The more stable the environment, apparently, the slower the turnover, other things being equal.

The most important fact that emerges from this analysis is that faunal turnover on islands is far more rapid than previously recognized and that this turnover is characterisic not only for very small islands but occurs on islands of any size. Various considerations indicate that extinction is by no means necessarily caused by competition from new colonists or by new pathogens introduced by them. Rather one must assume the existence of a general vulnerability to changes which includes weather factors (hurricanes), climatic fluctuations, and biotic changes of any kind.

Birds may well be unique in the rapidity of turnover, for the rich endemic floras of New Caledonia and the Venezuelan highlands indicate a very different situation for plants and perhaps for insects associated with plants.

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Isoprenoid Hydrocarbons in Recent Sediments: Presence of Pristane and Probable Absence of Phytane

Abstract. *Pristane (2,6,10,14-tetramethylpentadecane) has been isolated from two recent marine sediments. Unlike their ancient counterparts, these sediments contain no detectable phytane. These two facts suggest a biochemical origin for at least a fraction of the sedimentary pristane and a later, geochemical formation of phytane. Commercial reagent-grade solvents (pentane, isooctane, methanol) contain appreciable quantities of fossil pristane and probably phytane.*

Terpenoid hydrocarbons are among the most ubiquitous natural products. Pristane (2,6,10,14-tetramethylpentadecane), which occurs in some terrestrial plants and animals (*1*), is especially abundant in marine crustaceans (*2*) such as copepods. These copepods derive pristane from phytol in their food. As a relatively stable compound phytol passes through the marine food chain and accumulates in the fat of most marine fishes and mammals. Much interest centers around the recent discovery of pristane, phytane, and related isoprenoids in crude petroleum (*3*) and in ancient sediments (*4*), some of great antiquity. From petroleum and derived products, fossil isoprenoid hydrocarbons reenter the present-day environment.

The search for terpenoid hydrocarbons in recent marine sediments seemed of particular interest for closing one of the most extended biogeochemical cycles known. We obtained grab samples of sediment from the Wilkinson Basin, a depression in the shelf off Cape Cod, Massachusetts, and from Volden Fjord, Norway. The water column in both regions is rich in pristane-bearing Calanoid copepods. The sediments, preserved in the frozen state, were extracted first by methanol, then by methanol-benzene azeotrope. After dilution with water, the hydrocarbon-soluble fraction of the extracts was transferred to pentane. The solvents were removed at room temperature in a rotating evaporator. Silica-gel chromatography isolated the saturated hydrocarbons.

Great care was taken to reduce the contamination of the samples by fossil isoprenoids. Pristane was isolated and identified from a sample of commerical pentane (Phillips Petroleum Company, pure grade). Its concentration was 3 $\times 10^{-6}$ g/liter. The same contaminant occurs at lower concentration also in pure isooctane (2×10^{-7} g/liter) and reagent grade methanol (3×10^{-7} g/liter). Phytane appears to be present at comparable concentration; however, we have not isolated the corresponding chromatographic peak. Redistillation through an efficient, packed column lowered the pristane content of the solvents to 10^{-8} g/liter. Blanks carried through the entire procedure indicate that less than 3 percent of the pristane extracted from the sediments is contributed by all sources of contamination.

The hydrocarbon concentrate from the recent sediments was separated by gas chromatography on a strongly polar substrate for maximum resolution of the isoprenoids from the adjacent straight-chain hydrocarbons. The pristane and phytane regions were trapped in melting-point capillaries cooled by dry ice; etching of their internal surface and packing with steel wool to increase the condensation surface made the recovery quantitative.

The trapped pristane and "phytane" fractions were chromatographed again on a nonpolar column; infrared spectra of the pristane fractions were obtained with sampling equipment suitable for very small quantities. The retention indices on both gas chromatography columns together with the fine structure of the methyl-deformation band at 1370 cm^{-1} (Table 2) conclusively prove the presence of pristane. In both samples the pristane content (Table 2) is only slightly below that of the adjacent straight-chain hydrocarbons. On the nonpolar column, the sample collected in the phytane region off the polar column resolved into four major and several minor peaks; none had the retention index of phytane. We estimated that phytane would have been detected if it amounted to as little as 3 percent of the pristane.

Unlike ancient sediments these two recent pristane-bearing deposits con-

Table 1. Identification of pristane. Gas chromatograms, temperature programmed at 4°C/min; 1.8 m by 0.3 cm steel columns; 1.6 percent Apiezon L on Chromosorb G, acid-washed, dichlorodimethylsilane-treated; 3.5 percent RTV 502 (filler free) (Dow Corning) on the same substrate; 25 percent FFAP (Wilkens Instrument, Inc., Walnut Creek, Calif.) on Chromosorb W, acid-washed, trimethylchlorosilane-treated.

Retention index			Maxima of infrared spectra (cm^{-1})		
Apiezon L	RTV 502	FFAP			
		Pristane			
16.92	17.12	16.64	1360	1375	1382
		Phytane			
	18.15	17.73			
		Pristane (Wilkinson Basin)			
16.90		16.64	1360	1375	1382
		Pristane (Volden Fjord)			
	17.12	16.64	1360	1375	1382
		Phytane-fraction (Wilkinson Basin and Volden Fjord)			
	17.00	17.72			
	17.38				
	17.77				
	18.27				

Table 2. Pristane in recent marine sediments. Wilkinson Basin, Gosnold Cruise No. 65; 42°24′N, 69°29′W; depth, approx. 255 m. Volden Fjord, Norway, Chain Cruise No. 13, 63°09.5′N, Long. 5°59.8′E. Depth 659 m. All data are based on sediment dried at 110°C. The extract represents the benzene-soluble fraction of the methanol-benzene extraction. Saturated hydrocarbons were eluted from silica gel by normal pentane.

Constituent	Wilkinson Basin	Volden Fjord
$CaCO_3$ (%)	1.49	12.62
C (%)	1.03	2.68
Extract (ppm)	650	1300
Saturated hydrocarbons (ppm)	9.1	44
Pristane (10^{-3} ppm)	13	18

tain no detectable phytane. This suggests that recent oil pollution, which would introduce comparable quantities of pristane and phytane, played no role in the accumulation of the pristane. Rather, this hydrocarbon stems from recent organisms, most likely copepods, directly or through intermediates in the marine food chain. Like the sediments, these organisms contain no phytane.

Thus, based on limited data from two present sediments, phytane and isoprenoid hydrocarbons of lower molecular weight of ancient sediments appear to be postdepositional geochemical products. Phytane probably is formed by conversion of sedimentary phytol, for instance, by clay-catalyzed dehydration to phytadienes, followed by hydrogenation. Apparently, this process is too slow to generate detectable amounts of phytane in the uppermost sediment layer.

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Fast Reactions of Ascorbic Acid and Hydrogen Peroxide in Ice, a Presumptive Early Environment

Abstract. *Nonenzymatic decomposition of hydrogen peroxide proceeded more rapidly in ice than in liquid water. At 5×10^{-7}M ferric chloride or 10^{-8}M cupric chloride, breakdown of hydrogen peroxide was significant at $-11°$ and $-18°$ but negligible at $+1°$C. Ascorbic acid oxidation was faster in ice both with or without added metal ion. Nonparallel effects of metals and* pH *indicate mechanism changes in ice.*

Recent work has shown that several bimolecular reactions proceed more rapidly in ice than in liquid water (*1–6*). Kinetic analyses (*4, 5*) and inhibition by substrate analogs in frozen systems (*6*) suggest that the reaction mechanism has changed on freezing and that the ice structure may participate catalytically. These findings have possible implications in areas ranging from the storage of tissues and food at low temperatures to considerations of the origin of life on earth and elsewhere. We have now extended the studies in frozen solutions to metal ion–catalyzed reactions which behave similarly to enzymatic reactions. These include the breakdown of hydrogen peroxide and the oxidation of ascorbic acid.

For determination of hydrogen peroxide breakdown, an adaptation of the catalase assay method of Bonnichsen, Chance, and Theorell (*7*) was used. Solutions for storage were prepared in deionized distilled water and contained $0.0056M$ H_2O_2, $0.02M$ tris buffer at *p*H 7.2, or $0.02M$ acetate buffer at *p*H 5.5, and the desired amounts of $CuCl_2$ or $FeCl_3$. Freezing was initiated in a dry ice–acetone bath, and the samples were then transferred to $-11°$ or $-18°$C. At half-hour intervals over periods of 3 to 5 hours, samples were thawed rapidly in a bath at room temperature, in the presence of 1-percent sulfuric acid, and titration was performed with $0.006N$ potassium permanganate. The reaction was first-order at all temperatures to at least 50 percent decomposition.

Acceleration of hydrogen peroxide decomposition occurred in ice under all conditions studied. Table 1 shows that at $5 \times 10^{-5}M$ iron the rate in ice ($-11°$) exceeded that in water ($+1°$C) by a factor of 28. Both rates decreased with decreasing iron concentration, although not in parallel. At $5 \times 10^{-4}M$ iron, the rate at $-18°$ was 10 times that at 1°C. At $5 \times 10^{-7}M$ iron, the reaction rate was still significant at $-18°$, but zero at $+1°$C. Lowering the *p*H to 5.5 lowered the rates in the liquid and frozen solutions. The fall at $-18°$, however, was far more abrupt than that at $+1°$C, again indicating dissimilar reaction mechanisms.

Table 2 compares the rates for cupric chloride–catalyzed splitting of hydrogen peroxide. At $-11°$ copper was considerably more effective than iron, although iron catalyzed the reaction somewhat better at 1°C. At $10^{-8}M$ copper, the reaction was appreciable even at $-18°$C ($k = 28 \times 10^{-5}$ min^{-1}). An additional index of the rate enhancement on freezing is the extent of substrate decomposition after 4 days; at $10^{-8}M$ copper, this figure was 78 percent at $-11°$, 50 percent at $-18°$, and only 4 percent at 1°C.

Ascorbic acid oxidation, measured by the spectrophotometric method of Racker (*8*), also followed clean first-order kinetics in frozen solutions. Table 3 compares the rates in liquid and frozen systems containing $10^{-4}M$ ascorbic

Table 1. Rates of Fe(III)-catalyzed splitting of hydrogen peroxide in liquid and frozen systems.

$FeCl_3$ (M)	*p*H	Rate [$10^5 k_{obsvd}$ (min^{-1})]		
		1°C	−11°C	−18°C
5×10^{-5}	5.5	14.9	24.7	17.6
5×10^{-4}	7.2	23.0		227
5×10^{-5}	7.2	9.2	255	
5×10^{-6}	7.2	7.7	96.7	
5×10^{-7}	7.2	0.0	52.2	22.6

Table 2. Rates of Cu(II)-catalyzed splitting of hydrogen peroxide in liquid and frozen systems; *p*H 7.2.

$CuCl_2$ (M)	Rate [$10^5 k_{obsvd}$ (min^{-1})]	
	1°C	−11°C
10^{-5}	0.0	272
10^{-6}	0.0	166
10^{-7}	0.0	130
10^{-8}	0.0	61

Table 3. Rates of ascorbic acid oxidation in liquid and frozen systems. Absorbance read at 245 mμ.

$CuCl_2$ (M)	*p*H	Rate [$10^3 k_{obsvd}$ (min^{-1})]	
		1°C	−11°C
5×10^{-6}	5.5	15.9	56.4
0	5.5	5.0	14.2
5×10^{-6}	5.0	4.6	5.8
0	5.0	3.4	3.8