32,000 than that found in the emissions from the industrial powerhouse burning coal and fuel oil. One explanation for the large difference in TCDD concentration may be the nature of the fuel sources (including the total chlorine content). For the same reason, the findings of significant amounts of chlorinated dibenzo-*p*-dioxins in emissions from refuse and chemical waste incinerators (*2*, *16*) should not be used to infer that these compounds are also significant products of fossil-fueled power plants. In fact, we find that a commercial coal-fired power plant will emit less than 1 μg of TCDD per hour on fly ash particles from the combustion of 200 tons of coal. As this result is many times less than the amount found in the emissions from the chemical plant powerhouse, we believe it is invalid to extrapolate the latter result to the conclusion that ". . . fossil-fueled powerhouses are sources of both airborne and waterborne particulates which contain chlorinated dioxins."

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13. Sample 1 contained 10.022 g of fly ash; the internal standard was 22 μl of a 0.25 ng/μl solution of $^{37}Cl_4$-TCDD in benzene. Each sample was extracted four times with 20 ml of a mixture of hexane and acetone (equal volumes) and then centrifuged, and the supernatants were filtered. The solvent extracts were washed with aqueous KOH, water, concentrated H_2SO_4, water, and aqueous Na_2CO_3; the resulting hexane solutions were dried with anhydrous Na_2CO_3, concentrated under a stream of N_2, and fractionated on alumina columns. The TCDD fractions were evaporated to dryness, dissolved in 60 μl of toluene, and sealed under vacuum in a glass tube until analyzed by gas chromatography–high resolution mass spectrometry (Perkin-Elmer Sigma II and Kratos MS-50). The gas chromatographic column (180 cm by 2 mm inside diameter, glass) contained 0.60 percent OV-17 + 0.40 percent Poly S-179 coated on 100 percent methyl silicone bonded to 80/100 mesh Chromosorb W-AW and was operated with a helium flow rate of 15 ml/min. The temperature was held at 250°C for 1.5 minutes and then increased linearly to 300°C at a rate of 10°C per minute. The entire effluent from the gas chromatographic column was admitted to the mass spectrometer ion source and ionized with 70-eV electrons. The source temperature was 250°C, the accelerating voltage 8 kV, and the mass spectral resolution 10,000 (10 percent valley definition). The 2,3,7,8-TCDD and other isomers that elute at the same time (between 3.3 and 4.4 minutes) were quantitated by dual ion monitoring using peak matching. One channel was centered at *m/z* 327.8848 ($^{37}Cl_4$-TCDD, the internal standard) and the other at *m/z* 321.8936 (the most abundant molecular ion of TCDD having natural isotopic elemental abundances). The complete peak profiles were acquired by scanning at a frequency of 2 Hz, corresponding in each case to a mass range of 300 ppm (0.096 atomic mass unit). The output was accumulated with a signal averager (Nicolet model 1170), and the resulting signals were submitted to a three-point smoothing routine prior to printout (Fig. 1). The concentration of TCDD was calculated using the ratio of the intensities (maximum peak heights) at *m/z* 327.8848 and 321.8936; if no signal was observed, the detection limit was set at 2.5 times the noise amplitude [a 2.5:1 signal-to-noise criterion as described in (*2*)].
14. This assumption is consistent with the vapor condensation model proposed by D. F. S. Natusch [*Environ. Health Perspect.* **22**, 79 (1978)]. The model is substantiated by the measured concentrations of volatile trace elements [G. L. Fisher and C. E. Chrisp, in *Application of Short-term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures*, M. D. Waters, S. Nesnow, J. L. Huisingh, S. S. Sandhu, L. Claxton, Eds. (Publication EPA-600/9-78-027, Health Effects Research Laboratory, Environmental Protection Agency, Research Triangle Park, N.C., September 1978), p. 441] and by the relative mutagenic activities (*12*) that are enhanced for the smallest-sized particles because these are surface-associated parameters.
15. The measurements of surface area (in square meters per gram) for each of the fractions and the fractional weight contributions to an isokinetic sample were provided by A. R. Biermann (personal communication).
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Vertical Distribution and Isotopic Composition of Living Planktonic Foraminifera in the Western North Atlantic

Abstract. *Thirteen species of planktonic foraminifera collected with vertically stratified zooplankton tows in the slope water, Gulf Stream cold core ring, and northern Sargasso Sea show significant differences in their vertical distributions in the upper 200 meters of these different hydrographic regimes. Gulf Stream cold core rings may be responsible for a southern displacement of the faunal boundary associated with the Gulf Stream when reconstructed from the deep-sea sediment record. Oxygen isotope analyses of seven species reveal that nonspinose species (algal symbiont-barren) apparently calcify in oxygen isotope equilibrium, whereas spinose species usually calcify out of oxygen isotope equilibrium by approximately −0.3 to −0.4 per mil in $\delta^{18}O$ values. The isotope data indicate that foraminifera shells calcify in depth zones that are significantly narrower than the overall vertical distribution of a species would imply.*

The interpretation of species-specific differences in the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios in the calcite ($CaCO_3$) shells of planktonic foraminifera samples from deep-sea cores is still a fundamental question in marine geology (*1*). The oxygen isotopic composition of calcite that is precipitated in equilibrium with seawater has been predicted theoretically and verified experimentally (*2*). Although there is a general consensus that planktonic foraminifera do not deposit their calcite shells in carbon isotopic equilibrium, conflicting evidence exists concerning equilibrium versus nonequilibrium precipitation of oxygen isotopes measured in living planktonic foraminifera (*3*).

Answers to questions concerning species-specific isotopic differences are further complicated when they are derived from individuals taken from Holocene core-top sediments, which are a composite of species whose abundances in the overlying water are seasonally and vertically distributed in unknown proportions. Although the surface (upper 1 m) distribution and seasonal succession of planktonic foraminifera at particular localities have been determined (*4*), very

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little is known about the vertical distribution and abundance of planktonic foraminifera and how species abundances vary vertically throughout the year and during their life-span (*5*). In addition, we know little about the environmental control of these distributions.

We determined the quantitative distribution and isotopic composition of seven foraminiferal species with samples from a comprehensive set of vertically stratified zooplankton tows collected from distinct hydrographic regimes in the western North Atlantic. Our results suggest that spinose species of planktonic foraminifera calcify their shells out of oxygen isotope equilibrium. Nonspinose species (symbiont-barren) apparently calcify in oxygen isotope equilibrium within depth zones that are significantly narrower than the species overall vertical distribution would imply. Significant differences exist in the vertical distribution pattern of a given species in the different hydrographic regimes studied. In addition, in Gulf Stream cold core rings, which we have used to examine the effects of slowly changing environmental parameters on the absolute abundance and vertical distribution of planktonic foraminifera, we have been able to follow specific species populations through time.

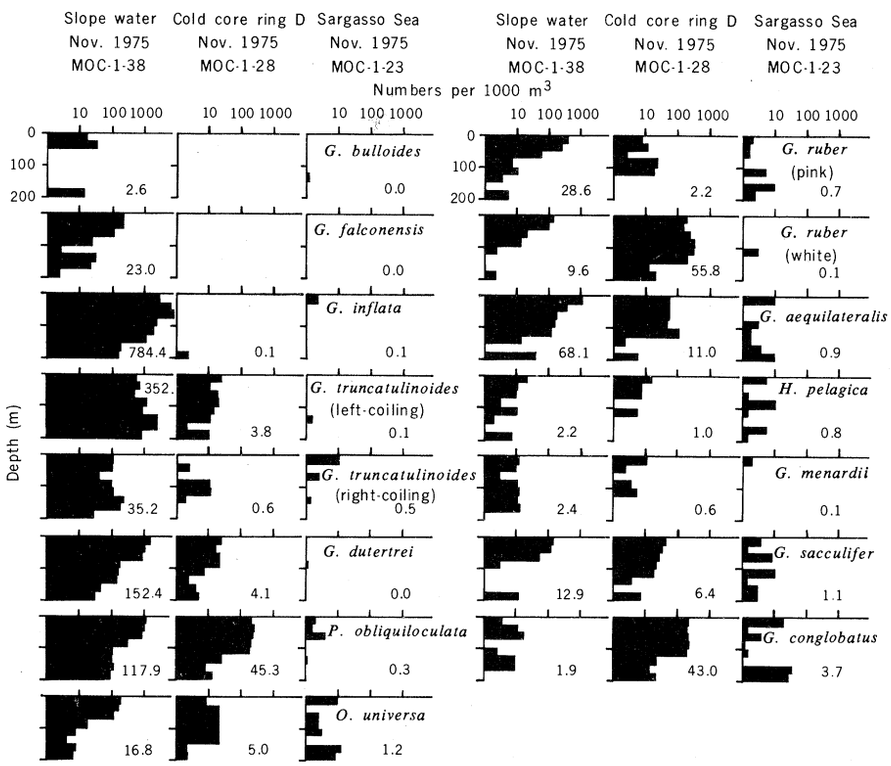

Fig. 1. Slope water, ring, and Sargasso Sea planktonic foraminifera distributions during daylight (numbers per 1000 m^3) during the November 1975 *Knorr* cruise 53. Values within each profile are integrated number of forams per square meter in the upper 200 m. Data are plotted for the following foraminifera: *Globigerina bulloides, G. falconensis, Globorotalia inflata, G. truncatulinoides, Globigerinoides conglobatus, G. ruber, Globigerinella aequilateralis, Pulleniatina obliquiloculata, Globoquadrina dutertrei, Orbulina universa, Globigerinoides sacculifer, Globorotalia menardii* and *Hastigerina pelagica*.

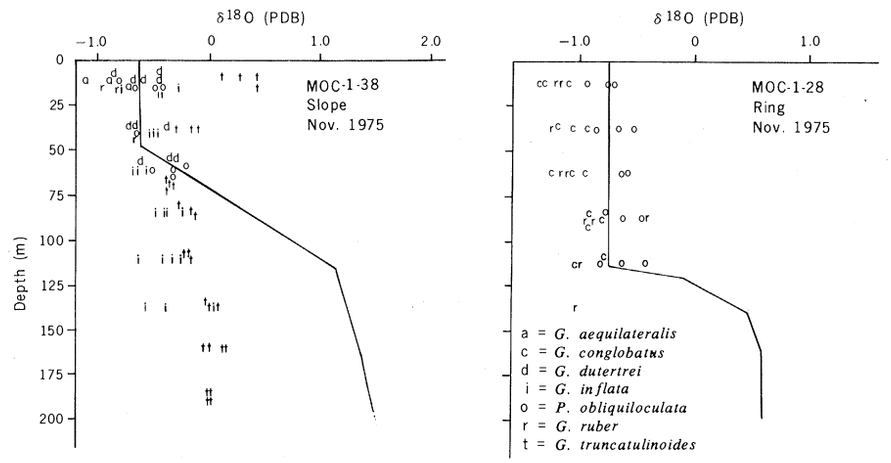

Fig. 2. Oxygen isotope composition of various size fractions of seven foraminifera species, as a function of depth in slope water and cold core ring D in November 1975. Size fractions are based on microscopic measurements of maximum diameter which range from 200 to 750 μm. Only *Globigerinoides conglobatus* showed small but consistent variations in $\delta^{18}O$ with increasing size fractions. Species were analyzed only at depths where their estimated shell mass exceeded 0.6 mg of $CaCO_3$. The solid line is the calculated equilibrium $CaCO_3$-^{18}O variation with depth.

Figure 1 illustrates the vertical distribution of living planktonic foraminifera ("living" here means full of protoplasm) sampled at three stations in November 1975: slope water (38°55′N, 67°53.7′W), cold core ring D (33°54.3′N, 71°46.7′W), and the Sargasso Sea (32°44′N, 71°09.8′W). We collected eight stratified oblique samples which integrated 25-m intervals from 0 to 200 m, using a multiple opening-closing net and environmental sensing system (MOCNESS) with 333-μm mesh nets (*8*).

Compared to the slope water fauna, ring D shows a substantial decrease in the colder-water species *Globigerina bulloides, G. falconensis, Globorotalia inflata*, and *G. truncatulinoides* and a concomitant increase in the relative and absolute abundance of warmer-water species, for example, *Globigerinoides conglobatus* and *G. ruber* (Fig. 1). Species vertical abundance profiles also change markedly, with a general decline in abundance from the surface to 200 m in MOC-1-38 (slope water) to relatively constant values from 0 to 125 m (surface to the base of the mixed layer) in MOC-1-28 (ring D). The exception to this trend is *Globorotalia truncatulinoides*, whose distribution we discuss separately below. These differences in vertical abundance correspond closely to the differences in chlorophyll distribution (food source) of the upper 200 m between MOC-1-38 and MOC-1-28 (*9*).

Ring D, which is estimated to have

been about 9 months old at the time of sampling MOC-1-28 (*10*), has physical and chemical properties in the upper 200 m that are more similar to the Sargasso Sea than to the parent slope water. However, the standing stock of planktonic foraminifera average 900 per 1000 m^3 in the upper 200 m of ring D as compared to 50 per 1000 m^3 in the upper 200 m of the Sargasso Sea. Since cold core rings may occupy between 6 and 13 percent of the surface area of the northern Sargasso Sea as defined by Ortner *et al.* (*11*), production of slope water assemblages in young cold core rings south of the Gulf Stream may cause an apparent southern shift of this important hydrographic boundary when reconstructed from the deep-sea sediment record. If we use our November standing crop data from MOC-1-28 and MOC-1-23 as being representative of an average ring and Sargasso Sea, respectively, then we calculate that foraminifera tests from cold core rings represent 50 to 75 percent of the tests arriving at the surface of the sediment in the northern Sargasso Sea. Although warm core rings form about as often as cold core rings, they generally have a shorter life-span and carry a very sparse foraminifera assemblage in the nutrient-poor Sargasso Sea water (Fig. 1). Therefore, Gulf Stream ring production may result in a southerly shift of the northern boundary of the central gyre foraminiferal assemblage found on the sea floor.

Globigerinoides ruber, G. conglobatus, and *Globigerinella aequilateralis*, all spinose species, have an oxygen isotope composition which averages −0.35 per mil different from the coexisting nonspinose species *Pulleniatina obliquiloculata, Globoquadrina dutertrei*, and *Globorotalia inflata*, which calcify in oxygen isotope equilibrium (*12*) (Fig. 2). The difference is significant and indicates that at least all the species under consideration cannot be simultaneously in oxygen isotope equilibrium with the mixed layer conditions. The isotope data from MOC-1-28 very weakly suggest that the departure of the spinose species from isotope equilibrium decreases with increasing depth, possibly because of the attenuation of light with depth and its effects on the activity of the algal symbionts. Alternately, the patterns may result from specimens of *Globigerinoides ruber* and *G. conglobatus* growing at cooler temperatures in the thermocline and subsequently mixed into the overlying water. *Globorotalia truncatulinoides* is isotopically heavier (enriched in ^{18}O) than equilibrium values when this species occurs above the thermocline, it appears to be in isotopic equilibrium when it is found on the thermocline, and it is markedly depleted with respect to ^{18}O when it is collected below the thermocline. *Globorotalia inflata* collected below the thermocline is also isotopically light with respect to equilibrium values.

The oxygen isotope data suggest to us that *G. inflata* found below the mixed layer are expatriated from the overlying main population. Furthermore, these individuals are not calcifying at their deeper habitat; otherwise, we would see a shift toward heavier oxygen isotopic values below 75 m. The main population of *Globorotalia truncatulinoides* is found between 125 to 175 m but has oxygen isotopic values comparable to those predicted for 75 m. It appears that *G. truncatulinoides* living between 125 and 175 m have descended from the top of the thermocline and that the *G. truncatulinoides* $\delta^{18}O$ values are distributed bimodally, with a group occurring from 25 to 125 m at $\delta^{18}O = -0.23 \pm 0.09$ per mil and a second group from 125 to 200 m at $\delta^{18}O = 0.05 \pm 0.06$ per mil. If we assume that the samples occurring below 125 m had an original composition of −0.23 per mil, then we can account for its new composition of 0.05 per mil by the addition of approximately 10 percent calcite in equilibrium with their new depth. We do not now understand the isotopically heavy values for this species at 0 to 25 m. Although it cannot be demonstrated from these data alone that *G. truncatulinoides* has migrated as opposed to having deposited its calcite at near constant $\delta^{18}O$ regardless of temperature, we have observed that during those times of the year when *G. truncatulinoides* occurs only in the mixed layer, it is found to be in oxygen isotopic equilibrium with ambient seawater (*13*). We suggest that this is strong support for the vertical migration or dispersion model presented above.

We conclude that six of the seven species calcified exclusively in the mixed layer and that *Globorotalia truncatulinoides* calcified at the top of the thermocline. Although *G. truncatulinoides* and *G. inflata* show a wide vertical range, they calcified over a very narrow temperature range. From a geological perspective, the histograms in Fig. 1 do not represent vertical distributions that are useful in interpreting the portion of the water column in which calcification is taking place. The ^{18}O data demonstrate a very restricted environment of calcification which offers promise that significant relationships will be identified between statistical comparisons of species absolute abundance and depth of calcification and physical, chemical, and nutrient phytoplankton and zooplankton distributions in the more than 120 such MOCNESS series sampled around the year.

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$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{reference}} - 1\right] 1000$$

We computed the $\delta^{18}O_{H_2O}$ by using the salinity relationship for North Atlantic waters derived from data given by S. Epstein and T. Mayeda [*Geochim. Cosmochim. Acta* **4**, 213 (1953)] (sample numbers 23, 41, 42, 43, 19, 56, 91, 90, and 93) with corrections for HCl addition to samples 23 and 19 as noted by H. Craig and L. I. Gordon [*Univ. R.I. Occas. Publ. No. 3* (1965), p. 277] and expressed relative to the Peedee belemnite (PDB) standard as

$$\delta^{18}O_{H_2O} = 0.59S - 20.68$$

where S is salinity (per mil). We ascribe a minimum uncertainty to the equilibrium predicted curve (Fig. 2) of ± 0.2 per mil, based on the estimated uncertainty of the original $\delta^{18}O$ water measurements by Epstein and Mayeda and the uncertainty in the original calcium carbonate $\delta^{18}O$ measurements and the corrections in the molecular to isotopic ratio from which the calcium carbonate $\delta^{18}O$ paleotemperature equation was derived.
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