column expressed in standard cubic meters) and in a water column 1 m^2 by 100 m are 3.15×10^{-6} g and 1.1×10^{-4} g, respectively. We define residence time as

$$\tau = N/(dN/dt)$$

where N is the quantity of a constituent present in a reservoir and dN/dt is its rate of addition to or removal from the reservoir. If $\tau_{\mathrm{PCB,water}} = 4$ years, $d(\mathrm{PCB})/dt = 1.1 \times 10^{-4}$ g per 4 years $= 2.8 \times 10^{-5}$ g/year, the rate of PCB transfer out of or into the mixed layer (assuming steady state). If the input is atmospheric, the apparent residence time of PCB in the Sargasso Sea atmosphere is $(3.15 \times 10^{-6}\ \mathrm{g})/(2.8 \times 10^{-5}\ \mathrm{g/year}) = 0.11$ year, or 40 days. A similar calculation, based on an estimated DDT concentration in the ocean mixed layer of 6×10^{-8} g/m^3 (*15*), gives an atmospheric DDT residence time of 51 days. These are much shorter times than a proposed atmospheric residence time for DDT of several years (*17*). Concentrations of PCB in Sargasso Sea water 10 to 20 times higher than our values have recently been reported (*3*). If these results are correct, and if our atmospheric PCB concentrations are representative of the entire Sargasso Sea, the residence time for PCB in the atmosphere could be an order of magnitude shorter than 40 days. Thus it seems to us that either (i) the residence time of PCB in the atmosphere is much shorter than previously estimated for DDT or (ii) the short apparent residence time is due to significant PCB inputs into Sargasso Sea water apart from atmospheric deposition.

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References and Notes

1. Abbreviations: DDT, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane; chlordane, the *cis*- and *trans*-isomers of 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene.
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15. Maximum and minimum values for subsurface PCB concentrations of 1.4 and 0.89 ng/liter, respectively, are obtained from the data in Table 2 by averaging the results from all stations, assuming (i) 0.9 ng/liter and (ii) 0.0 ng/liter for samples containing < 0.9 ng/liter of PCB. We have taken the intermediate subsurface PCB concentration of 1.1 ng/liter for our residence time calculation. If we calculate the average DDT concentration in the surface microlayer (0.64 ng/liter) and assume the same DDT/PCB ratio in the subsurface water as in the microlayer (0.053), the DDT concentration in subsurface water is estimated at 0.06 ng/liter, or 6×10^{-8} g/m^3.
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17. Using DDT production figures and assuming rainfall as the dominant method of removal from the atmosphere, G. M. Woodwell, P. P. Craig, and H. A. Johnson [*Science* **174**, 1101 (1971)] estimated the atmospheric residence time of DDT as 3.3 years.
18. We thank the U.S. Naval Underwater Sound Laboratory, Tudor Hill, Bermuda, for providing a site for the construction of the air sampling tower. This work was supported by the Office of the International Decade of Ocean Exploration, National Science Foundation, under NSF grant GX-33777. Contribution No. 1500 of the Rhode Island Experiment Station.

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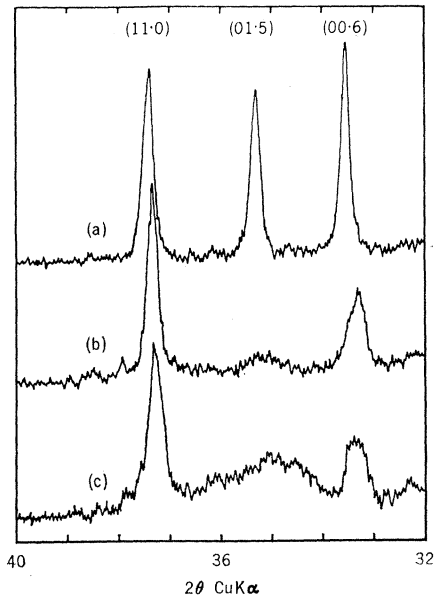
Protodolomite Synthesis at 100°C and Atmospheric Pressure

Abstract. *Ordered protodolomite, $CaMg(CO_3)_2$, has been synthesized at 100°C by reaction of metastable precipitated carbonates with aqueous magnesium-bearing solutions. Initial reaction products have expanded crystallographic cells, attributed to the presence of structural water. Longer reaction time produces a protodolomite approaching ideal composition and exhibiting order reflections in x-ray powder patterns.*

The long-standing problem of the origin of sedimentary dolomite has thus far successfully defied experimental studies. Attempts to synthesize dolomite under conditions approximating those encountered in natural sedimentary environments have consistently failed to produce ordered dolomite. Since ordering of the calcium and magnesium ions in dolomite is a requirement for stability (*1*), any experimental studies of dolomite formation must involve materials with demonstrable cation ordering.

Although dolomite and protodolomite exhibiting order reflections are readily synthesized at elevated temperatures and pressures, I believe this to be the first report of (ordered) protodolomite (*2*) synthesized under conditions sufficiently close to those of natural environments to allow direct comparison of the materials and of the processes of formation.

All syntheses were carried out at 100°C and atmospheric pressure in Pyrex reaction vessels. Temperature was maintained by a stirred, constantly boiling water bath. Aqueous solutions of calcium and magnesium chlorides (2 molal total cation concentration) with Mg/Ca (mole ratios) of 4 or 5 were brought to temperature in the water bath, and carbonate was introduced either as solid Li_2CO_3 or as an aqueous solution of Na_2CO_3. In order to minimize changes in solution chemistry due to the subsequent reactions, the total carbonate added amounted to less than 5 percent of the total magnesium plus calcium in solution. The reaction vessels were sealed after introduction of carbonate, but were periodically opened for sampling. Samples were removed by pipetting a portion of the suspension produced by vigorous shaking. Samples were washed with distilled water, dried at room temperature, and examined optically and by x-ray powder diffraction.



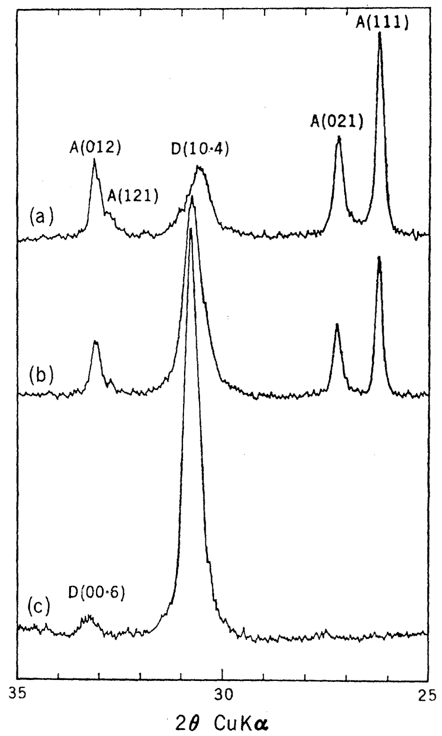


Fig. 1 (left). X-ray powder diffraction patterns of (a) natural dolomite, Gabbs, Nevada; (b) natural protodolomite, Andros Island, Bahamas; (c) synthetic protodolomite. Peaks are identified by Bravais-Miller indices. Abscissa: Bragg angle, CuKα radiation. Fig. 2 (right). X-ray powder diffraction patterns of reaction products (a) 1 hour, (b) 48 hours, and (c) 84 hours after addition of carbonate as solid Li_2CO_3. Peaks are identified as aragonite (*A*) or dolomite (*D*) with appropriate Bravais-Miller indices. Abscissa: Bragg angle, CuKα radiation.

The ultimate product in all experiments was a fine-grained, reasonably well crystallized protodolomite with attenuated basal plane and order reflections and with the *d* value of the major x-ray reflection between 2.89 and 2.90 Å. These synthetic materials are virtually indistinguishable from the natural modern protodolomites formed under hypersaline conditions. Figure 1 compares the x-ray powder diffraction characteristics of synthetic protodolomite with those of a natural protodolomite and a well-crystallized, perfectly ordered natural dolomite. Line broadening due to small particle size is comparable in all three materials, as evidenced from the similarity of the prism (11·0) reflections. Stacking disorder in the *c* direction results in attenuation and broadening of the basal (00·6) reflection as well as the cation-ordering (01·5) reflection.

The reaction proceeded by the slow alteration of metastable precipitates formed immediately after introduction of carbonate into the system. Although the ultimate product was essentially the same in every case, the nature of the initial metastable assemblage depended on the method of introduction of carbonate. Addition of solid Li_2CO_3 produced an initial assemblage consisting primarily of acicular aragonite, but containing a small amount of a poorly crystallized rhombohedral carbonate with *d* (10·4) = 2.92 Å (*3*). With increasing reaction time, the aragonite slowly disappeared and the rhombohedral carbonate increased proportionately. Concomitantly the *d* (10·4) reflection of the rhombohedral carbonate sharpened and shifted toward the position of ideal dolomite, and very weak (10·1), (01·5), and (0·21) order reflections ultimately appeared. This reaction sequence is illustrated in Fig. 2. All samples were approximately equal in size and were prepared and x-rayed under identical conditions; therefore, peak intensities may be compared semiquantitatively among the samples. The order reflections were visible in Debye-Scherrer photographs of a sample removed after 96 hours, and the synthetic sample illustrated in Fig. 1 was removed after 145 hours.

Addition of carbonate as Na_2CO_3 solution produced an initial assemblage of aragonite needles and a spherulitic magnesian calcite with *d* (10·4) = 2.94 Å. A second rhombohedral phase (protodolomite) with *d* (10·4) = 2.90 Å appeared in diffraction patterns after approximately 50 hours. With continued reaction, the protodolomite increased proportionately as the aragonite disappeared. Subsequently but much more slowly the initial magnesian calcite also disappeared with concomitant increase of protodolomite. Replacement of the aragonite by protodolomite was complete after approximately 100 hours, while complete replacement of the magnesian calcite required approximately 400 hours. Addition of LiCl to the system before introduction of Na_2CO_3 solution had no effect on the nature of the initial precipitates, but produced a significant acceleration of the replacement reactions. In the presence of 0.05 molal Li^+, replacement of aragonite was essentially complete after 50 hours of reaction, and the magnesian calcite was completely replaced after approximately 300 hours.

The expanded cells of protodolomites are usually attributed to the presence of excess calcium substituting for magnesium in the structure. However, an expanded cell could also result from the presence of small amounts of structural water (*4*). Since aqueous Mg^{2+} is known to be strongly hydrated, and since there is evidence that desolvation of the ions may be a rate-controlling factor in dolomitization (*5*), it seems likely that these low-temperature precipitates will contain some "trapped" structural water. Simultaneous differential thermal analysis and thermogravimetric analysis of a synthetic protodolomite sample showed a small endothermic weight loss near 300°C, similar to that ascribed by Glover and Sippel (*6*) to loss of water from precipitated magnesian calcites.

The existence of a chemically distinct surface phase has been proposed by Weyl (*7*) to explain the anomalous solubility effects of dolomite. The observations reported here are consistent with a growth model involving a partially hydrated surface phase. An initial precipitate with a high ratio of surface to volume might reflect the effects of such a phase (poor crystallinity, expanded cell); however, these effects would decrease continuously with growth of the crystallites. The catalytic effect of Li^+ is also consistent with this model. Kinetic control by desolvation of the surface phase predicts an inverse relation between the reaction rate and the activity of water. Introduction of a strongly hydrated ion such as Li^+ would reduce water activity and accelerate the reaction.

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2. I use "protodolomite" to refer to materials which deviate from ideal dolomite composition, or are imperfectly ordered, or both, but which show unambiguous evidence for a high degree of cation order.
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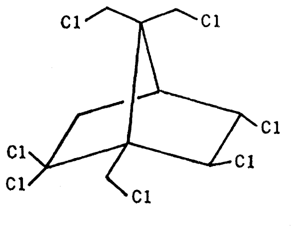
Toxaphene Insecticide: A Complex Biodegradable Mixture

Abstract. *Adsorption and gas-liquid chromatography separate toxaphene into at least 175 polychlorinated 10-carbon compounds including Cl_6, Cl_7, Cl_8, Cl_9, and Cl_{10} derivatives. One toxic component is 2,2,5-*endo,6-exo*,8,9,10-heptachlorobornane. Rats metabolically dechlorinate toxaphene, removing about half of the chlorine from the technical insecticide and from each of seven subfractions of varying composition and toxicity.*

Within the past 25 years 1 billion (10^9) pounds of toxaphene have been applied to crops and livestock for pest insect control. Its use continues at the rate of about 40 million pounds per year, in large part combined with methyl parathion for treatment of cotton. The toxaphene–methyl parathion combination has replaced the toxaphene–DDT combination employed until recently. Despite the fact that toxaphene is used in larger amounts in the United States than any other chlorinated hydrocarbon insecticide, there is insufficient information on several aspects of its chemistry, persistence, and environmental fate (*1*).

Toxaphene is produced by chlorination of camphene to about 67 to 69 percent chlorine by weight, yielding a reproducible but very complex mixture of compounds with an overall average elemental composition of $C_{10}H_{10}Cl_8$ (*2*). No individual component, toxic or otherwise, has previously been isolated in pure form. Despite the difficulties in evaluating toxaphene persistence, it is known from observations on its duration of effectiveness in insect control and from analyses of its residues by a variety of methods that many of the toxaphene constituents degrade under several different environmental conditions more rapidly than certain other chlorinated hydrocarbon insecticides, including DDT (*1*). Increased restrictions on the use of chlorinated insecticide chemicals and improved methodology for working with complex mixtures make it necessary and possible to define the nature of the toxaphene components and their metabolic fate in mammals. We have taken steps in this direction.

Analysis of chlorinated insecticides and other chlorine-containing environmental pollutants normally involves the use of gas-liquid chromatography (GLC) with an electron-capture detector. Technical toxaphene appears to contain 25 to 30 components when analyzed on appropriate GLC columns (*3*); however, many of the peaks detected are due to multiple components that do not separate on GLC. Fractionation of toxaphene on silica gel by thin-layer chromatography (TLC) with pentane as the developer or by column adsorption chromatography with hexane for elution resolves the toxaphene components on a different basis than GLC; the components elute from the GLC column in the general order of increasing degree of chlorination whereas this is not the case for elution from the adsorption column. Examination of the toxaphene fractions from silica gel column chromatography by combination gas-liquid chromatography–mass spectroscopy (MS) techniques (*4*) reveals a complex mixture of at least 175 C_{10} polychloro derivatives made up of $C_{10}H_8Cl_{10}$, $C_{10}H_{18-n}Cl_n$, and $C_{10}H_{16-n}Cl_n$ derivatives where the chlorine number (n) is 6, 7, 8, or 9. It appears likely that the majority of $C_{10}H_{18-n}Cl_n$ compounds are polychlorobornanes since one heptachlorobornane (**1**) has been identified, as described below, and 2-*exo*-10-dichlorobornane is a major intermediate (*5*) in the chlorination of camphene. The $C_{10}H_{16-n}Cl_n$ derivatives are likely to be polychlorobornenes or polychlorotricyclenes or both.



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A procedure was devised for isolating individual toxaphene components in pure, crystalline form. It involves separation on a partition column with β-methoxypropionitrile and heptane and then on the silica gel–hexane adsorption column, followed by a repetition of these two steps in sequence, and then preparative GLC and further purification by either sublimation or crystallization (*6*). With suitable monitoring, this sequence of chromatographic steps should permit isolation of any individual component provided it is stable under the chromatographic conditions employed.

By using intraperitoneal acute toxicity in the mouse as the monitoring criterion, two toxic crystalline compounds were isolated, one a $C_{10}H_{11}Cl_7$ and the other a $C_{10}H_{10}Cl_8$ component. These crystalline materials are, respectively, 6 times and 14 times more toxic to mice than technical toxaphene and 2 times and 4 times more toxic to houseflies treated topically. The $C_{10}H_{11}Cl_7$ component has been characterized by x-ray crystallography and by MS and nuclear magnetic resonance studies as 2,2,5-*endo*,6-*exo*,8,9,10-heptachlorobornane (**1**). Crystallization of the racemate from a mixture of hexane and acetone (5 : 1) appears to lead to the separation of the two enantiomers; however, these enantiomers could not be differentiated by the x-ray study. The $C_{10}H_{10}Cl_8$ component has not yet been obtained in crystalline form appropriate for x-ray structure determination. The $C_{10}H_{11}Cl_7$ and $C_{10}H_{10}Cl_8$ toxic components each constitute 2 to 6 percent of technical toxaphene, based on a combination of TLC and preparative GLC analyses, but they are in relatively large amounts compared with many other components. While it is already evident from our study that other toxic materials are present in toxaphene, the two components isolated to date appear to contribute significantly to the mammalian toxicity of commercial toxaphene.

The availability of preparations labeled with ^{36}Cl and ^{14}C (*7*) made it possible to carry out initial studies on the metabolic fate of toxaphene in mammals. Toxaphene labeled with ^{36}Cl was administered orally to rats at about