Oxygen Isotopic Analysis of the Size Fraction Between 62 and 250 Micrometers in Caribbean Cores P6304-8 and P6304-9

Abstract. *Oxygen isotopic analysis of the carbonate sediment fraction between 62 and 250 micrometers yields curves following the general trend of those obtained from* Globigerinoides sacculifera. *Warm stages 11, 13, and 15 are characterized by heavy postdepositional solution, which makes the sediment fraction between 62 and 250 micrometers rich in shell fragments of the more resistant, deeper-living species. As a result, oxygen isotopic analysis of these samples yields comparatively low temperatures, in contrast to those obtained from* Globigerinoides sacculifera.

Oxygen isotopic analysis of pelagic foraminiferal shells from deep-sea cores has greatly clarified the history of the Pleistocene (*1*-*5*). The number of major glaciations has been shown to be considerably greater than the classical four, as already evident from the work of Arrhenius (*6*), and work on land has now begun to confirm the evidence from the seafloor (*7*).

Oxygen isotopic analysis is usually performed on shells of foraminiferal species separated under the microscope. Because different species deposit their calcium carbonate at different depths or seasons, monospecific samples are generally used. Furthermore, sampling is usually restricted to specimens larger than 250 μm.

The carbonate sediment fraction between 62 and 250 μm consists almost exclusively of juvenile specimens of pelagic foraminifera plus varying amounts of fragments of larger shells of the same species produced by postdepositional solution. If postdepositional solution is slight, the juvenile shells strongly predominate in the sediment fraction mentioned. If solution is heavier, abundant fragments of the larger shells belonging to the more soluble species (*8*) are observed. If solution is very heavy, fragments of the larger shells belonging to the less soluble species predominate. In cores P6304-8 and P6304-9, postdepositional solution is negligible in all cold stages and in the temperate stage 3; it is slight in warm stages 1 and 5; it is appreciable in warm stages 7 and 9; and it is very heavy in warm stages 11, 13, and 15 [Fig. 1 in this report and figures 3 and 4 in (*2*)]. Heavy dissolution in these early warm stages of the Brunhes Epoch produced marked minima in the coarse fraction percentages [core P6304-8, 980 to 990 cm below the top; core P6304-9, 910 to 920, 1040 to 1060, and 1210 cm below the top; see figures 3 and 4 in (*2*)], a trend which is opposite to that generally observed in the Caribbean and equatorial Atlantic (*1*, *2*). It is apparent that conditions on the floor of the Caribbean during the earlier warm stages of the Brunhes Epoch were more conducive to post-

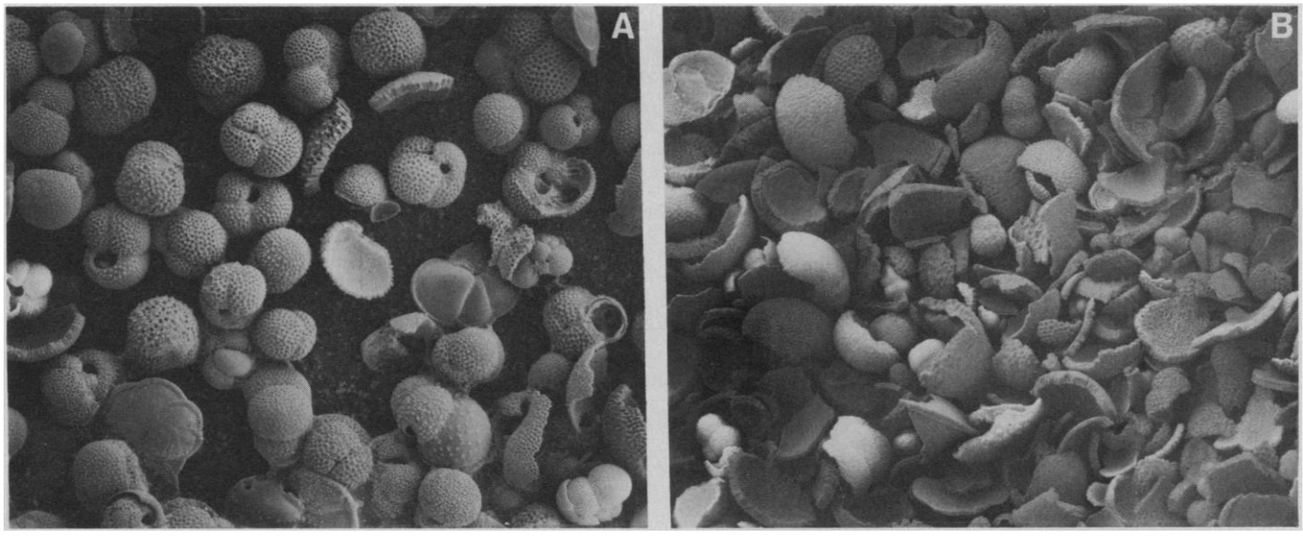

Fig. 1. Core P6304-9 sediment fraction between 62 and 250 μm (A) at the peak of stage 5 (320 cm below the top) and (B) at the peak of stage 13 (1040 cm below the top) (× 40).

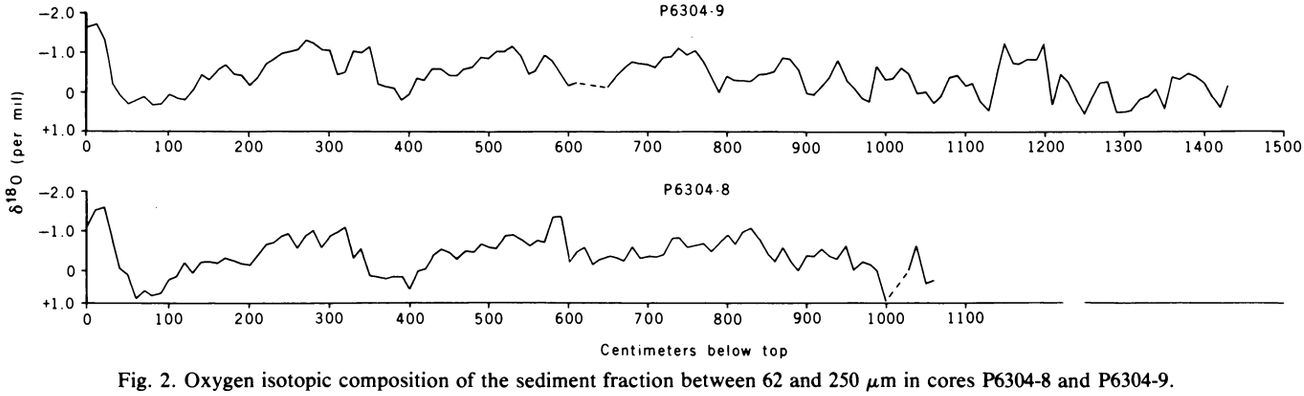

Fig. 2. Oxygen isotopic composition of the sediment fraction between 62 and 250 μm in cores P6304-8 and P6304-9.

depositional solution than those during the later warm stages. The rate of terrigenous sedimentation must have been particularly low. In contrast, higher rates of sedimentation led to excellent preservation of the smaller foraminiferal shells during all cold stages. During catathermal 3-2 and cold stage 2, even shells of pteropods were preserved in abundance (*9*).

Oxygen isotopic analysis was performed on samples of the carbonate sediment fraction between 62 and 250 μm at the usual 10-cm intervals (Fig. 2). The curves thus obtained reproduce the general trend of curves previously obtained using *Globigerinoides sacculifera* [figures 3 and 4 in (*2*)]. This is not surprising because it was shown (*10*) that the early stages of all pelagic foraminiferal shells are deposited in shallow water where *G. sacculifera* spends its entire life cycle. The strongest deviations from the *G. sacculifera* curves occur in correspondence with the sediment layers where postdepositional solution is heaviest. In these layers (core P6304-8, 1000 cm below the top, and core P6304-9, 910 to 920, 1060, and 1210 cm below the top) ^{18}O maxima occur while *G. sacculifera* shows minima. This is so because the layers with heavy solution are largely composed of shell fragments of the least soluble, deeper-living species. It is apparent that not only faunal analysis, but also isotopic analysis of bulk faunal samples [see (*5*)], is biased by postdepositional solution (*1, 8*). The need to limit isotopic analysis to monospecific samples is emphasized, although bulk faunal analysis of well-preserved juveniles is capable of producing meaningful results and may be used if larger specimens are not available.

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9. The occurrence of pteropod shells in abundance in a layer 1.4 m thick 30 cm below the surface of the Caribbean seafloor led early marine scientists to identify a portion of the Caribbean seafloor as being covered with pteropod ooze. The absence of pteropod shells in cold stages earlier than stage 2 together with increasing dissolution of forminiferal shells in the earlier warm stages may indicate that postdepositional solution is not limited to the sediment-water interface.
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Polychlorobornane Components of Toxaphene: Structure-Toxicity Relations and Metabolic Reductive Dechlorination

Abstract. *2,2,5-*endo,*6-*exo,*8,9,10-Heptachlorobornane and four derivatives of this heptachlorobornane, with an additional chlorine atom at position 3-*exo,*8, 9, or 10, account for a major portion of the acute toxicity of toxaphene and for up to 23 percent of toxaphene composition as analyzed by open tubular column gas-liquid chromatography with an electron capture detector. Both in several organisms and model environmental systems and on photolysis, this heptachlorobornane undergoes facile reductive dechlorination at the geminal-dichloro group and sometimes dehydrochlorination.*

Toxaphene is a complex insecticidal mixture containing heptachlorobornane **1** (*1, 2*), octachlorobornanes **2** and **3** (*3, 4*) (Fig. 1) and > 170 other $C_{10}H_{18-n}Cl_n$ and $C_{10}H_{16-n}Cl_n$ (n = 6 to 10) components (*5–7*). Compounds **2** and **3** are major contributors to the acute toxicity of toxaphene to mice, goldfish, and houseflies (*1, 3, 5*). Toxaphene is metabolized in rats (*5, 8*) and degraded in iron(II) protoporphyrin systems (*9*) by cleavage of about half of the carbon-chlorine bonds. It is important to define more precisely the relations between structure and toxicity for polychlorobornanes and the chemical nature of their initial metabolic products, since in the United States the amount of toxaphene used continues to be larger than that of any other insecticide. We find that compound **2** from chlorination of **1** is the most toxic of a series of newly prepared hepta-, octa-, and nonachlorobornanes. Further, we report that **1** undergoes metabolism and photolysis, in part, by reductive dechlorination at the geminal-dichloro substituent to form **4** and **5** and sometimes by dehydrochlorination to give **6** (Fig. 1).

Heptachlorobornane **1** was prepared (*10*) in gram quantities by photochlorination of 2-*exo*,10-dichlorobornane (*11*) in carbon tetrachloride solution to a chlorine content of 66.7 percent. It was isolated in 2 to 3 percent overall yield by chromatography on a silicic acid column with hexane (*1*), with bifluorenylidene (*7*) as a marker dye for the elution position of **1**. Further chlorination of **1** under the same conditions to an overall composition of $\sim C_{10}H_{10}Cl_8$ yields a mixture of unreacted heptachlorobornane (22 percent), **2** (13 percent), **3** (27 percent), and the 3-*exo*-chloro- (12 percent) and 10-chloro- (13 percent) derivatives of **1**. These hepta- and octachlorobornanes account for up to 23 percent of the composition of toxaphene as determined by open tubular column gas-liquid chromatography with an electron capture detector (*7, 10*). Additional minor products from the chlorination of **1** are its 5-*exo*-chloro-, 3-*exo*,10-dichloro-, and 8,10-dichloro-derivatives (*10*). These eight hepta-, octa-, and nonachlorobornanes were isolated by the same column chromatographic procedure used to obtain **1**. Their structures were assigned by proton magnetic resonance spectroscopy and mass spectrometry (*10*).

The structure-toxicity relations of polychlorobornanes and polychlorobornenes were examined with male albino mice treated intraperitoneally and with female houseflies of an insecticide-susceptible strain (SCR) treated topically (*1*), each in the presence and in the absence of the synergist piperonyl butoxide (*12*), and with goldfish exposed for 24 hours under static conditions (*3*) (Table 1). The potency of compounds resulting from introducing chlorine substituents into **1** generally decreases in the order: 9-chloro (**2**) > 8-chloro- (**3**) > no added chlorine (**1**) > 3-*exo*-chloro- or 5-*exo*-chloro- or 10-chloro (*10*). Addition of a 10-chloro substituent to the 3-*exo*-chloro or 8-chloro derivative of **1** reduces their potency. The toxicity of **1** is also decreased by reductive dechlorination at the geminal-dichloro group especially on conversion to **5** (*13*) and by dehydrochlorination, particularly at the 5,6 position on removing the chlorine from carbon-6 (*10*).

The reactions of heptachlorobornane **1** were examined in several chemical and biological systems (*13*). These systems included triphenyltin hydride in hexane in the presence of light (*6*), iron(II) hematin in both *N*-methyl-2-pyrrolidone-ace-