Simpson (*4*) synthesized hydroxylapatite in the presence of other calcium phosphate phases and a large excess of water and found the omega index of the apatite to be about 1.652. The reason for the difference is unknown. Possibly the previously studied material was phosphorus-rich or the $H_4O_4^{-4}$ ion has a significant role in either or both materials.

Thus, a coupled substitution of carbonate and hydronium ions for phosphate and calcium ions, respectively, takes place in apatite. Substitution of 2.29 percent carbon dioxide very slightly increases the a_0 dimension and decreases the omega index of refraction. Neither the index nor the lattice dimension show sufficient change to be useful for establishing the carbonate content of apatite.

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Lead Isotopes in Gasoline and Aerosols of Los Angeles Basin, California

Abstract. *The isotopic composition of lead isolated from antiknock gasolines and the aerosols of the Los Angeles basin was determined. The lead isotopic composition of the aerosols was similar to that of rural snow. The high concentration of lead in water of precipitation and that of the surface of the sea can be attributed to automobile exhausts.*

The lead content of rural snow, sampled at Lassen Volcanic National Park, California, is about 1.6 μg/kg (*1*). This high concentration of lead could not be accounted for by soil dust, and the contamination was attributed to industrial pollutants. The source of the lead contaminants can be identified by their isotopic composition because each lead ore has its characteristic isotopic composition (*2*). We now report on the isotopic composition of leads in antiknock gasoline and in the aerosols of the Los Angeles basin, California. The aerosols were collected from an electrostatic air filter at the Geochemistry Laboratory of the California Institute of Technology (Pasadena) during the spring of 1964. The sooty deposits consisted of about 5 percent ash, which contained about 50,000 parts of lead per million. Gasoline samples were purchased from service stations in the San Diego area in May 1964, and the aerosols were gathered during the same period. The lead content (mean) of antiknock gasoline is 2.1 g per gallon (*3*). The lead in the gasoline and in the air filtrate was extracted by refluxing with concentrated hydrochloric acid for several hours. This lead was then isolated and purified by dithizone extraction (*4*). Mass spectrometric analyses were performed at the California Insti-

Table 1. Isotopic composition of leads in gasoline and aerosols.

Sources	Ratio of Pb^{206} to		
	Pb^{204}	Pb^{207}	Pb^{208}
Gasolines			
Wilshire D	18.14	1.160	0.4771
Wilshire Regular	18.10	1.156	.4751
Douglas	18.05	1.152	.4745
Standard Oil Regular	17.92	1.142	.4724
Shell Oil Regular	17.38	1.115	.4650
Average	17.92	1.145	.4728
Other sources			
Los Angeles aerosols	18.04	1.154	0.4746
Lassen Volcanic Park snow (*1*)	18.01	1.144	.4690
1947 Tetraethyl lead (*6*)	18.69	1.204	.4880
Pacific sediment lead (*5*)	18.73	1.197	.4836