^{226}Ra in barite: Absolute dating of Holocene Southern Ocean sediments and reconstruction of sea-surface reservoir ages

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ABSTRACT

Absolute dating of marine sediments is necessary to achieve reliable correlations of paleoclimate records. The ^{226}Ra decay in barite separated from a deep-sea core of the Southern Ocean was used to determine absolute ages for the Holocene Epoch. Comparison with ^{14}C ages measured on planktic foraminifers provides the first past sea-surface reservoir ages in the Antarctic zone of the Southern Ocean. Throughout the middle to late Holocene, our results indicate a reservoir age of ca. 1100 yr, comparable to modern estimates. A significantly higher reservoir age (ca. 1900 yr) is obtained for the early Holocene, which suggests a major change in the Southern Ocean circulation at that time.

Keywords: paleoclimatology, Holocene, marine sediments, dating, radium, barite, radiocarbon, Southern Ocean.

INTRODUCTION

Knowledge of the phase relation between climatic events that take place in the two hemispheres is required to better understand the mechanisms driving global climate changes. However, interhemispheric teleconnections can only be investigated if paleoclimatic records are accurately and reliably correlated. Synchronization of ice-core records from Antarctica and Greenland was recently achieved by the measurement of methane concentrations in trapped air bubbles (Blunier et al., 1997, 1998; Steig et al., 1998). The radiocarbon method can be used for both continental and marine records. However, whereas the timing of events from ice cores and continental records may be directly compared, this step appears to be more problematic with marine records, thus complicating the understanding of the role of the ocean in regulating past climate.

The most common way to date Holocene marine sediments is through radiocarbon ages measured on planktic foraminifers. However, these ages must be corrected for the difference in the $^{14}C/^{12}C$ ratio between atmospheric CO_2 and ΣCO_2 contents of surface seawater (i.e., sea-surface reservoir age). Uncertainties on the reservoir-age correction are especially large in the Southern Ocean, where estimates of modern reservoir ages are sparse. Estimates for this region are high, to 1400 yr in high latitudes (Stuiver and Polach, 1977; Stuiver et al., 1981; Bard, 1988). Low ^{14}C concentrations in modern surface waters of the Southern Ocean are due to (1) mixing with deep waters that have been depleted in ^{14}C by isolation from the atmosphere and (2) sea-ice cover that strongly reduces CO_2 air-sea exchange. Past reservoir ages were likely different compared to those of the present ocean, as shown for subtropical and subpolar areas of the southwest Pacific Ocean (Sikes et al., 2000) and in the North Atlantic (Bard et al., 1994; Siani et al., 2001). The assumption of a constant reservoir-age correction may thus lead to severe bias in marine ^{14}C chronologies. An additional complication in establishing chronologies in Southern Ocean sediments comes from the scarcity of foraminifers that often simply precludes the standard use of carbonate radiocarbon dating.

A new radiometric method based on the measurement of ^{226}Ra activities ($t_{1/2}$ = 1602 yr) in marine barite (Paytan et al., 1996; van Beek and Reyss, 2001) was employed in a gravity core from the Atlantic sector of the Southern Ocean. This method provides absolute ages that allow us to estimate the reservoir correction in radiocarbon dating for the Holocene Epoch in the Antarctic zone of the Southern Ocean.

MATERIAL AND METHODS

Barite crystals were separated from core PS2102-2 (53°04′S, 04°59′W, 2390 m water depth) by using a protocol designed for opal-rich sediments. A heavy liquid at a density of 2.8 g/cm^3 (LST Fastfloat, which consists of low-toxicity sodium heteropolytungstates dissolved in water) was employed to separate the dense fraction of the sediment that contains barite crystals (4.5 g/cm^3) from opal (2.2 g/cm^3). Dense fractions (a few milligrams separated out of 3 to 5 g sediment) were then thoroughly washed with distilled water, centrifuged, dried, and measured for their gamma activity in high-efficiency, low-background, well-type detectors settled in the underground laboratory of Modane in the French Alps (Reyss et al., 1995). After gamma counting, the ^{238}U activities and the barite content (deduced from barium measurements) in the separated samples were determined using instrumental neutron activation analysis as described in van Beek and Reyss (2001). Errors on the Ba and ^{238}U contents are estimated as 5% and 20%, respectively. It is also important to stress that the protocol as employed in this work did not provide a quantitative separation of barite.

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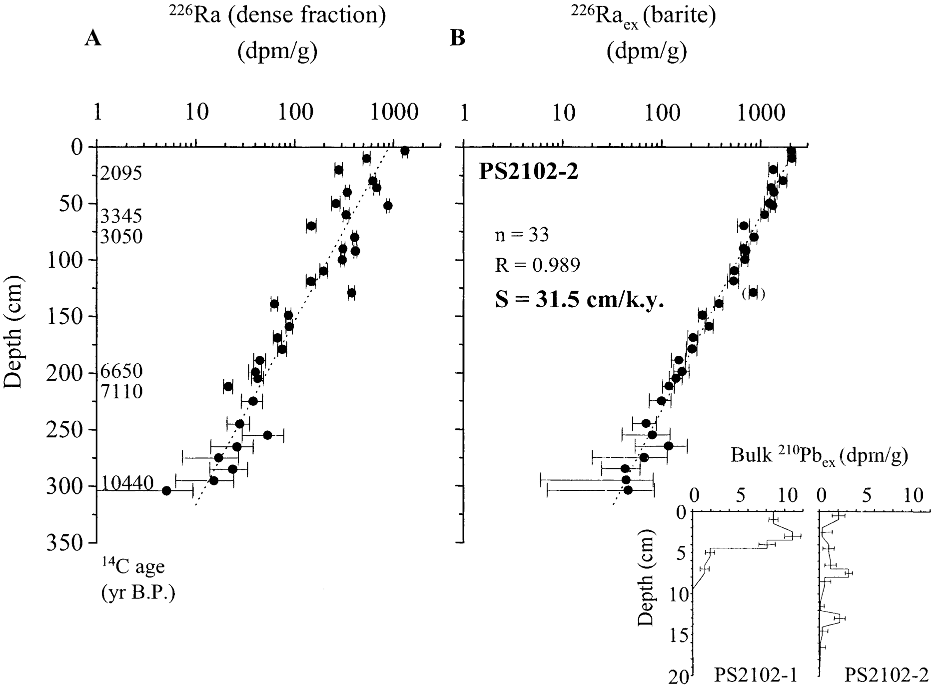

Figure 1. A: ^{226}Ra activities in dense fractions separated from core PS2102-2 (expressed in disintegrations per minute per gram, dpm). B: Excess ^{226}Ra activities normalized to barite content. Exponential decay of $^{226}Ra_{ex}$ activities in barite with sediment depth provides sedimentation rate of 31.5 cm/k.y. (error of 1.0 cm/k.y.) deduced from slope of 0.00597 ± 0.00016, estimated by taking error bars of ^{226}Ra activities into account (data point out of trend was ignored in calculation). Bulk $^{210}Pb_{ex}$ activities measured in core PS2102-2 and in surface samples from multicore collected at same location (PS2102-1) are also shown. Comparison between two profiles suggests that upper 17 cm of core PS2102-2 were disturbed during coring (trend that may also be indicated by first two upper $^{226}Ra_{ex}$ activities in barite that are similar). To estimate possible sediment loss of PS2102-2 core top, $^{210}Pb_{ex}$ inventory in this core was compared with that from multicore; result was that loss of 40% of total activities, which corresponds to sediment loss of 2–3 cm, cannot be excluded in gravity core. However, such sediment loss will not affect significantly ages deduced from sedimentation rate. Conventional ^{14}C ages are also reported.

TABLE 1. DETERMINATION OF SEA-SURFACE RESERVOIR AGES

Depth (cm)	^{226}Ra-in-barite age* (yr)	Conventional ^{14}C age* (yr B.P.)	Marine $\Delta^{14}C$* (‰)	$\Delta^{14}C$ difference with the marine curve* (‰)	Reservoir age† (yr)
26.5–27.5	855 ± 35	2095§ ± 40	−150.8 ± 5.7	−91.9 ± 5.7	1230 ± 100
70.5–71.5	2255 ± 75	3345§ ± 60	−139.0 ± 10.3	−91.1 ± 10.8	1210 ± 150
72–75	2335 ± 75	3050# ± 75	−98.1 ± 12.0	−51.8 ± 12.3	850 ± 170
207.5–210	6630 ± 220	6650# ± 70	−31.4 ± 27.9	−61.8 ± 27.9	900 ± 170
210.5–211.5	6700 ± 220	7110§ ± 90	−77.5 ± 27.3	−108.7 ± 27.4	1290 ± 210
300–302.5	9560 ± 320	10 440# ± 140	−138.6 ± 37.5	−180.5 ± 38.8	1930 ± 290

Note: Conventional ^{14}C ages were determined by accelerator mass spectrometry radiocarbon dating of planktic foraminifers (*Neogloboquadrina pachyderma*). Marine $\Delta^{14}C$ values were obtained by considering the ^{226}Ra-in-barite ages as absolute ages (transformed into ages B.P.—i.e., with 1950 A.D. as reference year—in the calculations). Comparison of our $\Delta^{14}C$ values with those from the marine calibration data set given by INTCAL98 (Stuiver et al., 1998) allowed us to estimate past sea-surface reservoir ages. The discrepancy with the marine calibration data set (see Fig. 2) reflects the regional difference (designated ΔR [Stuiver and Braziunas, 1993]) from the average global marine reservoir age (Stuiver et al., 1998, and references therein). Sea-surface reservoir ages were determined by adding 400 yr (i.e., the average global marine reservoir) to the ΔR value estimated from the $\Delta^{14}C$ difference with the marine calibration curve.

A mean reservoir age of 1100 ± 210 yr can be determined for the middle to late Holocene. The standard deviation of the mean reflects slight discrepancies in between ^{14}C ages given at similar core depths by two different laboratories. Errors on ages deduced from the ^{226}Ra activities in barite are given considering the uncertainty of 1.0 cm/k.y. on the sedimentation rate.

* 1σ error.
† 2σ error.
§ Laboratory of Kiel.
\# Laboratory of Aarhus.

RESULTS

The ^{226}Ra activities measured in the samples separated from core PS2102-2 decrease with sediment depth (Fig. 1A). However, some ^{226}Ra may be produced by both ^{238}U and unsupported (i.e., not produced by its parent isotope) ^{230}Th (Paytan et al., 1996; van Beek and Reyss, 2001). The ^{226}Ra activities decrease with depth until very low ^{226}Ra values are reached, suggesting no or negligible ^{226}Ra activities produced by unsupported ^{230}Th in the early Holocene samples (Fig. 1A). Assuming that this trend is valid throughout the Holocene Epoch, the ^{226}Ra activities have been corrected only for the ^{226}Ra activities in radioactive equilibrium with ^{238}U, even if ^{238}U activities are low (i.e., <5.6 dpm/g; Appendix Table DR1[1]). This correction thus provides excess ^{226}Ra activities (noted $^{226}Ra_{ex}$). In addition, large variations in the barite abundance were observed from one sample to another (values ranging from 11.1% to 65.8%; Appendix Table DR1 [see footnote 1]). These variations can be attributed to dilution by more or less nonbarite dense material that resulted from the use of a nonspecific and nonquantitative chemical separation. The obtained $^{226}Ra_{ex}$ activities were therefore normalized to the barite content to correct for dilution. This normalization results in a slope with a better linear fit that reflects more accurately the exponential decay of ^{226}Ra activities within barite crystals (Fig. 1B). Our results do not indicate any significant change in the slope over the investigated core section. Therefore a constant sedimentation rate was determined for the Holocene Epoch (i.e., 31.5 cm/k.y., with an error of 1.0 cm/k.y.).

Bulk $^{210}Pb_{ex}$ activities measured in the PS2102-2 core top indicate that no significant sediment loss occurred during coring (Fig. 1). Absolute ages in the core can therefore be directly deduced from the ^{226}Ra-derived sedimentation rate. Comparison with ^{14}C ages from the same core allows us to determine the sea-surface reservoir ages for the past 10 k.y. at the core location. Marine $\Delta^{14}C$ values that correspond to the difference between absolute and ^{14}C ages (Table 1) were calculated and compared to the marine calibrated $\Delta^{14}C$ record (Stuiver et al., 1998) (Fig. 2). The obtained values indicate a mean reservoir age of 1100 ± 210 yr throughout the middle to late Holocene and a significantly higher estimate of 1930 ± 290 yr at 9560 yr (Table 1).

[1]GSA Data Repository item 2002084, Results obtained on samples separated from core PS2102-2, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA, editing@geosociety.org, or at www.geosociety.org/pubs/ft2002.htm.

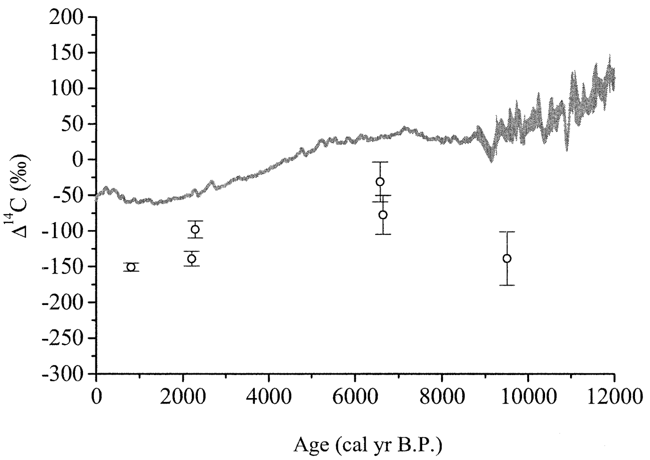

Figure 2. Holocene marine $\Delta^{14}C$ values derived from comparison between ^{14}C ages and ^{226}Ra-in-barite ages (open circles). Deviation from marine calibration data set (gray curve) allows us to estimate sea-surface reservoir ages for Holocene Epoch (see Table 1).

DISCUSSION

Except for the early Holocene value, the reservoir ages determined by coupling ^{226}Ra and ^{14}C analysis are similar within errors to modern estimates deduced from the measurement of the natural ^{14}C content (1) in the dissolved bicarbonate of surface water sampled in the South Atlantic between 50° and 60° (sea-surface reservoir ages ranging from 900 to 1200 yr based on $\Delta^{14}C$ values of −105‰ to −135‰; Broecker et al., 1985) and (2) in marine organisms from high southern latitudes (Stuiver and Polach, 1977; Gordon and Harkness, 1992; Berkman and Forman, 1996). The close agreement between the middle to late Holocene and modern reservoir ages suggests rather persistent hydrographic conditions in the Southern Ocean since 7000–8000 yr B.P., with surface-water temperatures and sea-ice cover comparable to those of the modern environment as indicated by the diatom record (Fig. 3). In contrast, the high reservoir age (ca. 1900 yr) estimated in the early Holocene coincides with the southern-latitude hypsithermal, a period characterized by increased atmospheric and sea-surface temperatures and a strong reduction of the Antarctic sea-ice field after the last glaciation (Fig. 3) (Gersonde and Zielinski, 2000; Masson et al., 2000; Hodell et al., 2001). It must be stressed, nevertheless, that because of the large error bars associated with the $^{226}Ra_{ex}$ activities below 250 cm (Fig. 1), a change in the sedimentation rate in the early Holocene cannot be ruled out. The assumption of a constant sedimentation rate may thus have biased the early Holocene reservoir-age estimate. However, evidence for a sedimentation-rate increase associated with the hypsithermal interval was found in a core collected at similar latitude and water depth in the Atlantic sector of the Southern Ocean (Hodell et al., 2001). A similar pattern in the PS2102-2 core would lead to a younger ^{226}Ra age at 300 cm that would provide a sea-surface reservoir age even older than the 1930 yr value.

The reduction of sea-ice cover favors air-sea CO_2 exchange and thus conflicts with an increase of reservoir age. Among the other processes that potentially influence reservoir ages, a change in the ocean circulation that would lower the $^{14}C/^{12}C$ ratio in the underlying waters would lead to an increase in the apparent age of surface waters (Bard et al., 1994; Siani et al., 2001). By using the equilibrium equation for a modern surface-water mass (Siani et al., 2001), a reservoir age of ca. 1900 yr as we determined for the early Holocene would be reached by mixing surface waters with deeper waters of ca. 3000 yr age. Similar reservoir ages in surface and intermediate waters were determined by Sikes et al. (2000) in the southwest Pacific (1990 yr and 3470 yr at 37°S, and 1970 yr and 5040 yr at 45°S) for the Last Glacial Maximum. As indicated by paleoclimate records, the ocean circulation is capable of abrupt changes from one mode to another (Bond et al., 1997; Adkins et al., 1998; Bianchi and McCave, 1999; Sikes et al., 2000; Siani et al., 2001). Results of modeling studies suggest that the temperature increase in the high southern latitudes at the onset of the Holocene could have been caused by a weakening of the thermohaline circulation, consistent with the so-called seesaw effect (Crowley, 1992; Stocker, 1998; Ganopolski et al., 1998). However, simulations performed with a zonally averaged circulation model that includes ^{14}C as a tracer show that either a reduction or a complete collapse of the thermohaline circulation does not increase the apparent age of surface waters from the Southern Ocean (Marchal et al., 1999). The high sea-surface reservoir age may

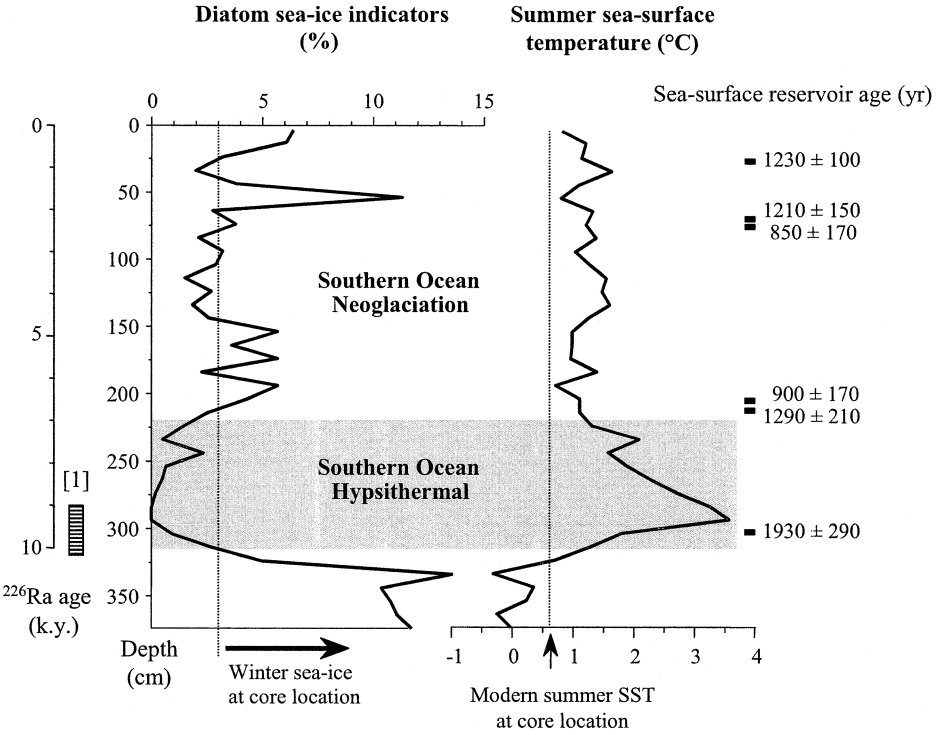

Figure 3. Estimation of Antarctic winter sea-ice cover and summer surface-water temperature (°C) variations reconstructed in core PS2102-2 based on diatom assemblages studies using methods described by Zielinski et al. (1998) and Gersonde and Zielinski (2000). SST is sea-surface temperature. Values exceeding 3% of diatom sea-ice indicator taxa are interpreted to represent presence of winter sea-ice at core location (Gersonde and Zielinski, 2000). Temperatures were estimated with transfer-function technique (standard error of estimates: 0.66 °C; Zielinski et al., 1998). For comparison, period characterized by temperature optimum as recorded in Antarctic ice cores (Masson et al., 2000) is also reported [1]. Age model derives from presented ^{226}Ra-in-barite dating method.

therefore document a local circulation change that would have affected the Southern Ocean water-mass structure at the onset of the Holocene.

CONCLUSIONS

Our results from core PS2102-2 indicate that ^{226}Ra activities measured in marine barite can be used as a tool for dating Holocene sediments from the Southern Ocean. Absolute ages given by this method offer a unique opportunity to determine past reservoir-age corrections in radiocarbon dating, with implications for the reconstruction of the past circulation pattern in the Southern Ocean. Such a temporal framework allows reliable interhemispheric comparisons of climate events to be made, thus leading to a better understanding of climate-driving mechanisms.

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