RADIOCARBON DATING OF POREWATER – CORRECTION FOR DIFFUSION AND DIAGENETIC PROCESSES

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ABSTRACT. Two simple algorithms are suggested here to correct for the effect of diffusion and diagenetic sulfate reduction on radiocarbon age determination of marine porewater. The correction algorithms were developed from mass balances of sulfate, dissolved inorganic carbon (DIC), and ^{14}C of the DIC ($^{14}C_{DIC}$) in vertical concentrations profiles in porewater starting from the sediment water interface. The algorithms were tested on data collected during our recent study of sediment porewaters extracted from the deep Eastern Mediterranean. The real ages of these porewaters varied from present (top of the core) to approximately 30 ka BP (bottom of the core) covering most of the dynamic range of the ^{14}C method (approximately 5 half lives). These ages were markedly older than the ages calculated from $^{14}C_{DIC}$ analyses by the regular age equation.

It is clearly demonstrated that in this case the correction of the apparent age for diffusion across the sediment/water interface is overwhelmingly larger than the correction for the effect of sulfate reduction. The correction for the effect of ^{14}C diffusion alone results in a perfect match between the calculated apparent ^{14}C ages and the real ages of porewater and therefore is the preferred algorithm for correcting apparent ages of porewater.

INTRODUCTION

It has been discussed in the literature that diffusion and diagenetic processes across interfaces may significantly distort age determination of groundwater by radiocarbon measurements of DIC (Mook 1980; Neretnieks 1980, 1981; Sudicky and Frind 1981; Walker and Cook 1991; Sanford 1997). An algorithm to correct for the effect of diffusion on the apparent ^{14}C age of groundwater in a hydrogeologic setting comprised of a stagnant zone surrounded by a flow zone was developed by Sanford (1997). He applied his algorithm to groundwater in Oahu, Hawaii and the Bangkok Basin, Thailand, that showed considerably older ^{14}C ages as compared to the estimations made by groundwater flow models. Accounting for diffusion of ^{14}C from the flow zone (rubble zone in Oahu and sand and gravel in Bangkok) into the stagnant layer (dense lava flow in Oahu and clay in Bangkok) the algorithm corrected the ^{14}C ages to be close to the ages predicted by the models. These rather crude whole basin averages showed that ^{14}C diffusion has the potential to markedly distort the dates of formation waters.

Our recent study on porewater trapped in deep-sea sediments (Sivan et al. 2001) used the "natural laboratory" conditions to supply the first set of field data that quantified the marked effect of diffusion across interfaces on ^{14}C dating. The sediment–seawater interface in the deep sea is an excellent setting to measure the effect of diffusion on ^{14}C age determination of porewater for the following reasons: 1) advection is usually negligible, 2) porewater is deposited with the sediments and hence, the age of porewater in each depth should be the same as the age of the sediment or even somewhat older due to compaction and squeezing, 3) the slow sedimentation rate (in the range of few cm ka^{-1}) enables measurement of the whole range of ^{14}C ages over one vertical profile extending a few meters below the sediment-seawater interface, and 4) biogeochemical processes affecting the distribution of ^{14}C can be identified from measurements of a suite of other relevant components.

The seawater-sediment interface study was based on data we collected from three cores taken in the Eastern Mediterranean about 150 km off the shores of Israel at water depth of about 1500 m (details

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in Sivan et al. 2001). Core D36, collected by a Benthos piston corer, was 230 cm long, core AT5, collected by a box corer, was 25 cm long and core MET215, collected by a multicorer, was 40 cm long. The cores were immediately sectioned and centrifuged under argon atmosphere to avoid contamination with atmospheric CO_2. Porewater from cores AT5 and D36 was sampled for DIC, total alkalinity (A_T), $\delta^{13}C$ of DIC ($\delta^{13}C_{DIC}$), ^{14}C activity of DIC ($^{14}C_{DIC}$) and for major ions (Cl^-, Br^-, SO_4^{2-}, Na^+, Mg^{2+}, Ca^{2+}) analyses. Porewater from core MET215 was analyzed only for major ion concentrations. The sedimentary inorganic carbon (SIC) and organic carbon (SOC) and foram skeletons (SKT) fractions were analyzed for their stable and radioactive carbon isotopic composition ($\delta^{13}C_{SIC}$, $\delta^{13}C_{SOC}$, $^{14}C_{SIC}$, $^{14}C_{SOC}$, $^{14}C_{SKT}$). Sediments from core D36 were sampled at intervals of 5 cm or less and skeletons of the foram *Globigerinoides ruber* (*GR*) were carefully picked for $\delta^{18}O$ ($\delta^{18}O_{GR}$) chronostratigraphy. Detailed description of the geochemical results is given in Sivan et al. (2001), and the main relevant results of that study are summarized below.

The $^{14}C_{SOC}$, $^{14}C_{SIC}$, and $^{14}C_{SKT}$ apparent ages at each depth were similar to each other and matched the independent $\delta^{18}O_{GR}$ stratigraphy. This strongly suggests that the ^{14}C dates of the sediment in each layer represent the real age of the layer. In our case, the sediment ages varied from recent (top of the core) to around 30 ka BP (bottom of the core), covering most of the dynamic range of the ^{14}C method (approximately 5 half lives) (Figure 1). These ages however were markedly older than the apparent ages of the porewater DIC, calculated directly from the radioactive age equation (Figure 1). Major ions and stable carbon isotope profiles proved that this marked apparent rejuvenation of the porewater was caused by diffusion of $^{14}C_{DIC}$ (mainly $H^{14}CO_3^-$) from bottom seawater into the sediments.
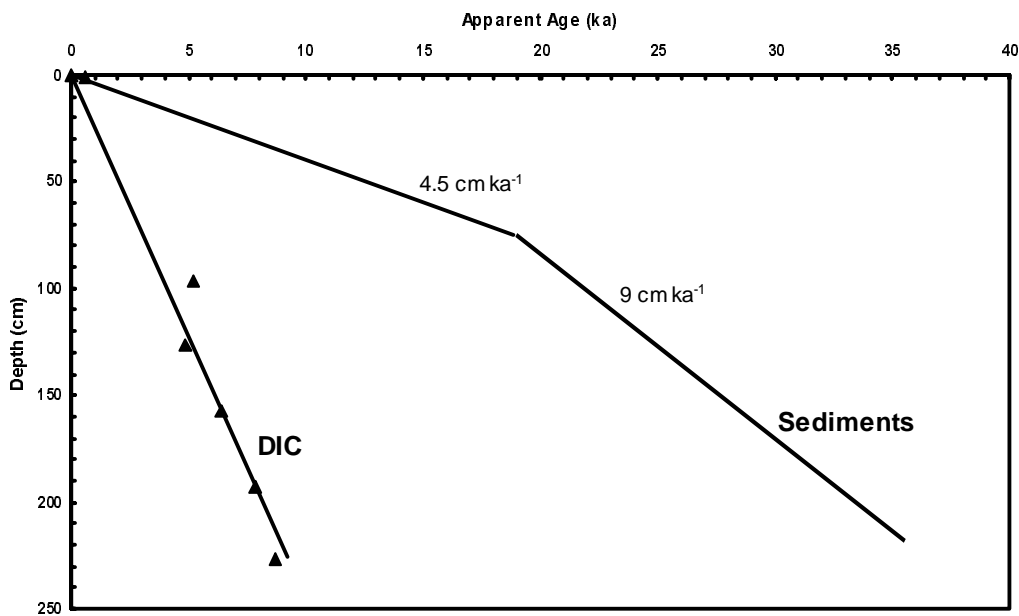

Figure 1 Radiocarbon apparent age profiles of DIC and sediments in cores D36 and AT5 calculated according the international convention (Stuiver and Polach 1977). The best fit to the sediment age profile shows a 7-cm-thick bioturbation zone of constant age at the top of the core, and two zones with different sedimentation rates, the upper zone (7–75 cm) with a rate of 4.5 cm ka^{-1} and the lower zone (below 75 cm) with a rate of 9 cm ka^{-1}. This line is considered to be the best estimate of the real age of the porewater deposited with the sediments. The data points represent the apparent ^{14}C age of the porewater as calculated by the regular age curve. The figure is modified from Sivan et al. (submitted).

Here, we apply a ^{14}C mass conservation model to develop simple algorithms to correct ^{14}C ages for the effect of diffusion and biogeochemical processes. Similar algorithms may be used to correct the apparent ages of groundwater types.

MASS CONSERVATION MODEL AND AGE CORRECTION ALGORITHMS

Deep-sea top cores are generally comprised of loose and young sediments in which DIC (and hence [14]C_{DIC}) is usually affected by physical mass transfer (compaction, advection and diffusion) and various diagenetic (biogeochemical) processes. Among the most common processes are degradation of organic matter by oxygenic bacterial respiration (in aerobic environment) or by bacterial sulfate reduction (in anaerobic environment) and precipitation/dissolution of $CaCO_3$. Therefore a mass conservation model that describes the porewater depth profiles of S (SO_4^{2-}), C (DIC, mainly bicarbonate in the pH range of marine porewaters) and [14]C ([14]C_{DIC}) was constructed in terms of the main physical and diagenetic processes. The model assumes that the concentration gradient along the depth profile of each of the above parameters is a result of a steady state between transport and reaction processes. It comprises three differential equations that describe the time variation in the porewater concentrations of each of the above components in any depth along the core. All three equations have the same general form (according to Berner 1978) and include terms for diffusion, sedimentation and advection, ^{14}C decay and sulfate reduction (the main biogeochemical process in our case), respectively:

$$\frac{\partial(\phi Y_i)}{\partial t} = \phi \frac{\partial}{\partial z}\left(D_s \frac{\partial Y_i}{\partial z}\right) - \phi(U + \omega)\frac{\partial Y_i}{\partial z} - \phi\lambda Y_i + n(1 - \phi)\rho_s k_s C_{org} \tag{1}$$

where Y_i is the concentration of a particular species i (S, C, and ^{14}C) in porewater (M·L^{-3}); z is the depth within the core (L); ϕ is the porosity; Ds is the diffusion coefficient of dissolved species i in sediments (L^2·T^{-1}), where $D_{s(i)} = D_{0(i)}\cdot\phi^2$ (after Lerman 1979) and D_0 is the diffusion coefficient of dissolved species i in seawater; U is the advection (L·T^{-1}); ω is the sedimentation rate (L·T^{-1}); λ is the radioactive decay constant (T^{-1}) that is zero for sulfate and C and greater than zero for ^{14}C; n is a stochiometric coefficient for the sulfate reduction term that is equal to 1 for C and ^{14}C and –0.5 for S. ρ_s is the density of the sediment (M·L^{-3}); k_s is the rate constant for sulfate reduction (T^{-1}); $C_{org}(z)$ is the concentration (M·L^{-3}) of organic matter ($C_{org}=C_{org[z=0]} \cdot \exp[-k_s/\omega]\cdot z$), where for ^{14}C this term is [14]C_{org} that is the concentration (M·L^{-3}) of ^{14}C in the organic matter owing to sulfate reduction ([14]$C_{org}=$[14]$C_{org(z=0)}\cdot\exp(-[(\lambda+k_s)/\omega]\cdot z)$.

The model does not contain porosity gradients to account for porewater flow due to compaction (included as a porosity depth derivative in the diffusion term). Instead it uses two constant porosities that simplify the mathematical expression. This is justified by the constant porosity measured in cores from the Eastern Mediterranean (Almagor and Schilman 1995) and the two ranges of constant sedimentation rates measured here (Figure 1). Constant sedimentation rate implies constant porosity (Berner 1978) and the two ranges in sedimentary rate found here correspond to porosities of 0.8 for the depth range from surface to 75 cm and 0.7 for the range from 75 cm to 230 cm. The effect of carbonate precipitation/dissolution on the ^{14}C budget in the studied sediments is minor and therefore its correction algorithm was not worked out in this study.

The differential equation was solved analytically for the steady state condition, $\frac{\partial(species)}{\partial t}=0$, a reasonable assumption for deep-sea sediments with relatively constant environmental conditions. The advection in this area is most probably negligible because it is far from any hydrothermal ridge

activity and the dominant transport process across the sediment-seawater interface is molecular diffusion in porous media.

The general solution for Equation 1 is

$$Y(z) = C_1 \cdot e^{0.5(-a+\sqrt{a^2-4b})z} + C_2 \cdot e^{0.5(-a-\sqrt{a^2-4b})z} + \frac{P}{b+aq+q^2} \cdot e^{qz}$$

(2)

where the mathematical expression of all constants for each component, sulfate, DIC and ^{14}C are given in Table 1.

This mass conservation model fits the measured data well. It is reassuring that the best fit to the data was achieved when substituting zero advection into the equations as expected in this environment (see above). Therefore, this solution can be used properly to correct the apparent ^{14}C porewater ages.

The effect of sulfate reduction and diffusion on the apparent ^{14}C ages can be tested by solving two different mass conservation equations for the porewater. The first contains terms for sedimentation, decay and sulfate reduction (without diffusion) and the second contains terms for sedimentation, decay and diffusion (without sulfate reduction).

The ^{14}C solution for sulfate reduction (without diffusion) is:

$$^{14}C(z) = \frac{P}{k_s} \cdot e^{qz} + \left(^{14}C_0 - \frac{P}{k_s}\right) \cdot e^{\frac{-\lambda_z}{\omega}}$$

(3)

while the ^{14}C solution for diffusion of $H^{14}CO_3^-$ across the sediment-water interface (without sulfate reduction) is:

$$^{14}C(z) = {}^{14}C_0 \cdot e^{\frac{1}{2}(\frac{\omega}{Ds} - \sqrt{(\frac{\omega}{Ds})^2 + 4\frac{\lambda}{Ds}})z}$$

(4)

by definition, the relationship between the real age of porewater (t_{real}) and the sedimentation rate for each depth z is:

$$z = \omega \cdot t_{real}$$

(5)

and the relationship between the apparent ^{14}C age of the porewater ($t_{apparent}$) and the $^{14}C_{DIC}$ content for each depth z is:

$$^{14}C(z) = {}^{14}C_0 \cdot e^{-\lambda t_{apparent}}$$

(6)

Substituting Equations 5 and 6 into Equation 3 yields an expression for $t_{apparent}$ as a function of t_{real} that is a correction age algorithm for the effect of sulfate reduction only:

$$t_{apparent} = \frac{1}{\lambda} \cdot \ln\left(\frac{P}{k_s \cdot {}^{14}C_0} \cdot (e^{(-\lambda+k_s)t_{real}} - e^{-\lambda t_{real}}) + e^{-\lambda t_{real}}\right)$$

(7)

Table 1 Parameters to model solution

	C1	C2	a	b	p	q
SO$_4$	Smax	$S_0 - S_{max} - \dfrac{\dfrac{\frac{1}{2} \cdot ks \cdot (1-\phi) \cdot \rho \cdot Corg}{DsS \cdot \phi}}{\dfrac{-(U+\omega)}{DsS} \cdot \dfrac{-ks}{\omega} + \left(\dfrac{-ks}{\omega}\right)^2}$	$\dfrac{-(U+\omega)}{DsS}$	0	$\dfrac{\frac{1}{2} \cdot ks \cdot (1-\phi) \cdot \rho \cdot Corg}{DsS \cdot \phi}$	$\dfrac{-ks}{\omega}$
DIC	Cmax	$C_0 - C_{max} - \dfrac{\dfrac{-ks \cdot (1-\phi) \cdot \rho \cdot Corg}{DsC \cdot \phi}}{\dfrac{-(U+\omega)}{DsC} \cdot \dfrac{-ks}{\omega} + \left(\dfrac{-ks}{\omega}\right)^2}$	$\dfrac{-(U+\omega)}{DsC}$	0	$\dfrac{ks \cdot (1-\phi) \cdot \rho \cdot Corg}{DsC \cdot \phi}$	$\dfrac{-ks}{\omega}$
^{14}C$_{DIC}$	0	$C14_0 - \dfrac{\dfrac{-ks \cdot (1-\phi) \cdot \rho \cdot C14org}{DsC14 \phi}}{\dfrac{-\lambda}{DsC14} + \dfrac{-(U+\omega)}{DsC14} \cdot \dfrac{-(\lambda+ks)}{\omega} + \left[\dfrac{-(\lambda+ks)}{\omega}\right]^2}$	$\dfrac{-(U+\omega)}{DsC14}$	$\dfrac{-\lambda}{DsC14}$	$\dfrac{ks \cdot (1-\phi) \cdot \rho \cdot C14org}{DsC14 \phi}$	$\dfrac{-(\lambda+ks)}{\omega}$

The correction depends on the rate constant for sulfate reduction, on the porosity, on the sediment density and on the concentration of the organic matter.

Substituting Equations 5 and 6 into Equation 4 yields an expression for t_{real} as a function of $t_{apprent}$ that is a correction age algorithm for the effect of diffusion only:

$$t_{real} = -\frac{\lambda}{\frac{1}{2} \cdot \omega \cdot \left(\frac{\omega}{Ds} - \sqrt{(\frac{\omega}{Ds})^2 + 4\frac{\lambda}{Ds}} \right)} \cdot t_{apparent}$$

(8)

according to Equation 8 the diffusion age correction coefficient, G, is defined as

$$G = -\frac{\lambda}{\frac{1}{2} \cdot \omega \cdot \left(\frac{\omega}{Ds} - \sqrt{(\frac{\omega}{Ds})^2 + 4\frac{\lambda}{Ds}} \right)}$$

(9)

G depends on the diffusion coefficient of $H^{14}CO_3^-$, the sedimentation rate and the decay constant. Substituting the numerical values of all constants into the sulfate reduction correction algorithm (Equation 7) shows that in the value range of the sulfate reduction rate constant (similar to the literature constant given by Brener 1978) and the organic matter concentrations in the sediments, the calculated $t_{apparent}$ is only 1% older than t_{real}. It seems that considering the effect of sulfate reduction yields only a trivial correction to the apparent age.

The diffusion age correction coefficient, G, is much larger than unity and depends on the values of λ, ω, and Ds. Therefore, the diffusion correction has potential to change the apparent ^{14}C age to fit the real age.

APPLICATION OF THE AGE CORRECTION ALGORITHMS TO THE DEEP EASTERN MEDITERRANEAN

The ^{14}C profile in the Eastern Mediterranean (Sivan et al. 2001) serves as our case study to test the applicability of the age correction algorithm. A plot of the real ages of porewater versus the apparent ^{14}C ages (Figure 2) shows that the sulfate reduction correction by Equation 7 yields no significant improvement to the apparent age. It seems that in the Eastern Mediterranean this correction is very small because of the low concentrations of the organic matter and the low constant rate for sulfate reduction.

Applying the diffusion correction algorithm (Equation 8) to the ^{14}C data yielded a perfect match between the apparent ages and the real ages: a line with slope of 1 instead of line with slope of 0.23! This clearly indicates that accounting for diffusion of $H^{14}CO_3^-$ from seawater into the sediment porewater to replenish the decayed ^{14}C in the porewater (Equation 4) corrects practically all the ^{14}C age distortion.
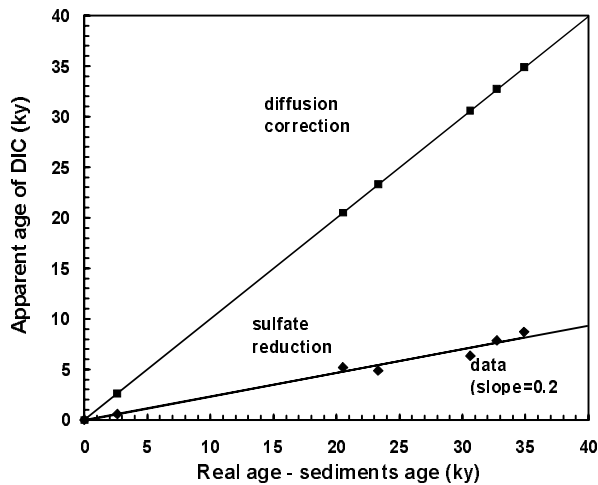
Figure 2 DIC apparent ages versus real age (the sediments age) in cores D36 and AT5. The figure presents the raw data (solid diamonds); the age correction algorithm for sulfate reduction (Equation 7) that practically does not change the apparent age and therefore its line pass through the data points; and the ages corrected for diffusion by Equation (8) (solid squares) that fall on a line with slope = 1. The diffusion coefficient of $H^{14}CO_3^-$ in the sediment porewater used in the correction is 2.3 cm^2 yr^{-1}.

CONCLUSIONS

The case study on porewater from the sediment-seawater interface in the deep Eastern Mediterranean demonstrates the importance for correcting the apparent ^{14}C age of water for the effect of diffusion of ^{14}C across the interface. The effect of diffusion on distorting the apparent ^{14}C age was much larger than the effect of sulfate reduction. The correction coefficient, G, developed here to correct porewater apparent ^{14}C ages for the effect of diffusion fits the real ages well, ages that were determined independently. We suggest that diffusion correction should be the first order correction for ^{14}C ages of porewater near the sea-sediment interface and similar natural environments.

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