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VARIATIONS IN ^{14}C RESERVOIR AGES OF BLACK SEA WATERS AND SEDIMENTARY ORGANIC CARBON DURING ANOXIC PERIODS: INFLUENCE OF PHOTOSYNTHETIC VERSUS CHEMOAUTOTROPHIC PRODUCTION

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ABSTRACT. Radiocarbon activity of dissolved inorganic carbon has been measured in the northwestern Black Sea. Both continental shelf and open-sea profiles show that surface waters are in equilibrium with the atmosphere. The observed distribution of ^{14}C activity shows a weak contribution of the deep ^{14}C-depleted CO_2 to the photic zone. Such a distribution of ^{14}C within the water column is unable to explain the aging of sedimentary organic matter and reservoir ages greater than 500 yr. A contribution of production by chemoautotrophic bacteria feeding on ^{14}C-depleted methane at the boundary of the oxic and anoxic zones is a realistic hypothesis. Also, a contribution to sedimentary organic carbon estimated at <15% of the photosynthetic primary production could explain ^{14}C reservoir ages greater than 1300 yr.

INTRODUCTION

The Upper Pleistocene Black Sea is thought to have been a continental basin oscillating between a fresh oxygenated lake and a brackish water lake when connected to the Mediterranean Sea (Sperling et al. 2003). The entry of dense, salty waters from the Mediterranean Sea induces stratification of the water column, leading to a well-developed suboxic zone at the transition between the oxic and sulfidic layers, characterized by many intermediate redox reactions (Murray et al. 1989, 1995). At present, only the upper 170 m of the Black Sea water is oxygenated (Murray et al. 1991; Murray 2006). The physico-chemical changes in, for instance, salt and oxygen contents modify the water mass residence time and consequently the dissolved mineral carbon radiocarbon age, leading to large uncertainties of the Black Sea reservoir age (R). Accurate chronology of the sediment deposition in the Black Sea and thus of the hydrological evolution of this basin are hampered by the lack of precise R values and data on their variability range. From an historical point of view, these uncertainties have contributed to controversial paleo-reconstruction interpretations concerning the last reconnection between the Black and Mediterranean seas, opposing a catastrophic view against the non-catastrophic features (Ryan et al. 1997, 2003; Aksu 2002a,b,c). These interpretations are strongly dependent on our ability to estimate very accurately the duration of the reconnection and thus on the precision of the calibrated ^{14}C dates.

Different methods have been used to determine ^{14}C reservoir ages ($R = {}^{14}C_{\text{age of lacustrine or marine sample}} - {}^{14}C_{\text{age of contemporaneous atmospheric sample}}$). Direct measurements of ^{14}C of marine or freshwater dissolved inorganic carbon (DIC) and shells of known age are the simplest approach. The past reservoir age value can also be quantified by paired measurements like bulk marine sediment ^{14}C age (or ^{14}C age of shell contained in sediment) versus varve chronology counts (expressed in ^{14}C ages), or of ^{14}C age differences between samples of terrestrial organic matter and marine samples. The latter need strict contemporaneous samples, which can be achieved by selecting terrestrial vegetal macrofossils and marine samples with the same instantaneous time marker like that of a volcanic eruption ash layer (Bard et al. 1994; Siani et al. 2001). The Black Sea R values found in the literature

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range from 0 to 2000 yr: this variability has not been fully understood up to now. The first estimations using varve counts provided reservoir ages around 2000 yr (Degens and Ross 1972; Calvert and Fontugne 1987; Calvert et al. 1987). Using Minoan eruption tephra, Guichard et al. (1993) reduced the reservoir age to 1280 ^{14}C yr, corresponding to about 2000 calendar yr. Geochemical studies and comparisons between carbonate and organic matter ages led Jones and Gagnon (1994) to suggest a reservoir age of 460 yr, to which a correction of detritical organic carbon contribution may be added. Measured ^{14}C of water column DIC shows that ages increase from 0 yr at the surface to about 1800 yr near the bottom sediments at ~2000 m depth (Östlund and Dyrssen 1986; Murray et al. 1991). ^{14}C ages of museum collection shells range from 415 to 0 ^{14}C yr for marine mollusks (Siani et al. 2000) and freshwater shells (*Dreissena rostriformis*), respectively (Major et al. 2002; Bahr et al. 2005). AMS ^{14}C dating of ostracod and gastropod shells from southwestern Black Sea cores combined with tephrochronology resulted in variable reservoir ages for the late glacial Black Sea basin (Kwiecien et al. 2005, 2006, 2008) from 0 to 1450 yr.

Here, we present new measurements of Black Sea water DIC ^{14}C collected on or near the continental shelf. These results are discussed for each kind of sample (shell or organic matter) and compared with literature data in order to examine the origin of the R value variability. We suggest that chemoautotrophic productivity contributing to the sedimentary organic matter can explain the variation of reservoir ages evident during the Holocene in the anoxic Black Sea.

MATERIAL AND METHODS

In 2004, during the MD139 cruise of the research vessel (R/V) *Marion Dufresne*, samples were collected along different profiles in the northwestern part of the Black Sea. Selected samples at different depths of the water column were collected for ^{14}C and ^{13}C analyses. The location of the sampling points is given in Figure 1. Two profiles were located on the continental shelf (50 and 350 m water column depths) with a third profile in the open Black Sea (1595 m).

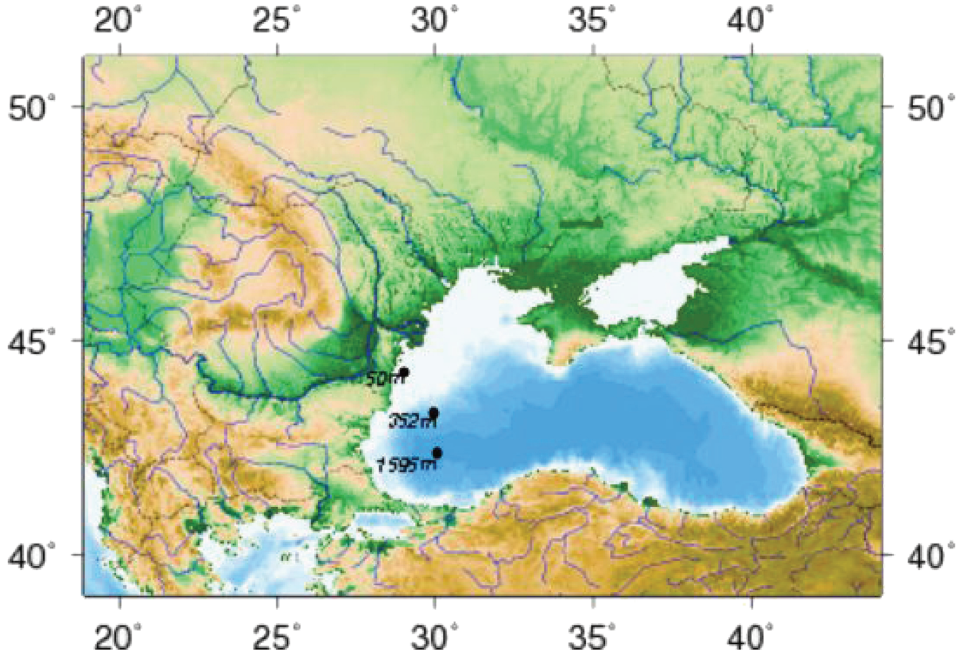

Figure 1 Location of water sampling station during the MD139 cruise of the R/V *Marion Dufresne*

After collection using CTD bottles, water samples were immediately poisoned with mercury chloride and stored hermetically in 250-cm^3 glass bottles until laboratory analysis according to the methods described by Duplessy (1972), Bard et al. (1987), and Leboucher et al. (2004).

In the laboratory, water samples between 50 and 100 cm^3 are introduced in a vacuum line, acidified with phosphoric acid, and bubbled with helium gas in order to optimize to the extraction of the total dissolved carbon dioxide (Bard et al. 1987; Leboucher et al. 2004). The evolved CO_2 was purified, trapped, and converted to graphite and put on a target prior its measurement for ^{14}C activity using the Saclay Accelerator Mass Spectrometry facilities. Results are expressed in percent modern carbon (pMC) or in ‰ (Stuiver and Polach 1977). An aliquot of CO_2 gas was also sampled to measure the stable carbon isotopic composition (δ^{13}C) with a Fison-OPTIMA mass spectrometer. The precision is better than 0.05‰.

RESULTS AND DISCUSSION

Results of ^{14}C activity and δ^{13}C with respect to depth for the 3 sites are reported in Table 1 and Figure 2. The δ^{13}C values in Figure 2 exhibit a decrease from –0.31‰ at the surface waters to –3.8% in deep anoxic waters, which is in good agreement with Fry et al. (1991). The data show a trend from enriched to depleted values (+0.8‰ at the surface to –6.3‰ at the bottom level). The low deep-water δ^{13}C values may be induced by inputs of carbon dioxide resulting from oxidation of either organic matter or methane (see Michaelis et al. 2002).

Table 1 Variations of ^{14}C activity and stable carbon isotopic ratios of the total CO_2 extracted from DIC versus water depth in the northwestern Black Sea.

Depth (m)	Δ^{14}C (‰)	δ^{13}C (‰)
Station MD04-2774H (44°57.46′N; 29°50.11′E, 50 m)		
1	56.4 ± 3.9	–1.82
30	63.1 ± 3.8	–1.35
Station MD04-2790H (43°12.80′N; 30°59.63′E, 352 m)		
2	62.5 ± 3.9	–0.31
100	58.1 ± 3.9	–1.17
250	–61.5 ± 3.7	–2.81
330	–125.2 ± 3.5	–3.4
MD04-2765H (42°23.49′N; 30°30.99′E, 1595 m)		
0	66.6 ± 3.8	nd
32	44.8 ± 4.1	–1.28
50	47.4 ± 3.9	–1.74
100	–15.9 ± 3.7	–2.96
250	–114.2 ± 3.4	–2.81
1500	–192.8 ± 3.3	–3.8

The MD04-2765H profile (Figure 2) presents a decrease of ^{14}C DIC activity with depth from Δ^{14}C = 66.6‰ to –192.8‰, corresponding to a shift in percent modern carbon of 106.6 to 80.7 pMC, respectively. The lower part of the profile matches previous results reported by Jones and Gagnon (1994) in the central Black Sea. Their data and ours show rather constant ^{14}C values below 200 m, representative of the anoxic zone. For these waters, the apparent ^{14}C age of total DIC is ~1750 yr BP.

The surface samples of the 3 profiles are clearly in equilibrium with the atmosphere, with Δ^{14}C values of ~60‰ (106 ± 1 pMC) representative of the atmospheric CO_2 ^{14}C activity of the year 2004.

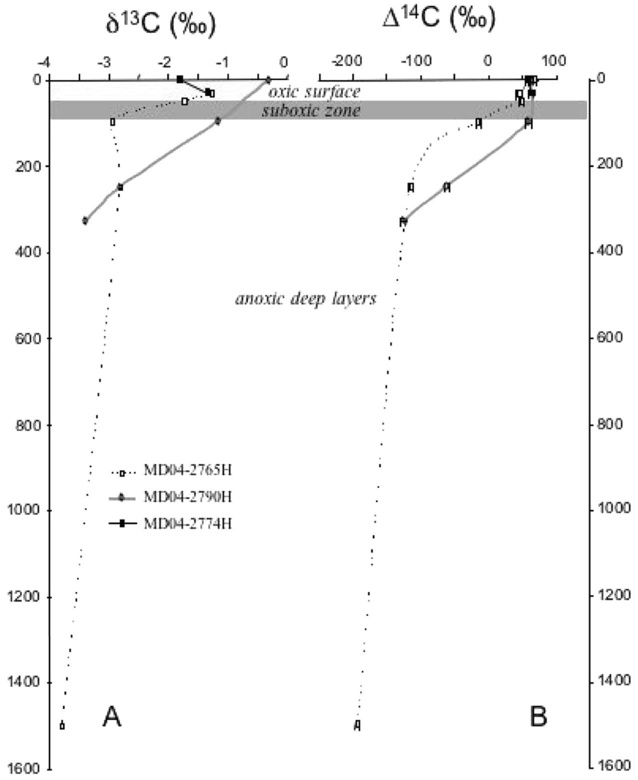

Figure 2 Variations versus water depth of dissolved inorganic carbon (DIC) ^{14}C activity and stable carbon isotopic ratios.

Δ^{14}C values measured at the shallowest profile MD04-2774 (0–50 m) are not significantly different, indicating well-mixed waters. For the intermediate profile MD04-2790H (0–350 m), the thickness of the well-ventilated water is <100 m; nevertheless, the lowest values representative of deep water are only reached at a depth of 330 m. For the deeper profile, a first decrease in ^{14}C activity occurs near 30 m depth and a second below 50 m. The deep-water values are encountered between 250 and 1500 m. From the shelf to the open sea, the onset in the decrease ^{14}C activity appears at shallower and shallower depths (around 100 m at profile MD04-2790H and <50 m at profile MD04-2765H). This indicates a greater contribution of older carbon to the base of the oxic waters when we move towards the open sea. This distribution of ^{14}C activity in the water column explains part of the reservoir age variability. It confirms that in the well-mixed waters of the shelf and especially near the mouth of rivers like the Danube, the reservoir age is negligible or very low, corroborating the Bahr et al. (2005) and Major et al. (2002) results. An increasing influence of old DIC of anoxic waters with depth can also explain why mollusks living at greater depth near the boundary between the oxygenated and anoxic zones would present higher reservoir ages than mollusks living near the shore in the well-mixed, ventilated waters. Such a pattern implies that the ecology of each species of mollusks has to be known in order to obtain reliable reservoir ages and chronology of sediment deposition. On the continental shelf, the phytoplankton-derived organic matter, which assimilates CO_2 in equilibrium with the atmosphere, would not need any reservoir age correction. Only correction of the detrital terrestrial material (if known) would be necessary. At depths greater than 200 m, in the anoxic waters of the Black Sea, no living mollusks exist. Thus, sedimentary organic matter is used as a substrate for ^{14}C dating or determination of reservoir ages.

In the central Black Sea and/or a few tens of km offshore, the contribution of terrestrial organic matter to deep sediment is negligible as evidenced by atomic C/N ratios or isotopic composition of organic carbon (δ^{13}C) (Deuser 1972; Calvert and Fontugne 1987; Strechie-Sliwinski 2007). It therefore becomes difficult to explain aging of the organic matter and reservoir ages reaching 1300 yr by terrestrial dead carbon of detrital origin.

An alternative explanation has to be proposed if the sediment organic matter has an algal origin and records an important reservoir age. However, the structure of the Black Sea water column cannot explain such a pattern since the influence of anoxic water and its resulting old CO_2 is not observed at this level in the photic layer (~70–80 m, Chu et al. 2005). As evidenced during recent cruises in the Black Sea by Chu et al. (2005) or that of Ediger et al. (2006) during the R/V *Knorr* cruise in 2001, there are no chlorophyll maxima below 40–50 m. Field experiments from Karl and Knauer (1991) suggest that the photoautotrophic production was limited to the upper 55 m of the water column.

A possible explanation for the reservoir age of organic matter could be the chemoautotrophic bacterial primary production. There is a complex microbial foodweb at the oxic/anoxic interface in such multilayer systems, and productive microbial communities live on the residual chemical energy (H_2S, CH_4, NH_{4+}, H_2, low molecular weight organics) that originates from the anoxic layer. Paradoxically, the importance of chemoautrophic production in the Black Sea has been known to biologists for several decades. Nevertheless, no attempt has been made to estimate if the phenomenon could have an impact on the ^{14}C reservoir age of sedimentary organic matter. Karl and Knauer (1991) estimated that "chemosynthesis within the oxic-anoxic interface zone 60–100 m is equivalent to ~15% of the rate of phototrophic production in the surface waters." During the R/V *Knorr* cruise in May–June 2001, Morgan et al. (2006) observed a high bacterial production reaching to 50% of the photosynthetic production. Furthermore, they noticed that below the suboxic boundary, large filamentous cells (>10 μm) contribute about 53% of the total bacterial biomass. During the same cruise in the Black Sea central gyre and in Sakarya canyon regions, Yilmaz et al. (2006) noticed the occurrence of chemoautotrophic organisms, which contributed between 30 to 89% of the overall water column production. This chemoautotrophic activity and the importance of the methanotrophic microbial mats in the anoxic Black Sea is now rather well documented (see Michaelis et al. 2002; Durisch-Kaiser et al. 2005; Treude et al. 2007). The methanotrophic bacteria that feed on a ^{14}C-depleted methane (~15 pMC, see Kessler et al. 2006) would present consequently a ^{14}C age around 15,000 yr. In these conditions, the amount of chemoautotrophic material required to yield sedimentary organic carbon with a realistic apparent age of 1300 yr (reservoir age) is rather low: between 12% with chemoautotrophic matter at 15 pMC and photosynthetic matter at 95 pMC and 17% with chemoautotrophic matter at 15 pMC and photosynthetic matter 100 pMC. Such amounts of chemoautotrophic material are realistic if we refer firstly to the estimates of Yilmaz et al. (2006) or Morgan et al. (2006) and secondly to the fact that photosynthetic organic matter is partly oxidized in the oxic part of the water column, enhancing the contribution of chemoautotrophic matter, which directly sink in the anoxic water column without any direct oxidation process.

Compared to the photosynthetic organic carbon, the chemoautotrophic carbon is different in terms of ^{14}C activity and δ^{13}C values. We can thus use δ^{13}C as an independent proxy to calculate the contribution of chemoautotrophic material to the deep sediment using a simple mixing equation and comparing it to that derived from ^{14}C:

$$\delta^{13}C_{SOM} = x \times \delta^{13}C_{COM} + (1-x) \times \delta^{13}C_{PSM}$$

where x is the fraction of chemoautotrophic carbon, and $\delta^{13}C_{SOM}$, $\delta^{13}C_{PSM}$, $\delta^{13}C_{COM}$ are the carbon isotopic composition end-members of the sediment organic matter, the photosynthetic matter, and chemoautotrophic organic matter, respectively. Few measurements of $\delta^{13}C$ of phytoplankton have been published for the Black Sea. The mean value obtained by Deuser (1970) from a spring bloom is –23‰ and needs to be corrected by about 2‰ for anthropogenic CO_2 influence to be comparable with pre-industrial and Holocene sediment values. With the increase of the summer sea surface temperatures, the dissolved CO_2 concentration decreases and $\delta^{13}C$ of phytoplankton increases; thus, the resulting exported primary production in deep sediment would give higher isotopic compositions. Therefore, a value between –21 and –22‰ would be more realistic for the phytoplankton end-member. Concerning the chemoautotrophic end-member, one can assume that $\delta^{13}C_{COM}$ reflects that of methane. For the upper water column, Kessler et al. (2006) give $\delta^{13}C$ values around –55‰ for the Black Sea.

Since the mid-Holocene, the Black Sea has reconnected to the Mediterranean, inducing sapropelic sediment deposits characterized by rather homogenous carbon isotopic values of about –25 to –26‰ (Deuser 1972; Calvert and Fontugne 1987; Strechie-Sliwinski 2007). Introducing these end-members into the mixing equation, we estimate a contribution of chemoautotrophic material of ~10–12%, which is in good agreement with what we get from ^{14}C estimates.

The results are summarized in Figure 3. Measurements of DIC ^{14}C activity in the Black Sea water column show that the surface waters are representative of the ^{14}C atmospheric concentration, suggesting no reservoir age correction. The ^{14}C activity in water decreases with depth and with offshore distance. The base of the well-mixed layer is marked by old CO_2 originating from deeper anoxic water. Such a water column structure on the continental shelf and on its slope to the deep sea sug-

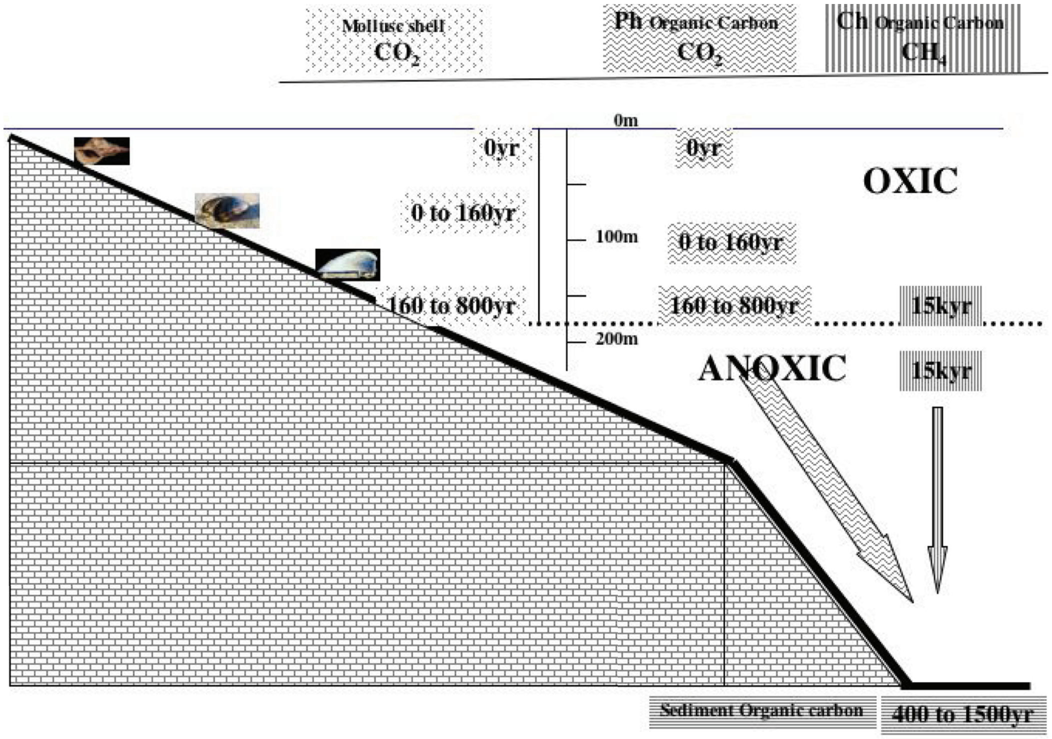

Figure 3 Variations of reservoir ages as a function of location and origin of carbon (mineral or organic (photosynthetic = Ph; chemoautotrophic = Ch) in the Black Sea during the anoxic periods.

gests that reservoir ages determined using mollusk shells depend on the living depth and the ecology (intra- or epi-benthic, for example) of these mollusks. However, the profile of ^{14}C activity in the water column is unable to explain reservoir ages older than 1000 yr since the influence of CO_2 coming from anoxic water is weak in the photic zone. Only a contribution of about 15% (or less) of chemoautotrophic material like methanotrophic microbial mats is able to explain a 1300-yr reservoir age value for deep sedimentary organic matter. Measurements of ^{14}C activity of these mats are needed if one wants to propose valuable reservoir age corrections and estimate this chemoautotrophic production.

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REFERENCES

Aksu AE, Hiscott RN, Kaminski MA, Mudie PJ, Gillespie H, Abrajano T, Yasar D. 2002a. Last glacial-Holocene paleoceanography of the Black Sea and Marmara Sea: stable isotopic, foraminiferal and coccolith evidence. *Marine Geology* 190(1–2):119–49.

Aksu AE, Hiscott RN, Mudie PJ, Rochon A, Kaminski MA, Abrajano T, Yasar D. 2002b. Persistent Holocene outflow from the Black Sea to the eastern Mediterranean contradicts Noah's Flood hypothesis. *GSA Today* 12(5):4–10.

Aksu AE, Hiscott RN, Yasar D, Isler FI, Marsh S. 2002c. Seismic stratigraphy of Late Quaternary deposits from the southwestern Black Sea shelf: evidence for non-catastrophic variations in sea-level during the last ~10000 yr. *Marine Geology* 190(1–2):61–94.

Bahr A, Lamy F, Arz H, Kuhlmann H, Wefer G. 2005. Late glacial to Holocene climate and sedimentation history in the NW Black Sea. *Marine Geology* 214(4): 309–22.

Bard E, Arnold M, Maurice P, Duplessy J-C. 1987. Measurements of radiocarbon in the ocean by means of accelerator mass spectrometry: technical aspects. *Nuclear Instruments and Methods in Physics Research B* 29(1–2):297–301.

Bard E, Arnold M, Mangerud J, Paterne M, Labeyrie L, Duprat J, Mélières M-A, Søstegaard E, Duplessy J-C. 1994. The North Atlantic atmosphere-sea surface ^{14}C gradient during the Younger Dryas climatic event. *Earth and Planetary Science Letters* 126(4):275–87.

Calvert SE, Fontugne MR. 1987. Stable carbon isotopic evidence for the marine origin of the organic matter in the Holocene Black Sea sapropel. *Chemical Geology* 66(3–4):315–22.

Calvert SE, Vogel JS, Southon JR. 1987. Carbon accumulation rates and origin of the Holocene sapropel in the Black Sea. *Geology* 15(10):918–2l.

Chu PC, Ivanov LM, Margolina TM. 2005. Seasonal variability of the Black Sea chlorophyll-a concentration. *Journal Marine Systems* 56(3–4):243–61.

Degens ET, Ross DA. 1972. Chronology of the Black Sea over the last 25,000 years. *Chemical Geology* 10:1–16.

Deuser WG. 1970. Isotopic evidence for diminishing supply of available carbon during diatom bloom in the Black Sea. *Nature* 225(5237):1069–71.

Deuser WG. 1972. Late Pleistocene and Holocene history of the Black Sea as indicated by stable-isotope studies. *Journal of Geophysical Research* 77(6):1071–7.

Duplessy J-C. 1972. La géochimie des isotopes stables du carbone dans la mer [PhD dissertation]. Paris: University Paris IV. 196 p.

Durisch-Kaiser E, Klauser L, Wehrli B, Schubert C. 2005. Evidence of intense archaeal and bacterial methanotrophic activity in the Black Sea water column. *Applied and Environmental Microbiology* 71(12):8099–106.

Ediger D, Soydomir N, Kideys AE. 2006. Estimation of phytoplankton biomass using HLC pigment analysis in the southwestern Black Sea. *Deep-Sea Research II* 53(17–19):1911–22.

Fry B, Jannasch HW, Molyneaux SJ, Wirsen CO, Muramoto JA, King S. 1991. Stable isotope studies of the carbon, nitrogen and sulfur cycles in the Black Sea and the Cariaco Trench. *Deep-Sea Research* 38 (Supplement 2):S1003–S1019.

Guichard F, Carey S, Arthur MA, Sigurdsson H, Arnold M. 1993. Tephra from the Minoan eruption of Santorini in sediments of the Black Sea. *Nature* 363(6430):610–2.

Jones GA, Gagnon AR. 1994. Radiocarbon chronology of Black Sea sediments. *Deep-Sea Research I* 41(3): 531–57.

Karl DM, Knauer GA. 1991. Microbial production and particle flux in the upper 350 m of the Black Sea. *Deep-Sea Research* 38 (Supplement 2):S921–S942.

Kessler JD, Reeburgh WS, Southon J, Seifert R, Michaelis W, Tyler SC. 2006. Basin-wide estimates of the input of methane from seeps and clathrates to the Black Sea. *Earth and Planetary Science Letters* 243(3–4): 366–75.

Kwiecien O, Bahr A, Arz H, Lamy F, Haug G. 2005. Paleoenvironmental history of the Black Sea during the last ca. 30 kyr. In: Michaelis W, Wong HK, Lericolais G, editors. 2nd *ASSEMBLAGE Workshop, Hamburg* (G). p 25–6.

Kwiecien O, Arz H, Lamy F, Bahr A, Wulf S, Haug G. 2006. Preliminary results on core MD04 2760 from the southwestern Black Sea. In: European Geosciences Union 2006 (editor). *Geophysical Research Abstracts*. Vienna: Ost. p 06947.

Kwiecien O, Arz HW, Lamy F, Wulf S, Bahr A, Röhl U, Haug G. 2008. Estimated reservoir ages of the Black Sea since the last Glacial. *Radiocarbon* 50(1):99–118.

Leboucher V, Jean-Baptiste P, Fourré E, Arnold M, Fieux M. 2004. Oceanic radiocarbon and tritium on a transect between Australia and Bali (eastern Indian Ocean). *Radiocarbon* 46(2):567–81.

Major CO, Ryan WBF, Lericolais G, Hajdas I. 2002. Constraints on Black Sea outflow to the Sea of Marmara during the last glacial-interglacial transition. *Marine Geology* 190(1–2):19–34.

Michaelis W, Seifert R, Nauhaus K, Treude T, Thiel V, Blumenberg M, Knittel K, Gieseke A, Peterknecht K, Pape T, Boetius A, Amann R, Jørgensen BB, Widdel F, Peckmann J, Pimenov NV, Gulin MB. 2002. Microbial reefs in the Black Sea fueled by anaerobic oxidation of methane. *Science* 297(5583):1013–5.

Morgan JA, Quinby HL, Ducklow HW. 2006. Bacterial abundance and production in the western Black Sea. *Deep-Sea Research II* 53(17–19):1945–60.

Murray JW. 2006. Introduction—Recent US research cruises to the Black Sea. *Deep-Sea Research II* 53(17–19):1737–9.

Murray JW, Jannasch HW, Honjo S, Anderson RF, Reeburgh WS, Top Z, Friederich GE, Codispoti LA, Izdar E. 1989. Unexpected changes in the oxic/anoxic interface in the Black Sea. *Nature* 338(6214):411–3.

Murray JW, Top Z, Ozsoy E. 1991. Hydrographic properties and ventilation of the Black Sea. *Deep-Sea Research* 38 (Supplement 2):S663–S689.

Murray JW, Codispoti LA, Friederich GE. 1995. Oxidation-reduction environments: the suboxic zone in the Black Sea. In: Huang CP, O'Melia CR, Morgan JJ, editors. *Aquatic Chemistry: Interfacial and Interspecies Processes*. ACS Advances in Chemistry Series. Volume 224. Washington DC: ACS. p 157–76.

Östlund HG, Dyrssen D. 1986. Renewal rates of the Black Sea deep water. In: *Report on chemistry of the seawater, XXXIII proceedings of the Chemical and Physical Oceanography of the Black Sea*. Göteborg.

Ryan WBF, Pitman III WC, Major CO, Shimkus K, Moskalenko V, Jones GA, Dimitrov P, Gorür N, Sakinçe M, Yüce H. 1997. An abrupt drowning of the Black Sea shelf. *Marine Geology* 138(1–2):119–26.

Ryan WBF, Major CO, Lericolais G, Goldstein SL. 2003. Catastrophic flooding of the Black Sea. *Annual Review of Earth Planetary Sciences* 31(1):525–54.

Siani G, Paterne M, Arnold M, Bard E, Metivier B, Tisnerat N, Bassinot F. 2000. Radiocarbon reservoir ages in the Mediterranean Sea and Black Sea. *Radiocarbon* 42(2):271–80.

Siani G, Paterne M, Michel E, Sulpizio R, Sbrana A, Arnold M, Haddad G. 2001. Mediterranean Sea surface radiocarbon reservoir age changes since the Last Glacial Maximum. *Science* 294(5548):1917–20.

Sperling M, Schmiedl G, Hemleben Ch, Emeis KC, Erlenkeuser H, Grootes PM. 2003. Black Sea impact on the formation of eastern Mediterranean sapropel S1? Evidence from the Marmara Sea. *Palaeogeography, Palaeoclimatology, Palaeoecology* 190:9–21.

Strechie-Sliwinski C. 2007. Enregistrement sédimentaire des changements environnementaux récents dans la zone Nord-ouest de la Mer Noire [PhD dissertation]. Paris: University Paris Sud. 422 p.

Stuiver M, Polach H. 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.

Treude T. et al. 2007. Consumption of methane and CO_2 by methanotrophic microbial mats from gas seeps of the anoxic Black Sea. *Applied Environmental Microbiology* 73(7):2271–83.

Yilmaz A, Coban-Yildiz Y, Telli-Karakoç F, Bologa A. 2006. Surface and mid-water sources of organic carbon by photoautotrophic and chemoautotrophic production in the Black Sea. *Deep-Sea Research II* 53(17–19):1988–2004.