RADIOCARBON IN POREWATER OF CONTINENTAL SHELF SEDIMENTS (SOUTHEAST MEDITERRANEAN)

O Sivan^{1,2,3} • B Lazar¹ • E Boaretto⁴ • Y Yechieli² • B Herut⁵

ABSTRACT. In this study, we aim to characterize the main processes controlling $^{14}C_{DIC}$ concentrations in porewater at the shallow shelf (water depth less than 120 m) off the Mediterranean coast of Israel. At these water depths, we expected to find evidence for seawater penetration toward the coast, since this area was flooded by seawater only some 18,000 yr ago (the end of the Last Glacial period).

Measurements of the chemical composition ($^{14}C_{DIC}$) and stable carbon isotopic composition ($^{51}C_{DIC}$) were performed in several sediment cores (40 – 250 cm long) at water depths between 6 and 115 m. At water depths of 60 m, represented by a 2.5-m-long sediment core, the porewater $^{14}C_{DIC}$ levels (85 – 87 pMC) were lower than the corresponding sediment values in each layer (92 – 95 pMC), mainly due to the oxidation of relatively old organic matter (about 70 pMC) with no evidence to advection. In contrast, sediment cores from water depths shallower than 50 m showed only slight anaerobic oxidation and high $^{14}C_{DIC}$ values of approximately 100 pMC, indicating possible downward advection. These geochemical observations support the perception that the penetration of seawater into the coastal aquifer occurs at the shallow water zone (850 m), while further verification by deeper cores is required.

INTRODUCTION

Radiocarbon dating of groundwater and marine sediment porewater is subjected to alterations due to several diagenetic-biogeochemical and transport (advection/diffusion) processes. While several studies stressed the need for correction schemes for diagenetic processes affecting $^{14}C_{DIC}$ levels of fresh groundwater (e.g. Mook 1980; Geyh 2000), it was only recently shown that in deep-sea sediments, diffusion of $^{14}C_{DIC}$ from the bottom water into the sediments is the main process altering porewater $^{14}C_{DIC}$ levels (Sivan et al. 2001, 2002). This process accounted for the gradual "rejuvenation" of porewater (up to 70% increase in $^{14}C_{DIC}$ concentrations) compared to their hosting sediment. An opposite trend of "aging" $^{14}C_{DIC}$ concentrations was observed in saline groundwater attributed to diagenetic processes (e.g. Mook 1980; Geyh 2000; Sivan et al. 2004).

This research aims to present the main processes affecting $^{14}C_{DIC}$ concentrations in porewater at the shallow shelf (water depth less than 120 m) off the Mediterranean coast of Israel. In contrast to the conditions in the deep sea, this area is subjected to heterogenic sediment composition, relatively high sedimentation rates, and possible advection. It is assumed that the potential zone of seawater penetration into the sediments (advection) toward the coastal aquifer is located in this region. This area was flooded by seawater some 18,000 yr ago (the end of the Last Glacial period), and seawater has intruded into coastal aquifers since then (e.g. Fairbanks 1989; Chappell et al. 1996). Examination of the diagenetic processes and $^{14}C_{DIC}$ characteristics in this environment can help in assessing potential areas of seawater penetration. Moreover, such information may add to a better understanding of the chemical evolution and $^{14}C_{DIC}$ values of the saline groundwater in the Israeli Mediterranean coastal aquifer (60–70 pMC at about 100 m from the shoreline and 50 m below sea level [Sivan et al. 2004]).

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In order to examine the biogeochemical processes, measurements of the chemical composition, $^{14}C_{DIC}$, and stable carbon isotopic composition ($\delta^{13}C_{DIC}$) were performed in several sediment cores (40–250 cm long) at water depths between 6 and 115 m. As far as we know, this preliminary study contains the first set of data that combines $^{14}C_{DIC}$ and major ion composition from short and intermediate cores in these shallow seawater sediments.

METHODS

Sediment cores (40–250 cm long) were collected at the shallow Mediterranean Israeli shelf (location in Table 1) at water depths between 6 and 115 m. The cores were collected with a Benthos piston corer and a box corer (Ocean Instruments model 700 AL) for the relatively deeper sediments (>40 m water depth), and in shallower waters by scuba divers using a Perspex mini-corer specially designed for this research. The cores were immediately sectioned and centrifuged under argon atmosphere to avoid contamination with atmospheric CO₂, except the core at 46 m water depth, which was centrifuged in the laboratory. At shallower depths, the corer was designed to enable a fast separation into closed 10-cm compartments immediately after coring. Each compartment was connected to an argon tank and pressurized to squeeze the water out into a sealed syringe. Seawater samples were collected using Niskin or plastic bottles from about 1 m above the sea floor.

Seawater samples were analyzed for their chemical composition, $^{14}C_{DIC}$, $\delta^{13}C_{DIC}$, and tritium activity. One surface seawater sample was analyzed for ^{14}C in the dissolved organic carbon ($^{14}C_{DOC}$). Due to the low volume of porewater samples, they were not always analyzed for all parameters. The porewater sample was split for major ion analysis (about 2 mL) and 3H (only the large samples). Then, 20 mL was filtered using 0.45-µm Nuclepore polycarbonate filters directly into plastic syringes containing HgCl₂ powder for analyses of DIC (1 mL), A_T (1 mL), $\delta^{13}C_{DIC}$, and $^{14}C_{DIC}$. The water samples were kept at 4 °C until the measurements.

Some of the sediment samples were dried at 30 °C and then picked for shell and other inorganic carbonate material. In particular, well-preserved spines of sea urchin ($Paracenstratus\ lividus$) were identified and analyzed for stable and radioactive carbon isotopes composition ($\delta^{13}C_{urc}$ and $^{14}C_{urc}$). Analysis by scanning electron microscopy (SEM) showed that the sea urchin spines from the core were in a very good state of preservation.

Analytical Methods

Major ions were analyzed using standard methods with precision of less than 3%. DIC was measured in a newly developed system, designed by Sass and Lazar (the Hebrew University, Israel, unpublished), which is able to analyze small volumes (1 mL) at an accuracy better than 1%. The water samples were acidified with concentrated HCl to transform total inorganic carbon to CO_2 gas, which was measured by an NDIR analyzer (LiCor 6252). Total alkalinity was measured on 0.50-mL samples by Gran titration (Stumm and Morgan 1996) using a micro-pH electrode (Orion 9863BN). The error, calculated by averaging numerous duplicate samples, was ± 0.03 meq L^{-1} .

 3 H (tritium) was analyzed by a LKB 1220 Quantulus scintillation counter in the Weizmann Institute. Tritium concentrations are expressed in tritium units (1 TU = 1 atom of 3 H per 10^{18} atoms of hydrogen [Faure 1986]), and the counting error was ± 0.3 TU. $\delta^{13}C_{DIC}$ and $^{14}C_{DIC}$ analyses were performed on inorganic CO_2 extracted from each water sample (Boaretto et al. 1998). A fraction of the extracted CO_2 was used for $\delta^{13}C_{DIC}$ measurement by conventional mass spectrometry. Another fraction was converted to graphite for $^{14}C_{DIC}$ determination at the Weizmann Institute according to Boaretto et al. (1998). ^{14}C measurements were performed at the Accelerator Mass Spectrometry

(AMS) Radiocarbon Dating Lab at Aarhus University (Denmark) and at the NSF-AMS Laboratory, Tucson (Arizona). $^{14}\text{C}_{DOC}$ was performed on organic CO₂ extracted and measured in Tucson according the procedure of Burr et al. (2001). The analyses of $^{14}\text{C}_{urc}$ were also performed in Tucson. $\delta^{13}\text{C}$ is reported on the PDB scale and its precision is $\pm 0.1\%$. The activity of ^{14}C is given in pMC (percent Modern Carbon) according to the international convention (Stuiver and Polach 1977). The precision of the measurement is ± 0.5 pMC.

RESULTS AND DISCUSSION

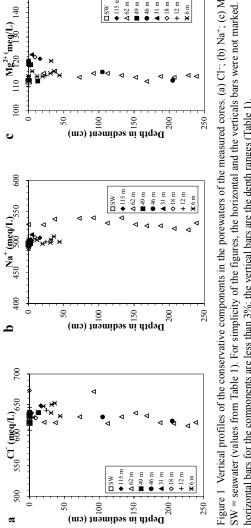
The chemical and the isotopic compositions of the bottom seawater and the porewater samples are given in Table 1.

Here, we test only the results from the upper 250-cm sediments in order to compare the different sites. The chemical profiles of Cl⁻, Na⁺, and Mg²⁺ in porewater slightly varied between sites, but in general, showed conservative behavior with respect to the bottom seawater concentrations (Figure 1). On the other hand, SO_4^{2-} , total alkalinity, DIC, Ca^{2+} , and Sr^{2+} showed non-conservative behavior along the cores (Figure 2). Ca²⁺ and Sr²⁺ (Figure 2a and 2b, respectively) were constant along the core in some sites and in the others showed slight decrease or slight increase with sediment depth (with no correlation to water depth), indicating precipitation/dissolution of CaCO₃. SO₄²⁻ slightly decreased in porewater at shallow water depths (<50 m), where the sediment is composed mainly from sand and silt. In deeper water depths (62-m core), where the sediments are composed mainly by clay, the gradient was much steeper (Figure 2c). In this case, SO₄²⁻ decreased by 30 meq/L along the top 250 cm (Figure 2c). The decrease was probably due to anaerobic oxidation of organic matter by sulfate reduction and maybe involved also other processes as well. The anaerobic oxidation is supported by the increase in the alkalinity and DIC (Figure 2d, e). The close values of total alkalinity and DIC indicate that the alkalinity is mostly from carbonates. The ratio between the alkalinity and DIC (Figure 3) is between 1 (in the 62-m core) to 1.5 in other cores. This indicates that the main process is sulfate reduction, resulting in a 1:1 ratio (aerobic oxidation would increase only the DIC without changing the alkalinity) combined with minor CaCO₃ precipitation/dissolution, giving a 2:1 ratio. Other processes might be involved in the sediments at about 60 m water depth, since the increase of the DIC and the alkalinity by 15 mM (and 15 meg/L if the alkalinity is mainly carbonatic) is not balanced by the decrease of the SO_4^{2-} by 30 meq/L. The processes might involve other diagenetic processes and different diffusion fluxes of these parameters.

The stable isotopic composition of the inorganic carbon ($\delta^{13}C_{DIC}$) at the 62-m core became lighter with depth of sediment to a value of -15% PDB at the bottom of the core (Figure 4a). These values are close to the levels of organic matter ($\delta^{13}C_{SOC}$) in deep-sea sediments (Sivan et al. 2002). The porewater $\delta^{13}C_{DIC}$ values are consistent with intensive anaerobic oxidation. The addition of 15 mM DIC from the decomposition of organic matter of -16% PDB to 2.5 mM DIC of seawater origin (0% PDB) would yield DIC with about -14% PDB [2.5 × (0%) + 15 × (-16%) = 17.5 × (-14%)], similar to the values measured in the deep porewater (Figure 4a). The $\delta^{13}C$ values of the carbonate ($\delta^{13}C_{urc}$) were close to the seawater values as expected (Figure 4a).

Tritium was sampled in 4 sites at the top 20 cm of the sediments (Table 1). The values show that the age of the porewater at the top of the sediments is the same as present-day seawater. The $^{14}C_{DIC}$ profiles (Figure 4b) support this conclusion. The top 50 cm of all cores had $^{14}C_{DIC}$ levels similar to present-day seawater (around 100 ± 10 pMC). Below 50 cm, the $^{14}C_{DIC}$ values were different at the 2 long cores (62 m and 46 m). $^{14}C_{DIC}$ values were high and similar to seawater values all along the 46-m core; whereas, in the 62-m core, they decreased with depth to 85 pMC at the bottom of the

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32 17.00 34 49.80 6 12.0 12.0 503 638 20.8 0.175 67.0 114.0 2.66 2.50 — 99.9 —		6/11/01	32	17.00	34	49.80	9	31.0	7.0	499	989	21.2	0.177	65.1	115.2	3.64	3.32	I	104.0		-4.3
		6/11/01	32	17.00	34	49.80	9	12.0	12.0	503	638	20.8	0.175	0.79	114.0	2.66	2.50		6.66		-4.3



□ SW ◆ 115 m △ 62 m ■ 49 m ● 46 m ◆ 18 m + 12 m ★ 6 m

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Figure 1 Vertical profiles of the conservative components in the porewaters of the measured cores. (a) Cl^- ; (b) Na^+ ; (c) Mg^{2^+} . SW = seawater (values from Table 1). For simplicity of the figures, the horizontal and the verticals bars were not marked. The horizontal bars for the components are less than 3%; the vertical bars are the depth ranges (Table 1).

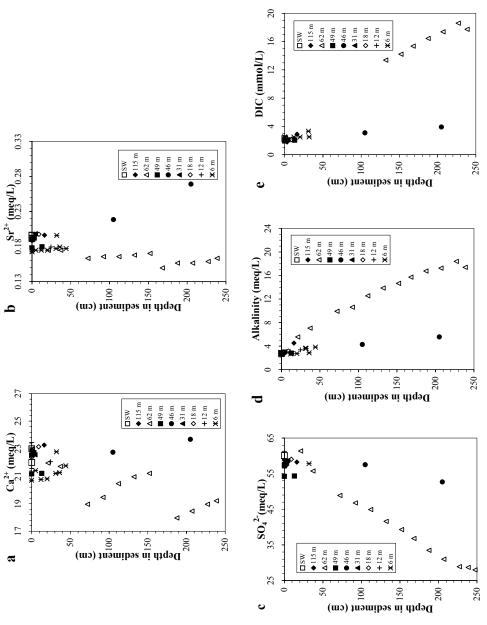
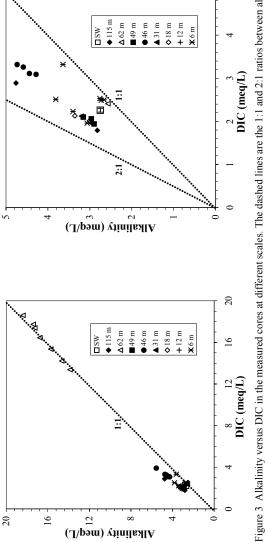


Figure 2 Vertical profiles of the non-conservative components in the porewaters of the measured cores. (a) Ca²⁺; (b) St²⁺; (c) SO₄²⁻; (d) total alkalinity; (e) DIC (dissolved inorganic carbon). SW = seawater (values from Table 1). For simplicity of the figures, the horizontal and the verticals bars were not marked. The horizontal bars for Ca^{2+} , SCa^{2-} are less than 3% for the alkalimity 0.03 meq L^{-1} and for the DIC 1%; the vertical bars are the depth ranges (Table 1).



linity and the DIC. The 62-m core fits to 1:1 ratio, indicating that there the major diagenetic process was anaerobic oxidation by sulfate reduction. Most of the cores' samples lie on about 1.5:1 ratio, indicating that CaCO₃ dissolution/precipitation is also significant (2:1 ratio) process beside sulfate reduction in those cores. Figure 3 Alkalinity versus DIC in the measured cores at different scales. The dashed lines are the 1:1 and 2:1 ratios between alka-

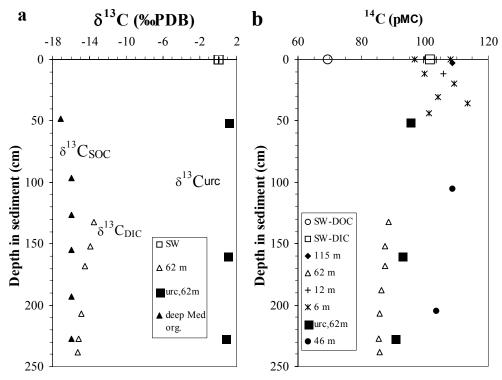


Figure 4 (a) Vertical profile of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{ure}$ (sea urchin spine) at the 62-m water depth core. A vertical profile of $\delta^{13}C_{SOC}$ (SOC-sediments' organic carbon) in the deep Mediterranean is also presented (data from Sivan et al. 2002) as well as the values of $\delta^{13}C_{DIC}$ of the seawater (SW, Table 1). (b) $^{14}C_{DIC}$ profiles at the measured cores and $^{14}C_{ure}$ at the 62-m water depth core. Also, the surface seawater values of $^{14}C_{DIC}$ (black square) and the $^{14}C_{DOC}$ (grey square) are presented. In both graphs, the horizontal bars are smaller than the symbols and the vertical bars (not marked) are the depth ranges (Table 1).

core. The present-day porewater $^{14}C_{DIC}$ levels at the 46-m core indicate that the slight anaerobic oxidation of organic matter with values lower than 100 pMC (assumed value, not measured due to technical problems) and the slight $CaCO_3$ dissolution had a minor effect on $^{14}C_{DIC}$ values. According to Sivan et al. (2002), diffusion alone is not capable of enhancing the $^{14}C_{DIC}$ to values measured at the core bottom (250 cm). We speculate that such relatively high $^{14}C_{DIC}$ values indicate advection of seawater into the sediment at this site.

On the other hand, at the 62-m site, porewater $^{14}C_{DIC}$ levels (85–87 pMC) were lower than seawater values and the corresponding sediment carbonate ($^{14}C_{urc}$) in each layer (92–95 pMC, Figure 4b). The shift of $^{14}C_{DIC}$ values in porewater to values lower than their sediment host probably resulted from the anaerobic oxidation of relatively old organic matter (about 70 pMC, calculated from a rough mass balance). The organic matter was not analyzed for ^{14}C as mentioned above, but $^{14}C_{DOC}$ in seawater in this area was measured as about 70 pMC. This value might be correlated to the organic matter values; the correlation between $\delta^{13}C_{DIC}$ and $^{14}C_{DIC}$ (Figure 5) supports the possibility. It seems that DIC derived from the oxidation of organic matter reduces both $^{14}C_{DIC}$ and $\delta^{13}C_{DIC}$ values. We would like to mention that the values of the sediments (92–95 pMC) probably represent the true ages of the layers. The good preservation of the sea urchin spine suggests that the spine was deposited shortly after the death of the animal. On the other hand, the shells fragments can be much older than the sediment layer. For example, shells collected from some Israeli beaches can be several thousand years older (E Boaretto, personal communication).

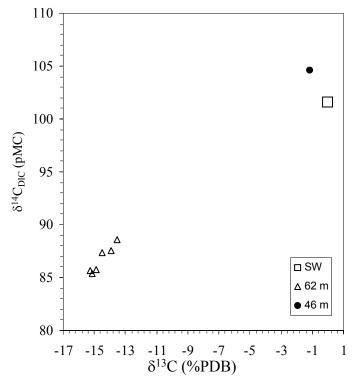


Figure 5 $^{14}C_{DIC}$ versus $\delta^{13}C_{DIC}$ at the 46-m and the 62-m water depth cores and in the seawater (SW). The horizontal and vertical bars are smaller than the symbols.

In general, the porewater $^{14}C_{DIC}$ characteristics showed a threshold between \sim 45 to \sim 60 m water depth. In the 62-m area, there is evidence of intensive anaerobic oxidation of organic matter (with ^{14}C values of 70 pMC) by sulfate reduction and slight $CaCO_3$ precipitation with no evidence of advection. The shallower sites showed much less anaerobic oxidation of organic matter and no or even slight dissolution of $CaCO_3$. In the 46-m site, there might be an evidence for fast advection of seawater into the sediments. In order to better validate this evidence, further study is suggested in this shallow sediment system by deeper coring and hydrological modeling.

The above results contribute to a better understanding of the saline groundwater age in the Israeli Mediterranean coastal aquifer. The saline waters in this aquifer contain relatively low $^{14}C_{DIC}$ values (60–70 pMC), mainly attributed to slightly DIC enrichment from the anaerobic oxidation of "dead" organic matter (Sivan et al. 2004). We think that these groundwaters are originated from porewater that has penetrated the aquifer from the shallow water zone (<50 m depth), where indeed there is evidence for advection and slight oxidation of organic matter, and its $^{14}C_{DIC}$ value is reduced only below the young marine (post-glacial) sediments, when it reaches the Pleistocene aquifer.

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