ably is a function of the carbon fixing by trace amounts of organic matter, as in conodonts (17). Demineralization of the spheres confirms the evidence provided by color banding; the dark color of the nucleus and the thin growth shells that surround it is due to the high concentration of organic matrix in these areas. Further arguments against the hypothesis that the spheres are inorganic precipitates are that they occur in a wide variety of lithofacies and that they are unknown after the Lower Carboniferous.

The only fossils invariably associated with the spheres are conodonts. Consequently, it can reasonably be assumed that the spheres belonged either to the conodont-bearing animal or to a group of organisms that possessed no other fossilizable hard parts. The identical chemical composition of conodonts and spheres tends to support the hypothesis that these two groups of structures were secreted by the same animal.

Despite evidence that the spheres belonged to the conodont-bearing animal, they cannot have represented a structure vital to that organism because of their sporadic association with the conodonts. Consequently, the speculation that they are conodont otoliths (7) or cnidarian statoliths (18) is untenable. Neither can they have been egg cases, because they are not hollow (19). An alternative explanation that appears compatible with all known facts is that the spheres are pearls secreted within the tissue of the conodont-bearing animal as a response to an organic or particulate irritant that formed the nucleus. Parasites provide the most common stimulus for pearl formation in bivalves growing under natural conditions (20), and the variability in the nuclei of our spheres may reflect the variety of infesting organisms. The dimple can be explained as the result of draping around a resistant area beneath the tissue that secreted the pearl. The depressed form of the largest conodont pearls may indicate that the height of the structure was close to the thickness of the tissue in which it was secreted.

Spherules within the basal plate of some Cambrian, Ordovician, and Silurian conodonts [for example (10), plate 16, figure 6] achieve diameters of only 20 μm before overgrowth by basal material but may have had a genesis similar to the conodont pearls described by us. Irrespective of this possible correlation, the spherules of the basal plate confirm the ability of the conodont-bearing animal to secrete concentric shells of apatite around a nucleus. Additional evidence that the conodont-bearing animal could respond to an irritant is the plugging of galleries burrowed into the conodont basal plate (10).

In conclusion, the mineralogy, structure, faunal associations, and geological occurrence of the spheres described by us suggest that they are pearls secreted by the conodont-bearing animal as a response to an organic or particulate irritant.

BRIAN F. GLENISTER
GILBERT KLAPPER
KARL M. CHAUFF
Department of Geology,
University of Iowa, Iowa City 52242

References and Notes

1. W. C. Sweet and S. M. Bergström, Eds., *Geol. Soc. Am. Mem.* 127 (1971).
2. M. Lindström, *Conodonts* (Elsevier, New York, 1964); G. Klapper and G. M. Philip, *Lethaia* **4**, 429 (1971); W. C. Sweet and S. M. Bergström, *Geol. Palaeontol.* **SB1**, 29 (1972).
3. M. Lindström, *Palaeontology* **17**, 729 (1974).
4. W. Melton and H. W. Scott, *Geol. Soc. Am. Spec. Pap.* **141**, 31 (1973).
5. C. R. Stauffer, *J. Paleontol.* **9**, 596 (1935); *ibid.* **14**, 417 (1940).
6. K. Leuteritz, H. Pietzner, J. Vahl, W. Ziegler, *Geol. Palaeontol.* **6**, 111 (1972).
7. W. Youngquist and A. K. Miller, *J. Paleontol.* **22**, 440 (1948).
8. F. H. T. Rhodes and D. L. Dineley, *ibid.* **31**, 353 (1957); D. L. Dineley, personal communication.
9. Paleozoic "hystrichospheres" are acritarchs according to the terminology of W. R. Evitt [*Proc. Natl. Acad. Sci. U.S.A.* **49**, 158 (1963)], among others, who indicated that many post-Paleozoic microfossils termed hystrichospheres are dinoflagellate cysts.
10. K. J. Müller and Y. Nogami, *Palaeontol. Z.* **46**, 68 (1972).
11. ———. H. Lenz, *Palaeontogr. Abt. A* **146**, 11 (1974).
12. J. B. Hayes, personal communication, 1962.
13. S. M. Bergström and R. L. Ethington have informed us that spheres are extremely rare in Ordovician strata of the North Atlantic and Midcontinent Provinces.
14. K. J. Müller, *Z. Dtsch. Geol. Ges.* **111**, 434 (1959).
15. R. G. C. Bathurst, "Carbonate sediments and their diagenesis," in *Developments in Sedimentology* (Elsevier, New York, 1971), vol. 12.
16. P. A. Sandberg, *Sedimentology* **22**, 497 (1975).
17. A. G. Epstein, J. B. Epstein, L. D. Harris, *U.S. Geol. Surv. Open File Rep. 75-379* (1975).
18. G. C. O. Bischoff, *Geol. Palaeontol.* **7**, 147 (1973).
19. Phosphatic calculi that resemble conodont spheres superficially are known to occur within the zooecia of certain Ordovician and Silurian ectoproct Bryozoa [W. J. Sollas, *Q. J. Geol. Soc. London* **35**, 500 (1879); K. P. Oakley, *Proc. R. Soc. London Ser. B* **116**, 296 (1935); *Bull. Br. Mus. Nat. Hist. Geol.* **14** (No. 1) (1966)]. Termed oakleyites [A. Eisenack, *Palaeontol. Z.* **38**, 170 (1964)] they apparently formed before the final disintegration of the zooids that occupied the zooecia. They are composed of the apatite species, dahllite (Oakley, 1935), and exhibit irregularities imposed by growth within a restricted chamber, thus differing from the conodont spheres.
20. W. J. Dakin, *Pearls* (Cambridge Univ. Press, London, 1913); L. R. Cox, in *Treatise on Invertebrate Paleontology,* part N, *Mollusca 6, Bivalvia*, R. C. Moore, Ed. (Geological Society of America, Univ. Press of Kansas, Lawrence, 1969), p. N2-129.
21. K. M. Chauff and A. Dombrowski, *Geol. Palaeontol.*, in press.
22. J. G. Johnson, *ibid.* **8**, 49 (1974).
23. G. Klapper and D. B. Johnson, *ibid.* **9**, 65 (1975).

24. Financial support was provided by the Graduate College at the University of Iowa, and by NSF grant GA-43791 to G.K. We thank S. M. Bergström, D. L. Clark, R. L. Ethington, W. M. Furnish, J. B. Hayes, K. J. Müller, W. C. Sweet, and W. Ziegler for critical review of the manuscript; S. R. Herr for early consultation; A. B. Bulatao and R. E. Sloan for loan of Stauffer's types; J. G. Johnson for contributing excellent study specimens from Nevada (Fig. IF); and K. Swett for consultation on ooids.

24 May 1976

Man-Made Carbon Tetrachloride in the Atmosphere

Abstract. *The emissions of man-made carbon tetrachloride and the rates of its removal from the atmosphere by natural sinks are evaluated. A large fraction, perhaps all of the carbon tetrachloride observed in the atmosphere, could be man-made, and carbon tetrachloride is a global atmospheric pollutant.*

In recent years, various halocarbon compounds including CCl_4 have been detected in the atmosphere (1, 2). The concentrations of CCl_4 in the stratosphere and troposphere are comparable to those of Fluorocarbon-11 ($CFCl_3$) and Fluorocarbon-12 (CF_2Cl_2). These three halocarbon compounds are photodissociated by ultraviolet (UV) radiation in the stratosphere. The resulting chlorine atoms can catalytically destroy O_3 (3). At present, CCl_4 is probably the major man-made source of chlorine in the stratosphere; CCl_4 provides perhaps three times as much chlorine in the stratosphere as the combined products from $CFCl_3$ and CF_2Cl_2 (4, 5).

There is an urgent need to identify the sources of halocarbons in the atmosphere and their natural loss mechanisms, as man-made halocarbon emissions may some day be sufficient to reduce the equilibrium O_3 concentration in the stratosphere and cause harmful biological effects as a result of the increased transmission of solar UV radiation (6). In earlier papers (1, 3–7), both man-made and natural sources of CCl_4 have been suggested. In this report I calculate the atmospheric concentration of CCl_4 due to man-made emissions.

Elevated CCl_4 concentrations of up to 1600 parts per 10^{12} (volume/volume) have been found in Los Angeles as compared with 50 to 200 parts per 10^{12} in clean background air over oceans (1, 2). Fluorocarbon-11, a known, man-made, atmospheric pollutant, and CCl_4 exhibit similar seasonal variations in concentration at Bowerchalke, United Kingdom, and Adrigole, Ireland (8). These results suggest that CCl_4, as well as Fluorocarbon-11, may be a man-made pollutant. The similar concentrations of CCl_4 found in background air in both hemispheres (*1*, *2*) are consistent with a long lifetime of CCl_4 in the atmosphere and a near equilibrium state of man-made emissions and destruction of CCl_4 in the atmosphere.

Man's emissions of CCl_4 into the atmosphere (Table 1) are estimated from data on production and usage in various countries, particularly the United States (*9*–*11*). The global production rates (column 4) are based on the percentages of the global production that originate in the United States (column 3) and on the U.S. production figures (column 2). It is assumed that for the period 1914 through 1955 the only significant production, apart from that in the United States, originated in the United Kingdom, France, and Germany. In subsequent years additional sources of production in Europe and Japan are included in the estimates. I know of no data on CCl_4 production in the U.S.S.R. and China. As a result, the final emission figures are probably somewhat underestimated as compared with the real emissions. The production estimates should be more reliable for the period 1945 through 1955 when most of the production was in the United States, and in 1972 and 1973 for which there are other estimates of the global CCl_4 production (*9*–*11*).

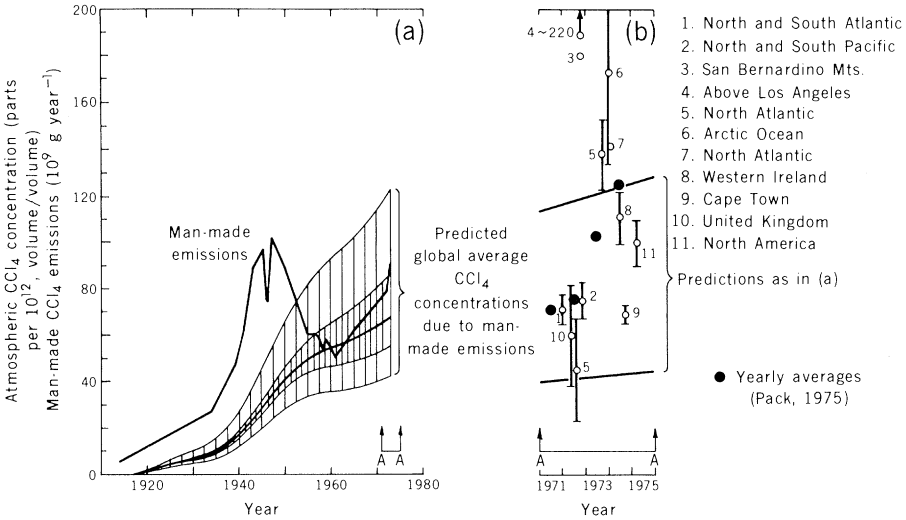

Fig. 1. (a) Predicted global average concentration of CCl_4 due to man-made emissions as presented in Table 1. The inner hatched area indicates the uncertainty due to loss mechanisms. The shaded area indicates the uncertainty due to loss mechanisms and a ± 30 percent variation in the emission rates. (b) Observed CCl_4 concentrations and predicted global average concentrations from (a).

Table 1. Global production and release of CCl_4 to the atmosphere.

Year	U.S. production		Global production (10^9 g/year)	Feedstock (%)	Remainder (10^9 g/year)	Emission (10^9 g/year)
	10^9 g/year	Percentage of global production				
1914	5	90	5	0	5	5
1934	27		30		30	27
1939	46		51		51	46
1941	62		69		69	62
1943	89		99		99	89
1945	98		108		108	97
1946	74		82		82	74
1947	102		113		113	102
1949				0		
1950	98		109		98	88
1954				50		
1955	130	90	145		67	60
1956	137		156		67	60
1957	144		170		66	59
1958	142		171		60	54
1959	167		206		64	58
1960	169		216		61	55
1961	174		229		55	50
1962	220		297	80	59	53
1965	269		408		69	62
1972	452	50	904	90	87	78
1973			998		100	90

I obtained values for man's emissions of CCl_4 to the atmosphere (column 7) by subtracting from the total production the amount used as chemical feedstock (column 5) and assuming that at least 90 percent of the remainder ultimately escapes to the atmosphere. This 90 percent loss by evaporation is based on the assumption that less than 10 percent of the CCl_4 used as a dry-cleaning solvent, fumigant, fire extinguisher, metal degreasing solvent, or in whatever other application is chemically transformed in the process. Storage and recycling of CCl_4 are neglected here because over periods of several years to a decade the production and loss of CCl_4 to the atmosphere will be much greater than the amount held in the various forms of storage (for example, solvent baths or fire extinguishers). Linear interpolation was used to provide data for those years for which production and usage figures were not available. No information is available for the period between 1915 and 1933. McCarthy and Jesson (*11*) have estimated CCl_4 production less feedstock usage for the United States for 1933 through 1973. Their average for the period is about 20 percent less than the value from this work based on the data in Table 1.

The uncertainty in these data is probably large, and a figure of ± 30 percent will be used. The CCl_4 emissions will probably remain constant or diminish in future years, because since the 1950's CCl_4 has been increasingly replaced in its various uses by other halocarbon compounds.

I estimated the concentration of CCl_4 in the atmosphere due to man-made emissions, using the mass balance equation for atmospheric CCl_4,

$$\frac{dM(\mathrm{CCl_4})_{\mathrm{atm}}}{dt} = E(t) - \sum_i L_i \qquad (1)$$

where $M(\mathrm{CCl_4})_{\mathrm{atm}}$ is the mass of CCl_4 in the atmosphere, $E(t)$ is man's emissions as a function of time, and L_i is the rate of loss of CCl_4 from the atmosphere (the different natural loss mechanisms are indicated by the subscript i). The mixing ratio (volume/volume) of CCl_4, C, is related to the atmospheric mass, $M(\mathrm{CCl_4})_{\mathrm{atm}}$, by the approximation that CCl_4 is uniformly mixed throughout the atmosphere from the surface to about 70 mbar (~18 km) with negligible amounts above this level [see (*1*, *4*, *5*)]. Thus

$$C = \frac{M(\mathrm{CCl_4})_{\mathrm{atm}}}{0.93\,M(\mathrm{air})_{\mathrm{atm}}} \times \frac{W_{\mathrm{air}}}{W_{\mathrm{CCl_4}}}$$

where W_{air} and $W_{\mathrm{CCl_4}}$ are the molecular weights of air and CCl_4, respectively, and where 0.93 corrects for the absence of CCl_4 above 70 mbar. This equation simplifies to

$$C = 3.84 \times 10^{-23} M(\mathrm{CCl_4})_{\mathrm{atm}} \qquad (2)$$

Generally the loss rates are proportional to the atmospheric concentration of CCl_4, and thus to its mass, so that

$$L_i = K_i M(\mathrm{CCl_4})_{\mathrm{atm}}$$

where K_i is the loss rate constant; Eq. 1 becomes

$$\frac{d\, M(\mathrm{CCl_4})_{\mathrm{atm}}}{dt} = E(t) - \Big(\sum_i K_i\Big)\, M(\mathrm{CCl_4})_{\mathrm{atm}} \qquad (3)$$

This equation has a simple solution (12).

Let us now evaluate the loss mechanisms. The four main mechanisms for the loss of CCl_4 from the atmosphere are: (i) reaction with active species in the gas phase; (ii) hydrolysis in water; (iii) photolysis by shortwave UV light; and (iv) absorption and decomposition in biological systems. The lifetime of CCl_4 in the environment is governed by the rates of these processes and the area or volume of the environment throughout which they are active. Other sinks, including adsorption on particulate matter or snow, have been suggested by various scientists (13). Because measurements are needed to evaluate the magnitudes of these sinks, I have omitted them from this discussion.

Gas-phase reactions that remove CCl_4 from the atmosphere and involve $O(^1D)$, $O(^3P)$, H, CH_3, and OH have been examined. In the calculations I have used the maximum concentration of the species present in either the troposphere or the lower stratosphere and the maximum value of the reaction rate applicable to the atmosphere (14). Only the $O(^1D)$ reaction is of significance. It gives a pseudo first-order CCl_4 removal rate of $K_1 = 1 \times 10^{-3}$ year^{-1}. This removal rate is the maximum rate that occurs anywhere in the troposphere or within the lower stratosphere to a height of 18 km. In the model (Eq. 3) it is applied throughout this region. Above 18 km the rate of the $O(^1D)$ reaction is less than 1 percent of the photodissociation rate; hence the $O(^1D)$ reaction is neglected above 18 km. The formation of CCl_4 from the CCl_3 radical in the gas phase is unlikely as CCl_3 is probably rapidly oxidized by O_2 (15).

The second mechanism for the loss of CCl_4 is hydrolysis in water. The amount of CCl_4 stored in the oceans is negligible as the mass of CCl_4 in the oceans is less than 1 percent of that in the atmosphere (1). The flux of CCl_4 from the atmosphere into the ocean (16) is large as compared with the amount of CCl_4 in the ocean. I calculate a lifetime of CCl_4 in the ocean of about 6 months. Hence the destruction of CCl_4 in the ocean will approximately equal the flux of CCl_4 from the atmosphere to the ocean and will be proportional to the atmospheric concentration of CCl_4. I calculated an atmospheric loss rate constant for CCl_4 due to the oceans of

$$K_2 = \frac{\text{air-ocean flux of CCl}_4}{M(\mathrm{CCl_4})_{\mathrm{atm}}} = 7 \times 10^{-3}\ \text{year}^{-1}$$

using data from Liss and Slater (16, 17).

In the stratosphere, CCl_4 is photodissociated by UV radiation mainly in the 195- to 225-nm window (4, 5). Molina and Rowland (5) developed a model of CCl_4 in the stratosphere incorporating a constant concentration of CCl_4 at the tropopause, varying vertical eddy diffusivity in the stratosphere, and photodissociation rates for CCl_4 varying with height in the stratosphere according to the degree of penetration of the different wavelengths of UV radiation. In the model, the loss of CCl_4 in the stratosphere is proportional to its tropospheric concentration. The model gives a latitudinal and diurnal averaged global loss rate of CCl_4 due to photodissociation of $(1.0 \pm 0.2) \times 10^6$ molecule cm^{-2} sec^{-1} for a tropospheric CCl_4 concentration of 73 parts per 10^{12}. Cicerone *et al.* (4) used a similar model and obtained a loss rate for CCl_4 of 6×10^5 molecule cm^{-2} sec^{-1} for a tropospheric CCl_4 concentration of 100 parts per 10^{12}. Thus, for the model developed here

$$K_3 = \frac{\mathrm{CCl_4}\ \text{loss in stratosphere}}{M(\mathrm{CCl_4})_{\mathrm{atm}}} = (1.7 \pm 0.8) \times 10^{-2}\ \text{year}^{-1}$$

based on the above data.

Land biota probably are a sink for CCl_4. I assume long-lived land biota are comparatively isolated from CCl_4 in the atmosphere. Plants and plant products currently have a CCl_4 content of about 10^{-8} g/g [McConnell *et al.* (10)]. Short-lived land biota have a mass of about 2×10^{17} g (18). Hence the present CCl_4 content of land biota is about 2×10^9 g, a negligible amount as compared with the approximately 10^{12} g of CCl_4 at present in the atmosphere. Thus, storage of CCl_4 in land biota is not important in the global balance of CCl_4, although the flux of CCl_4 into, or the destruction of CCl_4 within, the land biota may be important.

Table 2. First-order loss rates of CCl_4 in the environment (related to the atmospheric mass of CCl_4); K_i has the following values based on ± 50 percent errors in mechanisms 1, 2, and 4: most probable value, 2.7×10^{-2}; upper limit, 4.0×10^{-2}; and lower limit, 1.4×10^{-2}.

Mechanism	K_i (year^{-1})
1, Gas-phase reaction	1×10^{-3}
2, Hydrolysis in the oceans	7×10^{-3}
3, Stratospheric UV photolysis	$(1.7 \pm 0.8) \times 10^{-2}$
4, Loss in land biota	2×10^{-3}

The half-life of CCl_4 within land biota must be several months or more as the CCl_4 concentrations found in processed food are similar in range to those found in plants and plant products (10). If the CCl_4 has a half-life of 4 months within land biota, then the loss rate in land biota is 4×10^9 g of CCl_4 per year. Hence the atmospheric loss rate constant is

$$K_4 = \frac{\text{loss of CCl}_4\ \text{in land biota}}{M(\mathrm{CCl_4})_{\mathrm{atm}}} = 2 \times 10^{-3}\ \text{year}^{-1}$$

If CCl_4 has a longer lifetime in land biota, then use of this loss rate constant will give an overestimate of the CCl_4 destruction.

A tenth-order polynomial is fitted to the emission data for 1914 through 1973 in Table 1 by least-squares fit. It is assumed that the atmospheric concentration of CCl_4 was zero in 1914. The atmospheric concentrations of CCl_4 due to man's emissions calculated from Eq. 3 and the emission data are presented in Fig. 1a. The close-hatched area in Fig. 1a indicates the uncertainty in the predicted global CCl_4 concentration due to the uncertainty in the four loss mechanisms as given in Table 2. The shaded area indicates the uncertainty due to both loss mechanisms and a ± 30 percent variation in the emission rates.

In Fig. 1b are shown the observed and predicted CCl_4 concentrations for the period 1971 through 1974 (1, 2, 19). The error limits discussed previously were used.

It appears from Fig. 1 that perhaps all or at least a large fraction of the CCl_4 found in the atmosphere could be man-made. The shipboard observations showing identical CCl_4 concentrations of about 75 parts per 10^{12} in both hemispheres (1, 2) are consistent with an equilibrium concentration of CCl_4 in the atmosphere due to man-made emissions of about 50×10^9 g year^{-1}. This emission rate is similar to that estimated for the last decade (Table 1).

Assuming that this analysis is correct and that the future emissions of CCl_4 from all countries remain below 100×10^9 g year^{-1}, the model predicts a final equilibrium global average concentration of CCl_4 in the atmosphere not exceeding 280 parts per 10^{12} and probably lower.

The high concentrations of CCl_4 in Los Angeles, the North Atlantic, the Arctic Ocean, and western Ireland (Fig. 1b) could be due to the regional buildup of CCl_4 over populated areas in favorable meteorological conditions followed by advection of the polluted air to the area where measurements were made. Examination of monthly mean sea-level pressure charts for the time of the Los Angeles and North Atlantic observations indicates that such an interpretation is possible.

It has been suggested that the lifetime of CCl_4 in the atmosphere can be determined from the relative standard deviation of the atmospheric concentration of CCl_4 (*1*, *20*). However, this method is not applicable if the limit of instrument reproducibility for a measurement is comparable with the real variation in atmospheric concentration or if the atmospheric measurements are made in the vicinity of local sources or sinks. On the basis of the loss mechanisms described here, it appears that the atmospheric lifetime of CCl_4 is of the order of several decades.

I. E. GALBALLY

Division of Atmospheric Physics,
Commonwealth Scientific and Industrial
Research Organization, Aspendale,
Victoria, Australia

References and Notes

→ J. E. Lovelock, R. J. Maggs. R. J. Wade, *Nature (London)* **241**, 194 (19 → J. E. Lovelock, *ibid*. **252**, 292 (1974).

2. A. J. Murray and J. P. Riley, *ibid*. **242**, 37 (1973); → P. E. Wilkniss, R. A. Lamontagne, R. E. Larson, J. W. Swinnerton, C. R. Dickson, T. Thompson, *ibid*. **245**, 45 (197 → P. G. Simmonds *et al*., *Atmos. Environ*. **8**, 209 (1974); P. E. Wilkniss, J. W. Swinnerton, D. J. Bressan, R. A. Lamontagne, R. E. Larson, *J. Atmos. Sci*. **32**, 158 (1975); P. L. Hanst, L. L. Spiller, D. M. Watts, J. W. Spence, M. F. Miller, *J. Air Pollut. Control Assoc*. **25**, 1220 (1975); D. H. Pack, in "Geophysical monitoring for climatic change," J. M. Miller, Ed. [Summary Report No. 3 (1974), National Oceanic and Atmospheric Administration, U.S. Department of Commerce, Washington, D.C., 1975], pp. 99–107.

→ M. J. Molina and F. S. Rowland, *Nature (London)* **249**, 810 (1974); *Geophys. Res. Lett*. **1**, 309 (1974); P. Crutzen, *ibid*., p. 205; R. J. Cicerone, R. S. Stolarski, S. Walters, *Science* **185**, 1165 (19 → S. C. Wofsy, M. B. McElroy, N. D. Sze, *ibid*. **187**, 535 (1975).

4. R. J. Cicerone, D. H. Stedman, R. S. Stolarski, *Geophys. Res. Lett*. **2**, 219 (1975).
5. M. J. Molina and F. S. Rowland, *ibid*. **1**, 309 (1974).

→ F. S. Rowland and M. J. Molina, *Rev. Geophys. Space Phys*. **13**, 1 (1975).

7. R. J. Cicerone, *J. Geophys. Res*. **80**, 3911 (1974).
8. J. E. Lovelock and D. H. Pack, personal communications. Lovelock writes: "It is possible that carbon tetrachloride ultimately can be assigned a human source but it would appear that it is originating via some atmospheric or surface chemical processes from either halocarbons or the other chlorine carrying precursors." The alternative view presented in this report is that CCl_4 is man-made and subsequently released to the atmosphere.
9. P. S. Brallier, in *Kirk-Othmer Encyclopedia of Chemical Technology* (Wiley, New York, ed. 1, 1949), vol. 3, pp. 191–200; D. F. W. Hardie, in *Kirk-Othmer Encyclopedia of Chemical Technology* (Wiley, New York, ed. 2, 1964), vol. 5, pp. 128–139; J. W. Wyart and M. F. Dante, in *ibid*. (ed. 2, 1969), vol. 18, pp. 564–588; R. L. McCarthy, paper presented at the meeting of the American Geophysical Union, San Francisco, 13 December 1974.
10. G. McConnell, D. M. Ferguson, C. R. Pearson, *Endeavour* **34**, 13 (1975).
11. R. L. McCarthy and J. P. Jesson, paper presented at the annual meeting of the American Chemical Society, Philadelphia, 9 April 1975.
12. G. E. H. Reuter, *Elementary Differential Equations and Operators* (Routledge & Kegan Paul, London, 1958).
13. J. E. Lovelock, personal communication. Lovelock observed during the R.V. *Shackleton* cruise in 1971–1972 a decrease in the concentration of CCl_4 from 95 parts per 10^{12} to 70 parts per 10^{12} while the ship was passing through a region where the air was dense with Sahara dust. Visibility was in the range of 3 km, and the air was blowing from the African continent.
14. P. J. Crutzen, *Tellus* **26**, 47 (1974); P. Warneck, *ibid*., p. → M. B. McElroy, S. C. Wofsy, J. E. Penner, J. C. McConnell, *J. Atmos. Sci*. **31**, 287 (1974); H. S. Johnston, *Adv. Environ. Sci. Technol*. **4**, 263 (1974); R. K. M. Jayanty, R. Simonaitis, J. Heicklen, *J. Photochem*. **4**, 203 (1975); → A. Y-M. Ung and H. I. Schiff, *Can. J. Chem*. **40**, 486 (1962); V. N. Kondratiev, *Rate Constants of Gas Phase Reactions* (Publication COM-72-10014, National Bureau of Standards, Washington, D.C., 1972). I have estimated the upper limit of the OH + CCl_4 reaction rate from the molecular collision rate and enthalpy change limitations.
15. J. Heicklen, *Adv. Photochem*. **7**, 57 (1969).

→ P. S. Liss and P. G. Slater, *Nature (London)* **247**, 181 (1974).

17. I have obtained the same loss rate with a more complicated model involving air-ocean exchange, and vertical diffusion and destruction within the mixed layer of the ocean. Laboratory measurements [J. Hine, *J. Am. Chem. Soc*. **72**, 2438 (1950)] would indicate a slower rate of CCl_4 destruction by hydrolysis in water at the same *p*H as the oceans. These results indicate the influence of other constituents on CCl_4 destruction in seawater.
18. C. D. Keeling, in *The Chemistry of the Lower Atmosphere*, S. I. Rasool, Ed. (Plenum, New York, 1973), chap. 6.
19. J. E. Lovelock, unpublished data.
20. C. E. Junge [*Tellus* **26**, 477 (1974)] showed that the relative standard deviation of the concentration of an atmospheric constituent is related to its atmospheric residence time.
21. I thank N. E. Bacon for doing the model computations; I thank Dr. M. F. R. Mulcahy, Dr. J. E. Lovelock, and an anonymous referee for providing helpful comments.

1 December 1975; revised 16 March 1976

Volcanic Dust in Deep-Sea Sediments: Relationship of Microfeatures to Explosivity Estimates

Abstract. *Particle size variations in a series of volcanic ash layers, deposited in high latitudes of the South Pacific during the past 2.5 million years, were earlier analyzed by using a model in which source cloud height and minimum volcanic paleoexplosivity are derived from downwind ash distribution. Examination of submicrometer morphological features of the volcanic glass shards reveals a clear relationship between what appear to be impact features on the glass surfaces and the independently derived paleoexplosivities, which suggests that this may be a simple means to characterize ash horizons and estimate relative volcanic explosivities.*

Atmospherically transported volcanic glass in deep-sea sediments can be readily divided morphologically into categories representing highly explosive or relatively passive eruptions (*1*–*3*). With increasing distance downwind from a source, rhyolitic glass dust becomes the dominant volcanic constituent, reflecting the high explosivity involved in its production (*1*). Lisitzin (*4*) proposed that such volcanic glass makes up 99 percent of all atmospherically transported volcanic material at distances beyond 1000 km from the source. Megascopically distinguishable ash layers are very rarely found in deep-sea sediments beyond that distance.

We have developed a technique (*5*) for separating and counting fine volcanic glass in deep-sea sediments. By using conventional methods to measure ages and sedimentation rates of the host sediments, the apparent accumulation rate of such glass can then be computed in units of milligrams per 1000 years per square centimeter. Figure 1a shows our published results (*1*) for core E27-3, obtained east of the Balleny Islands (Fig. 1b, inset). We have shown that many of the ash horizons in E27-3 can be recognized in a series of six cores forming a 4000-km traverse east from the islands (*1*, *6*) and have used the observed downwind ash distribution to compute associated volcanic cloud heights, from which paleoexplosivities can be estimated in units of megatons of TNT equivalent (*7*, *8*). The published explosivities for the eruptions indicated in Fig. 1a are all minimum estimates (*9*) and range from 0.1 to 30.0 megatons of TNT equivalent (*10*). The results form the upper scale of Fig. 1b. Because of several ambiguities (such as the assumed net paleowind velocity limits and assumed simple variation of particle size with height in the volcanic cloud), the application of our data (*1*) to the explosivity model (*7*) is somewhat tenuous, and it is therefore desirable to derive independent means to check at least the relative explosivities computed. In this report we consider the merits of microfeature analysis for the resolution of this problem, since there is evidence linking microfeature character and impact velocity in certain natural glasses, particularly in lunar material (*11*–*17*).

We have noticed that volcanic glass of rhyolitic composition deposited in many deep-sea sediments is characterized mor-