

## $^{14}\text{C}$ excess in deep-sea sediments porewater driven by diffusion—Southeast Mediterranean

**Abstract**—Core profiles in the deep SE Mediterranean Sea revealed a significant  $\Delta^{14}\text{C}$  excess in the total dissolved inorganic carbon (DIC) of porewater as compared to the  $\Delta^{14}\text{C}$  of the sediments, below the bioturbation zone down to core bottom (>2 m). The main observation was that the age difference between porewater and sediments, as calculated from the excess, was not constant but rather increasing with depth. The porewater apparent age was younger by 10% than the age of the sediment at the core top and gradually became younger by about 70% at the bottom of the core. Flux calculations and mass balances of the chemical and isotopic data suggest that this  $^{14}\text{C}$  excess stems from a downward diffusive flux of  $95 \pm 15$  atoms of  $^{14}\text{C}_{\text{DIC}}$   $\text{m}^{-2} \text{s}^{-1}$  from the bioturbation zone and overlying bottom water into the sediment. The  $^{14}\text{C}_{\text{DIC}}$  flux is opposite in direction to the DIC flux out of the sediment. It is suggested here that the  $^{14}\text{C}_{\text{DIC}}$  flux may severely interfere with age determination of small submarine “brine lakes” formed in the deep Mediterranean. In addition, the  $^{14}\text{C}$  excess should show up in authigenic carbonate phases precipitating within the sediment and, hence, may serve as a tool to identify the extent and duration of authigenic carbonate precipitation.

Radiocarbon is a widely used nuclide for dating Quaternary sediments (Lowe and Walker 1997) and waters (e.g., groundwater [Mook 1980], oceanic water masses [Broecker and Peng 1982] and marine porewater [Bauer et al. 1995]). The dates are valid provided the  $^{14}\text{C}$  concentration is changed only by radioactive disintegration and not by a suite of diagenetic processes common in sedimentary environments (cf. Mook 1980). The development of the accelerator-mass-spectrometer (AMS) provided the sensitivity needed to measure  $^{14}\text{C}$  dissolved in small samples of marine porewater (as  $^{14}\text{C}$  of dissolved inorganic carbon,  $^{14}\text{C}_{\text{DIC}}$ , and dissolved organic carbon,  $^{14}\text{C}_{\text{DOC}}$ ) and stimulated several studies that use it as a tool for dating and identifying sediment–water interaction processes (cf. Bauer et al. 1995, 1998; Masuzawa et al. 1995; Eglinton et al. 1997; Martin et al. 2000). These studies used profiles of  $^{14}\text{C}$  in marine sediments and porewater in order to (1) estimate the fraction of sedimentary particulate organic carbon that was remineralized to DIC (Bauer et al. 1990); (2) show that part of the DIC originated from oxidation of old organic matter by bacterial sulfate reduction (Masuzawa et al. 1995); (3) estimate individual organic compounds’ ages in marine sediments (Eglinton et al. 1997); (4) point out that part of the dissolved organic carbon (DOC) in the bottom water of the Santa Monica Basin originates from very young sedimentary DOC (Bauer et al. 1995); and (5) estimate the age of dissolving calcite at the sea floor at two sites in the western equatorial Atlantic Ocean (Martin et al. 2000).

Beside a suite of diagenetic biogeochemical processes that may alter the  $^{14}\text{C}_{\text{DIC}}$ , transport processes such as advection and/or diffusion should be considered as well (Mook 1980;

Neretnieks 1980, 1981; Sudicky and Frind 1981; Walker and Cook 1991; Sanford 1997). For example Sanford (1997) demonstrated in a theoretical study the potential role of  $^{14}\text{C}_{\text{DIC}}$  diffusive transport in substantial distortion of groundwater ages. The suggestion that severe alteration of  $^{14}\text{C}_{\text{DIC}}$  concentration due to diffusion does exist (on top of the obvious processes of radioactive decay and diagenesis) was never clearly supported by direct field data to date.

This study is the first attempt to quantify the effect of diffusion of  $\text{H}^{14}\text{CO}_3^-$  on  $^{14}\text{C}_{\text{DIC}}$  profile in deep-sea sediments. This was achieved by measurements of stable and radioactive carbon isotopes in SE Mediterranean deep-sea sediment and porewater. This area serves as an ideal natural laboratory to investigate  $^{14}\text{C}$  processes due to its sole well-defined seawater end member, relatively homogeneous sediment, steady state conditions, and lack of significant advection.

**Methods**—Three cores, 25, 40, and 230 cm long (AT5, MET215, and D36, respectively) were collected in June and September 1996, and in April 1999 at ca. 1,500 m water depth in the SE Mediterranean (D36,  $32^\circ 51.59' \text{N}$ ,  $32^\circ 40.41' \text{E}$ ; AT5,  $32^\circ 54.96' \text{N}$ ,  $34^\circ 12.05' \text{E}$ ; MET215,  $32^\circ 36.81' \text{N}$ ,  $34^\circ 01.62' \text{E}$ ). The cores were collected with a Benthos piston corer (D36), a box corer (AT5), and a multicorer (MET215) and immediately sectioned (depth intervals are represented by the vertical bars in Figs. 1–3) and centrifuged under argon atmosphere to avoid contamination of the extracted porewater with atmospheric  $\text{CO}_2$ . Water samples were collected with 1.7-liter Go-Flo bottles mounted on a General Oceanic Rosette. At the same time, a Sea-Bird SBE 9+ electronic CTD was used to obtain continuous vertical profiles of temperature and salinity.

Porewater from cores AT5 and D36 and Mediterranean bottom waters were sampled for DIC, total alkalinity ( $A_T$ ),  $\delta^{13}\text{C}$  of DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ),  $^{14}\text{C}$  activity of DIC ( $^{14}\text{C}_{\text{DIC}}$ ), and for major ion ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) analyses. The samples for DIC,  $A_T$ ,  $\delta^{13}\text{C}_{\text{DIC}}$ , and  $^{14}\text{C}_{\text{DIC}}$  were filtered immediately after collection into plastic syringes, which contained  $\text{HgCl}_2$  powder using  $0.45 \mu\text{m}$  Nuclepore polycarbonate filters. Porewater from core MET215 was analyzed for major ion concentrations in order to obtain additional data on the 25–40 cm depth range. All water samples were kept at  $4^\circ\text{C}$  until analysis.

Sediments were analyzed for stable and radioactive carbon isotopic analyses in sediment total inorganic (SIC) and sediment total organic (SOC) fractions ( $\delta^{13}\text{C}_{\text{SIC}}$ ,  $\delta^{13}\text{C}_{\text{SOC}}$ ,  $^{14}\text{C}_{\text{SIC}}$ ,  $^{14}\text{C}_{\text{SOC}}$ ) and in foram skeletons ( $^{14}\text{C}_{\text{SKT}}$ ). Sediments from core D36 were sampled every 5 cm or less for  $\delta^{18}\text{O}$  chronostratigraphy by picking the foram *Globigerinoides ruber* (GR) in accordance to the procedures of Duplessy (1972).

$\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were analyzed by Ion Chromatography (Dionex 4000i) with  $< \pm 1\%$  precision.  $\text{Br}^-$  was analyzed by

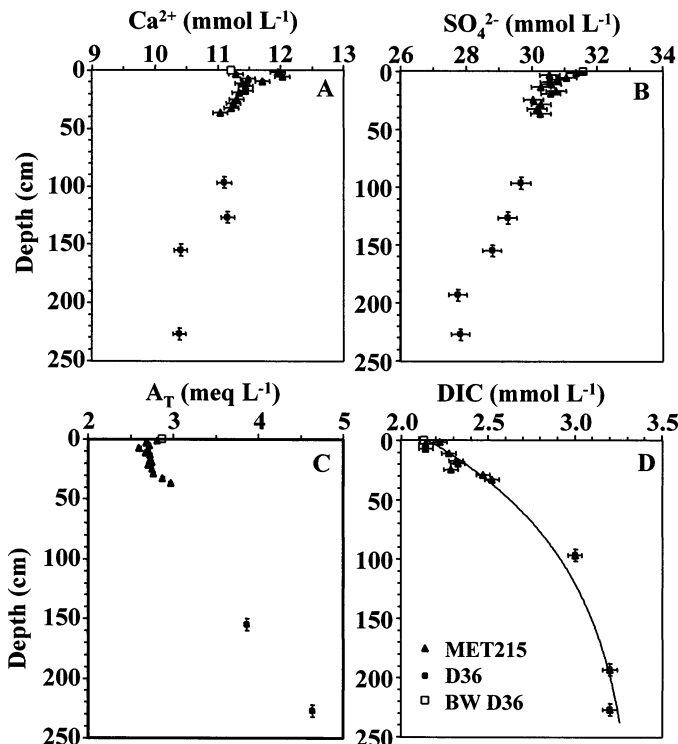


Fig. 1. Vertical profiles of nonconservative components in pore-water constructed from analyses of cores MET215 and D36. (A)  $\text{Ca}^{2+}$ ; (B)  $\text{SO}_4^{2-}$ ; (C) Total alkalinity ( $A_T$ ); (D) Dissolved inorganic carbon (DIC) (the line is the calculated best-fit:  $\text{DIC} = -1.2201 \times e^{-0.0098z} + 3.3739$ , where  $z$  is the depth in cm). Fig. 1D contains explanation of the markers; BW—bottom water from the top of several cores taken in studied area.

ICP-MS (P-E Sciex Elan6000) with  $\pm 3\%$  precision.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  were analyzed by ICP-AES (P-E Optima 3300), with  $\leq \pm 2\%$  precision. DIC was measured using a computerized carbon analyzer at accuracy better than 1% on 1-ml samples.  $A_T$  was measured on 0.5-ml samples by Gran titration with 0.01 N HCl as a titrant using a Metrohm titrator and a micro pH electrode (Orion 9863BN) as a sensor; the precision was  $\leq \pm 1\%$ .

$\delta^{13}\text{C}_{\text{DIC}}$ ,  $^{14}\text{C}_{\text{DIC}}$ ,  $\delta^{13}\text{C}_{\text{SIC}}$ , and  $^{14}\text{C}_{\text{SIC}}$  analyses were performed on inorganic  $\text{CO}_2$  extracted from both the water and the SIC fraction by adding phosphoric acid (Boaretto et al. 1998).  $\delta^{13}\text{C}_{\text{SOC}}$  and  $^{14}\text{C}_{\text{SOC}}$  measurements were performed on  $\text{CO}_2$  produced from the SOC, pretreated with the acid-alkali-acid procedure (AAA, 1 M HCl–1 M NaOH–1 M HCl, *see* details in De Vries and Barendsen 1954; Hatté et al. in press), by high temperature oxidation (900°C) with CuO. About 40 individuals per sample of the foram *G. ruber* were picked, cleaned, and dissolved and their  $\text{CO}_2$  was analyzed for  $\delta^{13}\text{C}_{\text{SKT}}$  and  $\delta^{18}\text{O}_{\text{SKT}}$  (Duplessy 1972; Shackleton 1974). Each  $^{14}\text{C}_{\text{SKT}}$  measurement was performed on  $\text{CO}_2$  extracted from 1,000 skeletons of spinosed foraminifera using phosphoric acid (AAA protocol). The conversion of  $\text{CO}_2$  to graphite was done with a catalytic condensation process, where cobalt was used as a catalyst (Vogel et al. 1984).

The isotopic analyses were performed at the Science Institute, Reykjavik, Iceland ( $\delta^{13}\text{C}$ ), at the Aarhus University,

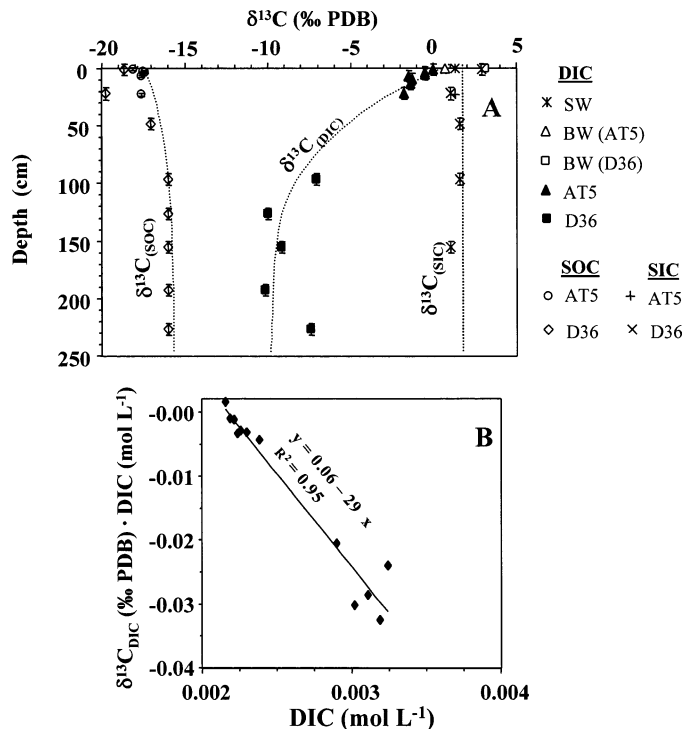


Fig. 2. (A) Depth profiles in cores AT5 and D36 of  $\delta^{13}\text{C}_{\text{DIC}}$ ,  $\delta^{13}\text{C}_{\text{SIC}}$ , and  $\delta^{13}\text{C}_{\text{SOC}}$ ; and (B)  $\delta^{13}\text{C}_{\text{DIC}} \times \text{DIC}$  product as a function of DIC. The slope of the line ( $-29\%$ ) is the carbon isotopic composition of the added dissolved inorganic carbon. SW—seawater; BW—bottom water sampled from the top of the cores. Vertical bars (depth ranges) and horizontal bars ( $\pm 1 \sigma$  of  $\delta^{13}\text{C}$ ) are smaller than the symbols. The lines in panel A were fitted manually.

Denmark ( $^{14}\text{C}$ ), and at the Geological Survey of Israel ( $\delta^{18}\text{O}$  of *GR*) using standard methods (Duplessy 1972; Shackleton 1974; Boaretto et al. 1998). The precision of the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  analyses was  $\pm 0.1\%$ , and that of  $^{14}\text{C}$  was  $\pm 0.5$  pmc. The activity of  $^{14}\text{C}$  is given in percent modern carbon (pmc) or  $\Delta^{14}\text{C}$  ( $\%$  units), in accordance with the International Convention (Stuiver and Polach 1977).  $^{14}\text{C}$  ages were calculated in conventional  $^{14}\text{C}$  years before 1950 in accordance with the International Convention (Stuiver and Polach 1977).

**Results and discussion**—Porewater concentrations of  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Br}^-$  along the cores were similar to the Mediterranean bottom water and conservative with respect to the bottom water salinity of 38.72‰. On the other hand, the concentrations of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $A_T$ , and DIC were found to be nonconservative (Fig. 1). It appears that their depth profiles are rather smooth, simple, and less noisy in the range below the bioturbation zone (Fig. 1). Therefore, down-core mass balances and flux calculations were restricted to this zone; simplifying also prevented the need to modify the diffusion coefficients due to fast solutes transport within the bioturbation zone and enabled use of the literature values.  $\text{Ca}^{2+}$  concentration profile (Fig. 1A) revealed a slight increase ( $\text{CaCO}_3$  dissolution) within the bioturbation zone (upper 5–7 cm) followed by a gradual decrease ( $\text{CaCO}_3$  precipitation) with depth (from  $12.0 \pm 0.2$  mmol  $\text{L}^{-1}$  to  $10.4 \pm 0.3$  mmol  $\text{L}^{-1}$ ).  $\text{SO}_4^{2-}$  decreased from  $31.5 \pm 0.2$  mmol  $\text{L}^{-1}$

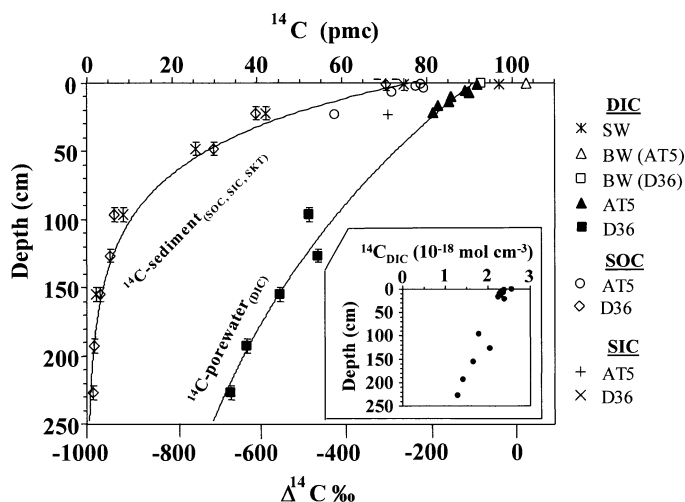


Fig. 3. Activity profiles of  $^{14}\text{C}_{\text{DIC}}$ ,  $^{14}\text{C}_{\text{SIC}}$ ,  $^{14}\text{C}_{\text{SOC}}$ , and  $^{14}\text{C}_{\text{SKT}}$  expressed in pmc and  $\Delta^{14}\text{C}$  units in cores AT5 and D36. DIC—dissolved inorganic carbon in porewater; SKT—skeletons of spined planktonic assemblages; SIC—sediment inorganic carbon; and SOC—sediment organic carbon. The inset in the lower right shows the  $^{14}\text{C}_{\text{DIC}}$  porewater profile expressed in concentration units.  $^{14}\text{C}_{\text{DIC}}$  concentrations were calculated by the equation:

$$^{14}\text{C} \left( \frac{\text{mol}}{\text{cm}^3} \right) = ^{14}\text{C} \text{ (pmc)} \frac{7,358,400 \left( \frac{\text{dpy}}{\text{g}^{12}\text{C}} \right)}{100 \text{ (pmc)}} 12 \left( \frac{\text{g}^{12}\text{C}}{\text{mol}} \right) \text{DIC} \left( \frac{\text{mol}}{\text{cm}^3} \right) \times \lambda^{-1} \text{ (yr)} \frac{1}{6.02 \times 10^{23}} \left( \frac{\text{mol}}{\text{atoms}} \right)$$

where the DIC was taken from the best-fit line,  $\lambda$  of  $^{14}\text{C}$  is  $1.21 \times 10^{-4} \text{ yr}^{-1}$ , and  $7,358,400 \text{ dpy g}^{-1}$  denotes disintegration per year per gram of carbon (Stuiver and Polach 1977). SW—seawater; BW—bottom water sampled from the top of the core. Vertical bars (depth ranges) and horizontal bars ( $\pm 1 \sigma$  of  $\Delta^{14}\text{C}$ ) are smaller than the symbols.

at the surface to  $27.8 \pm 0.3 \text{ mmol L}^{-1}$  at 227 cm owing to sulfate reduction (Fig. 1B).  $A_T$  and DIC increased gradually from  $2.87 \text{ mmol L}^{-1}$  to  $4.63 \text{ mmol L}^{-1}$  and from  $2.1 \text{ mmol L}^{-1}$  to  $3.2 \text{ mmol L}^{-1}$ , respectively (Fig. 1C and D).

These data suggest that the down-core increase in DIC and  $A_T$  (Figs. 1D, 1C, respectively) is a result of their production by anaerobic oxidation of organic carbon (by bacterial sulfate reduction) and slight consumption by  $\text{CaCO}_3$  precipitation (shown by the down-core  $\text{Ca}^{2+}$  decrease, Fig. 1A). The stoichiometry of sulfate reduction combined with some carbonate precipitation would require the down-core change in sulfate to be balanced by the changes in  $\text{Ca}^{2+}$  and DIC/or  $A_T$  ( $\Delta\text{SO}_4^{2-} = \Delta\text{Ca}^{2+} - (\frac{1}{2}\Delta\text{DIC}$  or  $\frac{1}{2}\Delta A_T$ ) because in the pH range prevailing in the core the change in carbonate alkalinity equals changes in DIC. Down-core balances show that the changes in sulfate are balanced by the changes in  $\text{Ca}^{2+}$  and  $A_T$ , but the change in DIC is too small to make up the sulfate balance against the changes in  $\text{Ca}^{2+}$  and DIC (indeed, Fig. 1 shows that deep down-core  $A_T$  is higher than the DIC by about  $1 \text{ meq L}^{-1}$ ). We suggest that accumulation of acetate by sulfate-reducing bacteria of the nonacetate-oxidizers group (Madigan et al. 2000) may be a possible reason

for this discrepancy. Acetate is a weak acid and is therefore part of the total alkalinity but not part of DIC. The presence of weak organic acids as part of the total alkalinity in natural waters is a well-known phenomenon (Morel and Hering 1993).

Identifying sulfate reduction and carbonate precipitation as the main diagenetic processes responsible for down-core DIC change is supported independently by the  $\delta^{13}\text{C}$  profiles of DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ) and sediments (Fig. 2A). The  $\delta^{13}\text{C}_{\text{DIC}}$  decreased considerably with depth from  $\sim 1\text{‰}$  at the surface of the core to approximately  $-10\text{‰}$  below 100 cm (Fig. 2A), while the values of  $\delta^{13}\text{C}_{\text{SOC}}$  and  $\delta^{13}\text{C}_{\text{SIC}}$  changed only slightly with depth and are similar to values measured on other deep-sea eastern Mediterranean sediments (Fontugne and Calvert 1992). The  $\delta^{13}\text{C}_{\text{DIC}}$  decrease from the bottom of the bioturbation zone to 1 m down core represents a balance between the following DIC sources or sinks: (1) Source from original bottom seawater ( $2.1 \text{ mmol L}^{-1}$  and  $\delta^{13}\text{C}_{\text{DIC}} \sim 0\text{‰}$ ); (2) Source from sulfate reduction (about  $2 \text{ mmol L}^{-1}$  and  $\delta^{13}\text{C}_{\text{SOC}}$  of ca.  $-18\text{‰}$ ); and (3) Sink to carbonate precipitation (about  $1 \text{ mmol L}^{-1}$  fractionated by  $+2\text{‰}$  with respect to  $\delta^{13}\text{C}_{\text{DIC}}$ ). In details, sulfate reduction would modify seawater DIC to be  $4.1 \text{ mmol L}^{-1}$  with  $\delta^{13}\text{C}$  of  $-8.8\text{‰}$  ( $2.1 \times (0\text{‰}) + 2.0 \times (-18\text{‰}) = 4.1 \times (-8.8\text{‰})$ ). After DIC removal by carbonate precipitation the final isotopic composition of the  $\delta^{13}\text{C}_{\text{DIC}}$  is  $-9.5\text{‰}$  ( $4.1 \times (-8.8\text{‰}) - 1.1 \times (-6.8\text{‰}) = 3.0 \times (-9.5\text{‰})$ ), very close to the measured  $\delta^{13}\text{C}_{\text{DIC}}$  value (ca.  $-10\text{‰}$ ). Omitting carbonate precipitation sink from the calculation will yield an unreasonably light  $\delta^{13}\text{C}_{\text{SOC}}$  value of  $-33\text{‰}$  ( $2.1 \times (0\text{‰}) + 0.9 \times (-33\text{‰}) = 3.0 \times (-10.0\text{‰})$ ). The role of these processes in causing the DIC profile is verified also by the slope of the plot of  $\delta^{13}\text{C}_{\text{DIC}} \times \text{DIC}$  versus DIC (after Martin et al. 2000). The slope of such a plot (Fig. 2B) represents the average  $\delta^{13}\text{C}$  of the added DIC to porewater ignoring any DIC removal. The value of this slope,  $-29\text{‰}$ , gives an unreasonable value for  $\delta^{13}\text{C}_{\text{DIC}}$  if carbonate precipitation is ignored.

It should be noted here that the diffusion of  $^{13}\text{C}$  might be neglected in the mass balance calculations because of its similarity to the diffusion of  $^{12}\text{C}$ . Although there is a decrease in  $\delta^{13}\text{C}_{\text{DIC}}$ , the concentrations of both  $^{13}\text{C}_{\text{DIC}}$  and  $^{12}\text{C}_{\text{DIC}}$  show an increase with depth. The relative change in the concentrations of  $^{13}\text{C}_{\text{DIC}}$  along the profile is similar to the relative change of  $^{12}\text{C}_{\text{DIC}}$  ( $\sim 1\%$  difference between the two), and both increase downward by approximately a factor of 1.5.

The  $\Delta^{14}\text{C}_{\text{SOC}}$ ,  $\Delta^{14}\text{C}_{\text{SIC}}$ , and  $\Delta^{14}\text{C}_{\text{SKT}}$  values at each depth were similar to each other and therefore were combined to a single depth profile (Fig. 3). The values were constant in the upper  $\sim 5$  cm, indicating the depth of the bioturbated mixed layer. Below the bioturbation layer,  $\Delta^{14}\text{C}$  in all sediment components decreased exponentially with depth from  $-200$  to  $< 970\text{‰}$  below 150 cm. The sedimentation rate ( $\omega$ ) based on this decay is between  $4.5$  and  $9 \text{ cm kyr}^{-1}$  (Fig. 4), similar to other deep-sea sediments (Berner 1980).  $\Delta^{14}\text{C}_{\text{DIC}}$  decreased smoothly with depth, from approximately  $-100\text{‰}$  in the mixed layer to  $-660\text{‰}$  in 227 cm. Strikingly, water values at each depth were much higher than those of the sediments, having, therefore, much younger apparent ages than those of the sediments results also in an unreasonably fast sedimentation rate of  $27 \text{ cm kyr}^{-1}$  (Figs. 3 and 4).

An independent control of the quality of sediments chro-



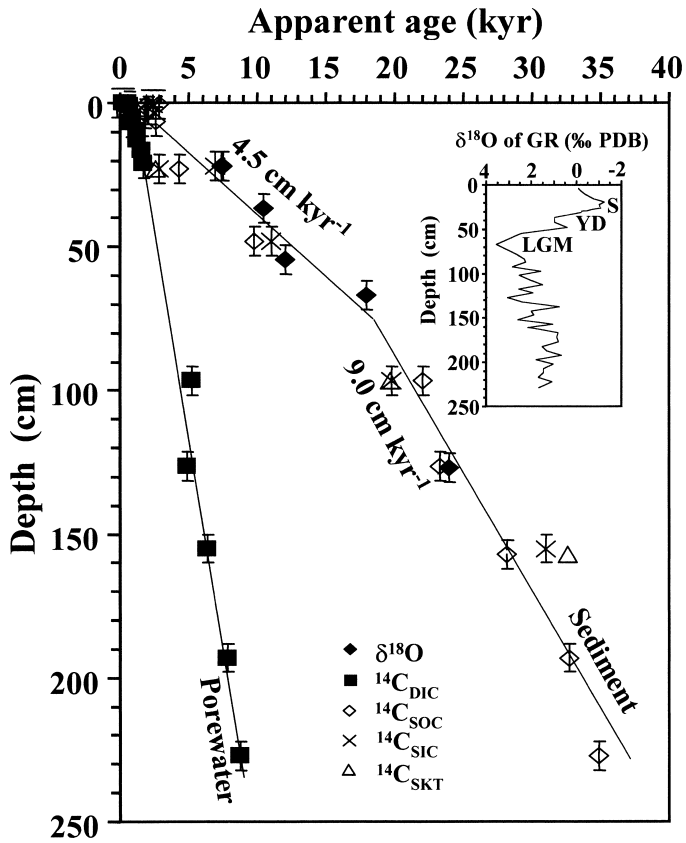


Fig. 4. Radiocarbon and  $\delta^{18}\text{O}$  apparent ages as a function of depth in core D36.  $\delta^{18}\text{O}$  ages are based on the global events found in  $\delta^{18}\text{O}$  depth profile of the planktonic Foraminifera *Globigerinoides ruber* (inset in the upper right). The identified horizons in this profile are marked as S—S1 sapropel, YD—Younger Dryas, LGM—last glacial maximum.  $^{14}\text{C}$  apparent ages were calculated for the DIC in porewater, for the inorganic and the organic sediment fractions (SIC and SOC, respectively), and for the carbonate skeletons (SKT). The  $^{14}\text{C}$  sediment's ages of SIC, SOC, and SKT and the  $\delta^{18}\text{O}$  ages are similar to each other at each depth. Their profile shows constancy down to  $\sim 5$  cm due to bioturbation. A sedimentation rate of  $4.5 \text{ cm kyr}^{-1}$  (the slope of the best-fit line) was calculated for the 5 to 75 cm depth interval and  $9.0 \text{ cm kyr}^{-1}$  below it.

nology along core D36 was provided by  $\delta^{18}\text{O}$  values of the planktonic foraminifera *G. ruber* ( $\delta^{18}\text{O}_{\text{GR}}$ ) (upper right in Fig. 4). It can be seen that all the known isotopic events back to the last glacial are clearly identified in the core (Grazzini et al. 1997; Fairbanks 1989). These “ $\delta^{18}\text{O}_{\text{GR}}$  ages” were coherent (significantly correlated) to the sediments  $^{14}\text{C}$  apparent ages. In summary, the three following observations on the sediments—(1) similarity in  $\Delta^{14}\text{C}$  values of SOC, SIC, and SKT; (2) coherency between  $^{14}\text{C}$  ages and “ $\delta^{18}\text{O}_{\text{GR}}$  ages”; and (3) reasonable sedimentation rate—clearly indicate that the  $^{14}\text{C}$  depth-age profile of the sediments represents the real ages along the cores. Apparently, the “younger” age of porewater indicates that in any layer within the core  $(^{14}\text{C}/\text{C})_{\text{DIC}} > (^{14}\text{C}/\text{C})_{\text{SIC,SOC}}$ , i.e., excess of  $^{14}\text{C}$  in porewater DIC. In the following section we discuss the possible mechanisms that drive this  $^{14}\text{C}$  excess.

Possible mechanisms for  $^{14}\text{C}$  excess in porewater: The  $^{14}\text{C}_{\text{DIC}}$  profile (Fig. 3) represents a steady state, i.e., a flux balance between transport and reaction (diagenetic) processes. The main processes that transport dissolved  $^{14}\text{C}$  are sedimentation and diffusion (assuming negligible advection as common in deep-sea sediments). Radioactive decay is the sink term responsible for complete depletion of  $^{14}\text{C}$  deep below sediment–water interface. The main diagenetic sink/source processes controlling porewater DIC (deduced from the chemical profiles presented in Fig. 1) are  $\text{CaCO}_3$  precipitation and dissolution and organic matter oxidation by microbial sulfate reduction. In any particular sedimentary horizon these processes may change  $^{14}\text{C}_{\text{DIC}}$  concentration but not necessarily the  $\Delta^{14}\text{C}_{\text{DIC}}$  that represents the normalized  $^{14}\text{C}/\text{C}$  ratio. Precipitation of  $\text{CaCO}_3$  reduces porewater DIC without changing its  $\Delta^{14}\text{C}_{\text{DIC}}$ , while both  $\text{CaCO}_3$  dissolution and sulfate reduction would reduce the porewater  $\Delta^{14}\text{C}_{\text{DIC}}$  by adding DIC from carbon pools with lower  $\Delta^{14}\text{C}$  (Fig. 3 demonstrates that for any depth level within the core, the values of  $\Delta^{14}\text{C}$  of SIC and SOC are always lower than the value of  $\Delta^{14}\text{C}_{\text{DIC}}$ ). This implies that within any particular sediment layer the main diagenetic processes cannot produce the observed  $\Delta^{14}\text{C}_{\text{DIC}}$  excess; hence, an out of layer  $^{14}\text{C}_{\text{DIC}}$  diffusive transport (in lack of advection) must occur.

$^{14}\text{C}_{\text{DIC}}$  that was diagenetically produced from dissolution of SIC and decomposition of SOC can be transported by diffusion only down core as shown by its depth gradient (inset of Fig. 3). The maximum depth of layer that may be the diagenetic source of the diffusively transported  $^{14}\text{C}_{\text{DIC}}$  is found on the  $\Delta^{14}\text{C}$  curve for the sediments by the intersection with a vertical line that connects this curve with the  $\Delta^{14}\text{C}$  curve for DIC (Fig. 3). For example, diagenesis of the sediments that lay shallower than 50 cm and their diffusive transport down core can be the source of the  $^{14}\text{C}_{\text{DIC}}$  present at 250 cm. It is very likely that the observed  $\Delta^{14}\text{C}_{\text{DIC}}$  excess is not the result of preferential addition (fractionation) of  $^{14}\text{C}$  that occurred within the sediments, as suggested by the striking similarity in the shape of  $^{14}\text{C}_{\text{DIC}}$  concentration profile (inset of Fig. 3) to the shape of  $\Delta^{14}\text{C}_{\text{DIC}}$  curve (Fig. 3).

The major role of diffusion in transporting  $^{14}\text{C}_{\text{DIC}}$  down core is corroborated by the comparison between the rate at which  $^{14}\text{C}_{\text{DIC}}$  is added to porewater by sulfate reduction to the rate of its disappearance from porewater in the same sedimentary horizon by radioactive decay. The decay rate is simply calculated by the equation  $\lambda \times ^{14}\text{C}_{\text{DIC}}$ ; and the addition via sulfate reduction is calculated according to the equation  $k_s(1 - \phi)\rho_s \times ^{14}\text{C}_{\text{org}}e^{[z(\lambda + k_s)/\omega]}$  (Bernier 1980), where the sulfate reduction rate constant,  $k_s$ , is  $1.4 \times 10^{-6} \text{ yr}^{-1}$  (estimated from the sulfate depth profile and the sediment age profile),  $\phi$  is the porosity (decreasing from 80% to 70% along the core, after Almagor and Schilman 1995), and organic matter content of the sediments ( $\text{C}_{\text{org}}$  is ca. 0.5%). The calculations show that the rate at which  $^{14}\text{C}_{\text{DIC}}$  is added to porewater by sulfate reduction is ca. tenfold smaller than its disappearance by radioactive decay in most layers below the bioturbation zone. Hence, in order to maintain the observed steady state  $^{14}\text{C}_{\text{DIC}}$  excess, it should be replenished by transport from layers having higher  $^{14}\text{C}_{\text{DIC}}$  content, meaning down-core diffusion from shallower layers. The labile organic matter within the bioturbation zone and the huge  $^{14}\text{C}$

content of bottom waters are probably the external  $^{14}\text{C}_{\text{DIC}}$  sources that replenish the down-core decaying  $^{14}\text{C}$  by downward diffusive flux of  $\text{H}^{14}\text{CO}_3^-$ .

The downward  $^{14}\text{C}_{\text{DIC}}$  flux was estimated to be  $95 \pm 15$  atoms  $\text{m}^{-2} \text{s}^{-1}$  by averaging the fluxes obtained from the equation  $F(z) = \phi \cdot (-D_{\text{S}(\text{H}^{14}\text{CO}_3^-)} \cdot [d^{14}\text{C}_{\text{DIC}}(z)/dz] + \omega \times ^{14}\text{C}_{\text{DIC}}(z))$  for the depth range of  $50 < Z < 250$  cm ( $D$ s of  $\text{H}^{14}\text{CO}_3^-$  is  $3.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [calculated from Berner 1980] and the depth derivative of  $^{14}\text{C}_{\text{DIC}}$  was calculated from the best-fit line of the data shown in the inset of Fig. 3) assuming that the mass-transfer within the bioturbation zone is very fast. The calculations show that diffusion makes up more than 95% of the total  $^{14}\text{C}_{\text{DIC}}$  flux; thus, a conservative estimate of the diffusive flux would be  $90 \pm 15$  atoms  $\text{m}^{-2} \text{s}^{-1}$ , and sedimentation plays only a minor role in transporting  $^{14}\text{C}_{\text{DIC}}$  deep into porewater. It should be noted that the  $^{14}\text{C}_{\text{DIC}}$  downward flux (mostly as  $\text{H}^{14}\text{CO}_3^-$ ) is counter to the significant upward diffusive flux of total DIC (mostly as  $\text{H}^{12}\text{CO}_3^-$ ). It is estimated that  $\text{H}^{14}\text{CO}_3^-$  is being transported by diffusion 14 m down into the sediments and still maintains detectable radioactivity. The  $^{14}\text{C}_{\text{DIC}}$  travel distance is calculated by the equation  $\sqrt{D_{\text{S}(\text{H}^{14}\text{CO}_3^-)} \cdot t}$ , (where the time,  $t$ , is set to three half lives of  $^{14}\text{C}$ ), which will estimate the depth at which one-eighth of the original  $^{14}\text{C}$  atoms will be found.

*Oceanographic implications*—The idea that  $^{14}\text{C}$  diffusive transport across a distinct interface may significantly alter the dissolved  $^{14}\text{C}$  content of a water body adjacent to that interface opens some new interesting possibilities. Two examples for possible oceanographic implications of porewater  $^{14}\text{C}$  excess are presented below.

Discovery Basin brine lake, deep eastern Mediterranean: Discovery Basin is a small submarine brine lake (with an area of  $7.5 \times 10^6 \text{ m}^2$  and a volume of  $2 \times 10^8 \text{ m}^3$ ) that advects downward into the sediment of the deep Mediterranean at a rate,  $v$ , of ca.  $0.3 \text{ cm yr}^{-1}$  during the last 2,000 yr (Wallmann et al. 1997). During this period Discovery lake surface moved downward due to brine advection by ca. 6 m above bottom ( $vt = [0.3 \text{ (cm yr}^{-1}) \times 2,000 \text{ (yr)}]/100 \text{ (cm m}^{-1})$ ). The lake surface is characterized by a sharp density gradient (seawater–brine interface) across which material exchange is maintained mainly by diffusion. It is likely therefore that  $^{14}\text{C}_{\text{DIC}}$  would diffuse down from the  $^{14}\text{C}$  enriched deep-sea bottom waters, across the interface, into the  $^{14}\text{C}$ -depleted old brine and significantly decrease its  $^{14}\text{C}$  apparent age. The postulated rejuvenation of  $^{14}\text{C}$  apparent age is based on comparison between the travel distances of bicarbonate ion by diffusion ( $\sqrt{D_{0(\text{H}^{14}\text{CO}_3^-)} \cdot t}$ ) to advection ( $vt$ ) during  $t = 2,000$  yr of lake existence. The downward diffusive transport  $^{14}\text{C}_{\text{DIC}}$  across the lake surface is estimated to be

$$8 \text{ m} \left( \sqrt{\frac{1.05 \times 10^{-5} \text{ (cm}^2 \text{ s}^{-1}) 2000 \text{ (yr)} 3.15 \times 10^7 \text{ (s yr}^{-1})}{10,000 \text{ (cm}^2 \text{ m}^{-2})}} \right)$$

while the lake advected over that period 6 m (*see above*). Therefore, diffusion can almost equilibrate the lake with bottom water  $^{14}\text{C}$  (even if the original brine is completely depleted of dissolved  $^{14}\text{C}$ ) and substantially distort its  $^{14}\text{C}$  age.

*Authigenic carbonate phases*: The substantial  $^{14}\text{C}_{\text{DIC}}$  excess in deep-sea porewaters as compared to the  $^{14}\text{C}$  content of the sediments in the same level could be used to detect authigenic (secondary) carbonate phases that precipitate within the sediments and to estimate the duration of the diagenetic process. Precipitation of diagenetic carbonate, mainly as high Mg calcite, is a rather common phenomenon in the Mediterranean Sea and Red Sea (Milliman et al. 1969; Milliman and Mueller 1973; Luz et al. 1984; Almogi-Labin et al. 1986). The secondary carbonate phases are expected to be enriched in  $^{14}\text{C}$ , and hence rejuvenated, as compared to the associated primary biogenic carbonate particles because they were precipitated from porewater solutions that contain excess  $^{14}\text{C}_{\text{DIC}}$ . This implies that a separable carbonate component suspected to be diagenetic could be identified by its high  $^{14}\text{C}$  content as compared to all other carbonate components from the same sedimentary layer. The growth rate of the secondary carbonate phase can be estimated from the activity difference between the secondary phase and the associated porewater. The effect of such phase on the apparent  $^{14}\text{C}$  age of SIC should depend on its fraction in SIC, which in the studied core is small.

In summary, reconstructing  $^{14}\text{C}$  mass balance of either terrestrial or oceanic aquatic reservoirs separated by a distinct interface may require the consideration of  $^{14}\text{C}_{\text{DIC}}$  diffusion. Severe age error may result if estimating the  $^{14}\text{C}$  age of the smallest reservoir without considering transport and diagenetic processes. The  $^{14}\text{C}$  excess in porewater should show up in authigenic carbonate phases and may be used to identify the extent and duration of authigenic carbonate precipitation.

Orit Sivan

Institute of Earth Sciences  
Hebrew University  
Jerusalem 91904, Israel;  
Geological Survey  
Jerusalem 95501, Israel

Boaz Lazar<sup>1</sup>

Institute of Earth Sciences  
Hebrew University  
Jerusalem 91904, Israel;  
The Moshe Shilo Minerva Center for  
Marine Biogeochemistry  
Hebrew University  
Jerusalem 91904, Israel

<sup>1</sup> Corresponding author (boazl@vms.huji.ac.il).

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Geological Survey  
Jerusalem 95501, Israel

*Yoseph Yechieli*

*Elisabetta Boaretto*

Kimmel Center of Archeological Science  
Weizmann Institute  
Rehovot, Israel

*Jan Heinemeier*

<sup>14</sup>C-AMS Dating Laboratory  
Institute of Physics and Astronomy  
Aarhus University  
Aarhus C, Denmark

*Barak Herut*

Israel Oceanographic and Limnological Research  
National Institute of Oceanography  
Haifa 31080, Israel

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