A METHOD FOR QUANTIFYING DEEP-SEA CARBONATE DISSOLUTION USING ^{14}C DATING

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ABSTRACT. We quantified the rate of carbonate dissolution with increasing water depth by taking the difference in the carbonate mass accumulation rate of deep (3393–4375 m) core top sediments from the shallowest one (3208 m), which we assumed was unaffected by dissolution. This method depends on high quality ^{14}C dates that we calibrated to calendar years for calculating sedimentation rates. Our results show low (ranging from 0 to 0.3 g cm^{-2} ka^{-1}) and high (ranging from 1.5 to 1.7 g cm^{-2} ka^{-1}) carbonate dissolution rates, above and below 4000 m, respectively. Therefore, we interpret the sudden increase in the carbonate dissolution rate at 4000-m water depth to mark the lysocline.

INTRODUCTION

Calcium carbonate deposition in the world's oceans is an important component of the global carbon cycle. Because changes in the rate of carbonate dissolution affect carbonate accumulation, they must be quantified. Previous attempts to estimate carbonate dissolution by means of percent carbonate (Balsam 1983; Farrell and Prell 1989), selective dissolution of foraminiferal (Berger 1970; Parker and Berger 1971: Berger and von Rad 1972; Berger 1976), and coccolith assemblages (McIntyre and McIntyre 1971; Berger 1973a; Roth and Berger 1975; Schneidermann 1977), benthic to planktonic foraminifera ratios, percent fragments or a combination of these methods (Arrhenius 1952; Thunell 1976; Malmgren 1983) were qualitative. Francois, Bacon and Suman (1990) quantified carbonate dissolution using [230]Th; de Vernal *et al.* (1992) used the relative abundance of CaCO$_3$ shells and organic linings of benthic foraminifera. We present here a simple method for quantifying carbonate dissolution using the decrease in the carbonate mass accumulation rate with increasing water depth. Note that our carbonate dissolution rate estimates reflect only the amount of calcite dissolved and not aragonite. A slight change in sedimentation rate affects the carbonate mass accumulation rate and eventually the carbonate dissolution rate estimate. Thus, it is essential to have high-quality ^{14}C dates.

METHODS

We used six box-core sediment tops recovered in the Northeast Atlantic between 44°–47°N and 20°–24°W from 3208–4375 m water depths (Fig. 1, Table 1). These cores were collected during JGOFS, Leg 4 cruise aboard R/V *Tyro* in June 1990. Carbonate dissolution quantification involves ^{14}C dating of two sediment samples taken from the top and from a deeper level in each box core, respectively (Fig. 2, Table 2). These ages were calibrated to calendar dates using the marine bidecadal data set (Stuiver and Braziunas 1993) of CALIB 3.0 (Stuiver and Reimer 1993), which already includes a modeled, time-dependent reservoir correction of *ca.* 402 yr for the global ocean (Stuiver and Braziunas 1993). We assume that our Northeast Atlantic planktonic foraminifera samples come from an environment similar to the model world ocean, thus the regional reservoir age correction (ΔR) = 0 (Stuiver and Braziunas 1993).

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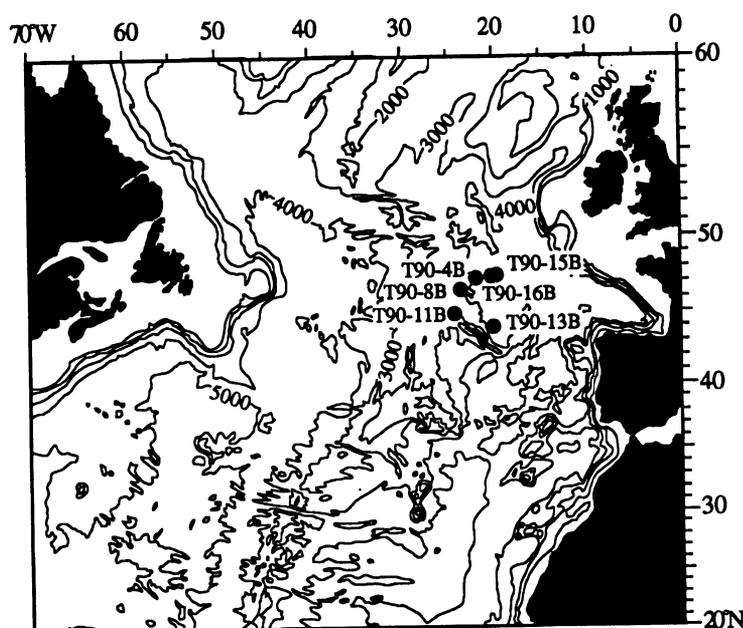
Fig. 1. Physiographic map of the Northeast Atlantic Ocean showing the position of the box cores between 44–47°N and 20–24°W. These cores were recovered from 3208–4375-m water depths. Depth contours are given in meters.

TABLE 1. Location, Water Depth and Length of the Recovered Box Cores

Box core	Latitude	Longitude	Water depth (m)	Core length (cm)
T90-11B	44°59.8′ N	24°39.6′ W	3208	23
T90-8B	46°12.8′ N	23°42.9′ W	3393	30
T90-4B	47°10.3′ N	21°42.9′ W	3945	34
T90-13B	43°59.9′ N	20°01.0′ W	4016	31
T90-15B	47°37.2′ N	20°55.3′ W	4177	43
T90-16B	47°39.5′ N	20°55.8′ W	4375	45

We calculated sedimentation rate by dividing the sediment thickness by the difference in the calendar calibrated ^{14}C ages for each box core, therefore assuming a constant sedimentation rate between these age-control points. Carbonate mass accumulation rate was calculated using

$$cMAR = SR \times DBD \times \%CaCO_3 \times 0.01 \tag{1}$$

where cMAR = carbonate mass accumulation rate (g cm^{-2} ka^{-1})
  SR = sedimentation rate (cm ka^{-1})
  DBD = dry bulk density (g cm^{-3}).

Assuming that the initial carbonate deposition rate preserved in the shallowest core is the same for all cores, the difference in the carbonate accumulation rate with the deeper cores will give the rate of carbonate dissolution as a function of depth expressed as

$$cDR = cMAR(\text{shallowest core}) - cMAR(\text{deeper core}). \tag{2}$$

These assumptions are viable because the cores were recovered from a small geographic area governed by the same water masses and ecological regimes. Also, the shallowest core contains pteropods and juvenile foraminifera, indicating that it lies above the aragonite compensation depth and has undergone little, if any, carbonate dissolution. Therefore, its carbonate (calcite) mass accumulation rate can be taken as the original carbonate (calcite) deposition rate. We considered aragonite as negligible in our shallowest core because we found only a few pteropod fragments and the bulk of the carbonate consists of calcite. Our carbonate dissolution rates estimate only the amount of calcite dissolved.

We determined dry bulk density by weighing 12 cm³ of wet sediment after drying at 50°C. This sediment was then wet-sieved through 32 μm mesh screen and both the fine (<32 μm) and the coarse (>32 μm) fractions were collected and weighed.

The percent carbonate by weight of the bulk sample and the fine fraction was determined by a Scheibler-type gasometric technique (Bruin 1937), with a precision of ± 2%. Based on these measurements and the weights of the different fractions, the carbonate content of the coarse fraction was calculated. Using accelerator mass spectrometry (AMS) ^{14}C measurements, we dated 12 >250-μm samples consisting of handpicked, excellently preserved, mixed planktonic foraminifera (Table 2).

TABLE 2. ^{14}C Dates of 12 >250 μm Samples of Mixed Planktonic Foraminifera

Box core	Depth in core (cm)	Lab no. (UtC)	δ^{13}C (‰PDB)*	^{14}C (BP)†	Calendar age BP‡	1σ cal BP
T90-11B	0–2	2948	0.11	2430 ± 50	2050	2116–1983
T90-11B	8–10	2949	0.97	3640 ± 100	3530	3460–3403
T90-8B	0–2	2918	0.64	2890 ± 50	2696	2723–2645
T90-8B	10–12	2919	0.56	4230 ± 50	4235	4393–4241
T90-4B	0–2	2912	0.55	3640 ± 140	3530	3690–3363
T90-4B	16–18	2913	0.50	5670 ± 50	6065	6153–5987
T90-13B	0–2	2953	0.82	2450 ± 50	2079	2133–2003
T90-13B	16–18	2954	0.96	6240 ± 70	6695	6753–6615
T90-15B	0–2	2955	0.85	2980 ± 110	2741	2843–2683
T90-15B	18–20	2956	0.73	6640 ± 70	7150	7196–7044
T90-16B	0–2	2957	0.52	3070 ± 70	2815	2896–2751
T90-16B	18–20	2958	0.86	7150 ± 60	7559	7619–7523

*Values measured at the Geology Department, Utrecht
†Age in years before present for ^{14}C activity after normalization to δ^{13}C = −25‰
‡Converted to calendar dates using the marine bidecadal data set with ΔR=0 (Stuiver and Braziunas 1993) of CALIB 3.0 (Stuiver and Reimer 1993)

RESULTS AND DISCUSSION

The sediments are calcareous oozes and marls, with the three deepest cores containing some volcanic rock fragments reaching a maximum diameter of 4 mm (Fig. 2). The surface sediments are carbonate oozes with a coarse carbonate fraction of planktonic foraminifera and pteropods with minor amounts of benthic foraminifera and ostracods, and a fine carbonate fraction of coccoliths and foraminiferal fragments. Only the shallowest surface sample collected at 3208-m water depth contained fragments of pteropods. The bulk carbonate content of the box core top samples varies from 90% down to 77% by weight, with a higher fine than coarse carbonate content (Fig. 3). The percent by weight of bulk carbonate generally decreases gradually with increasing water depth, though there is no distinct trend for the individual fine and coarse carbonate fractions (Fig. 3).

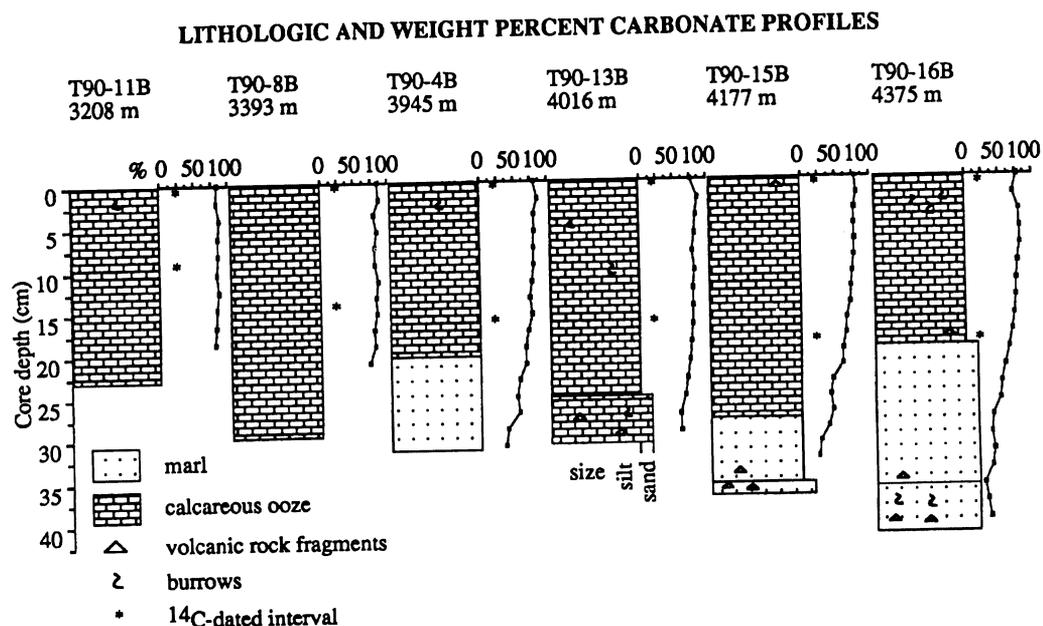## LITHOLOGIC AND WEIGHT PERCENT CARBONATE PROFILES

Fig. 2. Lithologic and percent carbonate by weight profiles of the box cores

Carbonate mass accumulation rate decreases with increasing water depth (Fig. 4), with a distinct drop at 4000 m. Here, the drop in the coarse carbonate accumulation rate is about twice that of the fine carbonate, implying that dissolution affects the former more than the latter. However, we cannot say this for certain because we find fragments of planktonic foraminifera incorporated in the fine fraction.

Carbonate dissolution rate increases with increasing water depth (Fig. 5). These rates are very low, ranging from 0 to 0.3 g cm^{-2} ka between 3208 and 3945 m and suddenly increasing to 1.5 g cm^{-2} ka at 4016 m, reaching a maximum of 1.7 g cm^{-2} ka in the deepest sample (4375 m) when calculated using sedimentation rates based on calendar ages. In relative percentages, the carbonate loss increases from 0–7% to 42–48%. The carbonate dissolution rate shows a remarkable increase at 4000-m water depth, which we interpret to mark the lysocline. This is in contrast to previous studies based on percent carbonate by weight, which show the lysocline to be several hundred meters deeper.

Previous studies (e.g., Heath, Moore and Dauphin 1976; Pisias 1976; Thiede, Suess and Müller 1982; Kuehl, Fuglseth and Thunell 1993) calculated sedimentation rates without converting the ^{14}C dates to calendar years. Our data show that these sedimentation rates can be about 14–20% higher. These differences are reflected in the carbonate mass accumulation rate and eventually in the dissolution rate estimates.

The carbonate dissolution rate shows a remarkable increase at about 4000-m depth, which we interpret to mark the lysocline. This depth coincides with Berger's (1977) lysocline position for this area. However, other studies based on percent carbonate by weight (Biscaye, Kolla and Turekian 1976) and degree of planktonic foraminifera fragmentation, absence of fragile forms, pitted tests, and eroded apertures or internal walls, and large numbers of benthic foraminifera (Kipp 1976; see also Broecker and Takahashi 1978) show the lysocline at 4900 m. Crowley (1983) estimated the lyso-
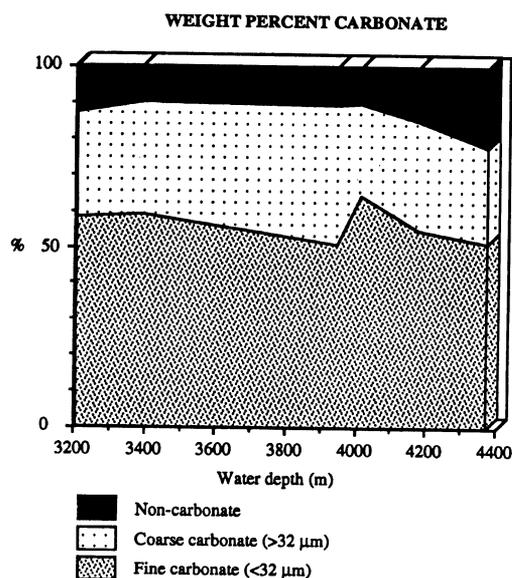
WEIGHT PERCENT CARBONATE

Fig. 3. The sediment core tops are composed of calcareous oozes with carbonate content varying from 90% down to 77% by weight

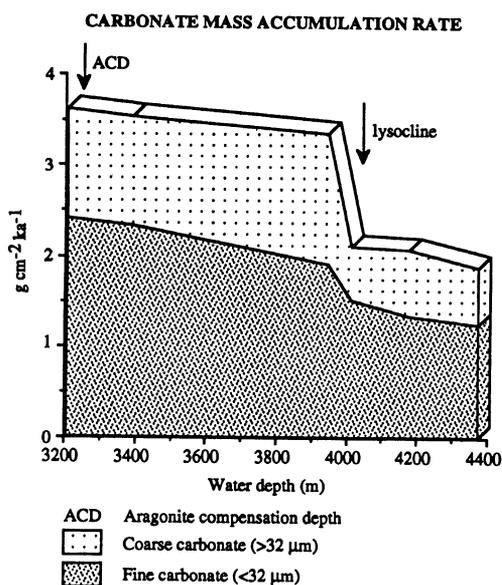**CARBONATE MASS ACCUMULATION RATE**

Fig. 4. Coarse (>32 μm) and fine (<32 μm) mass accumulation rate given in g cm^2 ka^{-1} plotted against water depth

cline depth at 4500 m in the Canary Basin, based on the planktonic foraminifera fragmentation and percentage of benthic foraminifera.

The different methods used to estimate carbonate dissolution give various lysocline depths. The one based only on percent carbonate by weight underestimates the amount of carbonate dissolved because for sediments with high initial carbonate content, little change in the percent carbonate by weight occurs until about 50% of the carbonate has dissolved (Morse 1973; Morse and Mackenzie 1990). From our data, we observe only a 13% decrease in percent carbonate by weight when 48%

CARBONATE DISSOLUTION RATE

ACD   Aragonite compensation depth
Uncertainty in the carbonate
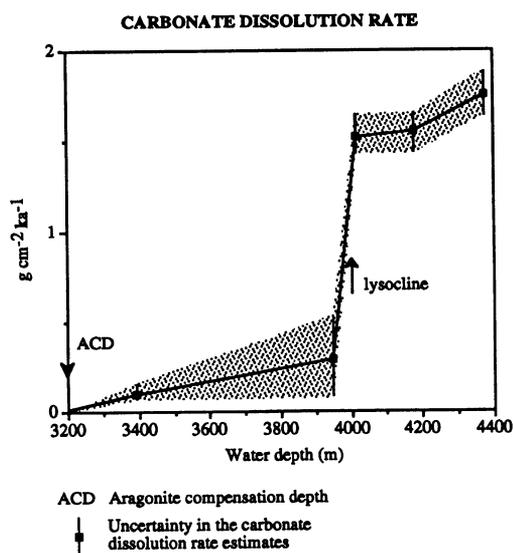dissolution rate estimates

Fig. 5. Carbonate dissolution rate shows a remarkable increase at 4000-m water depth, which we interpret to mark the lysocline. The uncertainty in the carbonate dissolution rate estimate is calculated using the 1 σ range of the calendar-calibrated age (Table 2) to calculate sedimentation rates and errors in the percent carbonate by weight and dry bulk density measurements.

of the carbonate has been dissolved (compare Figs. 3 and 5), consistent with Morse's (1973) estimates.

Likewise, the benthic to planktonic foraminifera ratio may underestimate carbonate dissolution. Benthic foraminifera are generally more resistant than planktonic foraminifera (Arrhenius 1952; Berger 1973b); therefore, an increase in the former may indicate enhanced dissolution. However, laboratory experiments show that some calcareous benthic foraminifera are less resistant than their most resistant planktonic counterparts (Adelseck 1978; Boltovskoy and Totah 1992). Additionally, Corliss and Honjo (1981) found varying dissolution susceptibilities among different benthic foraminiferal taxa by suspending specimens of various species in a deep-sea mooring. The use of the benthic to planktonic foraminifera ratio as a dissolution index probably accounts, in part, for the difference in our lysocline depth with those of Crowley (1983) and Kipp (1976).

Past carbonate dissolution estimates using percent carbonate, solution susceptibility of planktonic foraminifera and coccoliths, benthic-to-planktonic foraminifera ratios, and degree of fragmentation were qualitative (Ruddiman and Heezen 1967; McIntyre and McIntyre 1971; Berger 1976; Tappa and Thunell 1984; Peterson and Prell 1985; Naidu, Malmgren and Bornmalm 1993). We expect our results to allow for the calibration of these qualitative estimates in the study area. This calibration has to be repeated for each ecological province because carbonate dissolution is species-dependent and each zone has a distinct faunal/floral composition.

CONCLUSION

Deep-sea carbonate dissolution quantification is possible using the methodology presented here provided the cores are recovered from a small geographic area, so that the initial carbonate deposition rate can be assumed the same for all cores. It is also essential to have sufficient ^{14}C dates for calculating sedimentation rates. Our carbonate dissolution rate estimates show a remarkable increase at the 4000-m water depth, which we interpret to be the lysocline.

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