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Analysis of the atmospheric ^{14}C record spanning the past 50,000 years derived from high-precision $^{230}Th/^{234}U/^{238}U$, $^{231}Pa/^{235}U$ and ^{14}C dates on fossil corals

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Abstract

Changes in the geomagnetic field intensity, solar variability, and the internal changes of the carbon cycle are believed to be the three controlling factors of past atmospheric radiocarbon (^{14}C) concentrations (denoted as $\Delta^{14}C$). Of these three, it is believed that the field intensity is the dominant factor. We analyze an atmospheric $\Delta^{14}C$ record spanning the past 50,000 years based on previously-published $^{230}Th/^{234}U/^{238}U$ and ^{14}C dates of fossil corals from Kiritimati, Barbados, Araki and Santo Islands, and identify the role of the Laschamp geomagnetic field excursion on the long term trend of the $\Delta^{14}C$ record. There is a general consistency between the coral $\Delta^{14}C$ record and the $\Delta^{14}C$ output from carbon cycle models based on the global ^{14}C production estimates. High-precision, high-accuracy $^{230}Th/^{234}U/^{238}U$ dates and redundant $^{231}Pa/^{235}U$ dates anchor the timing of this $\Delta^{14}C$ record. We propose that a significant fraction of the long-term $\Delta^{14}C$ trend may be due to inaccuracies in the generally accepted ^{14}C decay constant. The uncertainty in estimating the shape of ^{14}C beta spectrum below 20 keV leads to one of the greatest errors in decay constant estimates. Once the ^{14}C half-life is validated via redundant techniques, $\Delta^{14}C$ records will provide a better opportunity to examine the roles of carbon cycle and ^{14}C production influences.

1. Introduction

Long-term variations in atmospheric ^{14}C production are believed to be primarily controlled by the geomagnetic shielding effect (Fig. 1a) (Elsasser et al., 1956; Lal, 1988; Bard et al., 1990) while smaller-scale variations are influenced by solar activity (Stuiver, 1961; Stuiver and Quay, 1980) and short-term carbon cycle changes (Edwards et al., 1993; Hughen et al., 2000). Many studies have been conducted to reconstruct the global paleomagnetic field intensity record using deep-sea sediments (Guyodo and Valet, 1996; Guyodo and Valet, 1999; Laj et al., 2000; Laj et al., 2004). Despite of the difference in length and resolution of individual sediment cores and the uncertainties in their chronologies, the reconstructed paleointensity stacks have a common feature: a decreasing trend in paleointensity from the highest value (close to the modern values) at ~50,000 years BP to the lowest value at ~40,000 years BP (Fig. 1b), corresponding to the well-known Laschamp event when the Earth's field intensity reached very low values.

The ^{14}C production is controlled by the interaction of the Earth's deep interior with cosmic rays produced inside and outside of our solar system (Elsasser et al., 1956; Lal, 1988). The solar wind and the Earth's carbon cycle induce secondary effects. Solar magnetic activity and sunspot occurrence have century-scale and decadal variability and are linked to high-frequency variations in the $\Delta^{14}C$ record (Stuiver, 1961; Stuiver and Quay, 1980). The high-frequency $\Delta^{14}C$ variations are best documented in detailed and continuous tree-ring records (Stuiver et al., 1998; Reimer et al., 2004).

Many studies have debated the role of ocean circulation changes in controlling the $\Delta^{14}C$ anomaly observed during the Younger Dryas climatic event (Edwards et al., 1993; Hughen et al., 1998; Goslar et al., 2000; Muscheler et al., 2000; Marchal et al., 2001) although according to Delaygue

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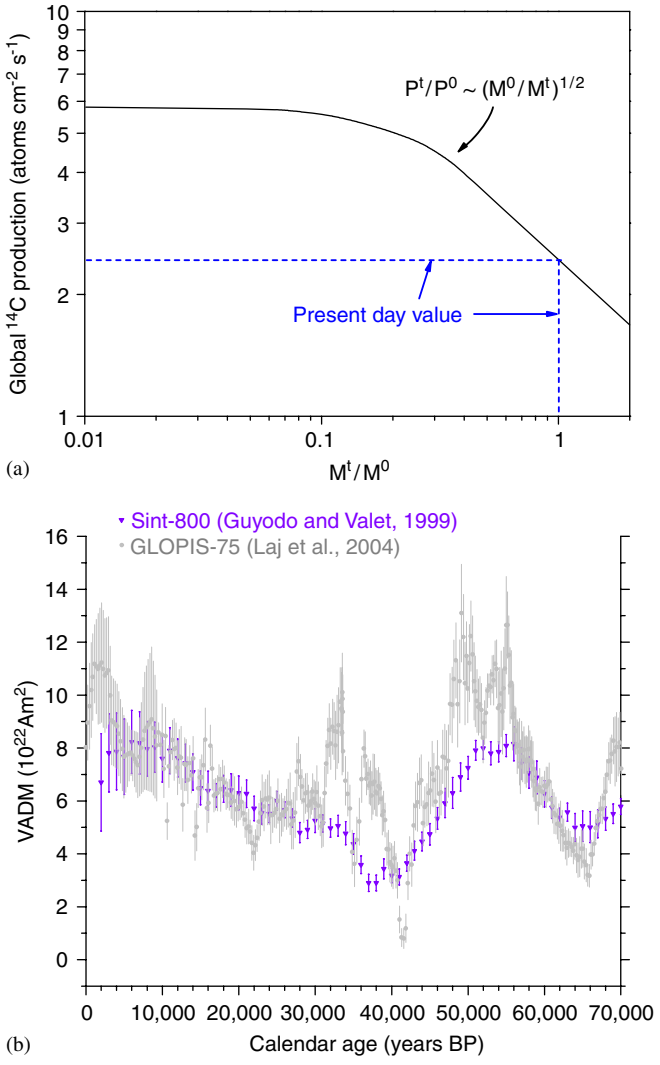

Fig. 1. (a) Graphic representation of the relationship between the global ^{14}C production and the geomagnetic field (Elsasser et al., 1956; Lal, 1988; Bard, 1998). P^0 is modern-day production value. P^t is production value at time t in the past. M^o is modern-day value of geomagnetic field intensity. M^t is the geomagnetic field intensity value at time t in the past. The absolute values may differ based on different physical model calculations (Lal, 1988; Masarik and Beer, 1999). (b) Paleointensity stacks GLOPIS-75 and Sint-800 from 0 to 70,000 years BP. GLOPIS-75 is the extended version of NAPIS-75 (Laj et al., 2000), and its initial chronology was based on GISP2 ice cores. GLOPIS-75 was calibrated to recent archeomagnetic compilation and volcanic data for the past 20,000 years and at the Laschamp event to obtain the absolute values, virtual axial dipole moments (VADMs) (Laj et al., 2004). Sint-800 was extended from Sint-200 (Guyodo and Valet, 1996) and the chronology is mainly based on marine Oxygen Isotope Stages. Sint-800 was converted to absolute values by using volcanic data for the past 40,000 years over 5000-year intervals (Guyodo and Valet, 1999).

et al. (2003), most of them fall short in explaining the magnitude of the Δ^{14}C anomaly. Δ^{14}C variations induced by solar activity and carbon cycle changes become less detectable through time as the Δ^{14}C record loses its resolution due to the increasing relative errors of radiocarbon dating and/or the availability of continuous archived records.

The Δ^{14}C value inherits the uncertainties from both ^{14}C age and calendar age of the dated archive, and thus accurate and precise dating is crucial to reconstructing past atmospheric Δ^{14}C records. Sediment cores at ODP Site 1002, Cariaco Basin, provide a Δ^{14}C record for the past 55,000 years (Hughen et al., 2004). However, ^{14}C dates and calendar age determinations were not obtained from the same materials in the Cariaco Basin cores. The Cariaco Basin record has an estimated calendar age chronology based on correlation of color changes in the sediment with Greenland ice core oxygen isotope record and assignment of tie points using the Greenland ice core age models. Any inaccuracies in the correlation, age model, and number of calendar years between tie points will automatically induce a "trend" in the Δ^{14}C record between tie points. Therefore, uncertainties in the assignment of ice core chronology tie points may generate artificial Δ^{14}C changes that distort the true "amplitude" and "shape" of the Δ^{14}C record. We believe the Cariaco Basin Δ^{14}C record exhibits such short-term Δ^{14}C trends between each set of tie points. If real, they require geochemical and geophysical explanations different from the smoother coral Δ^{14}C record described below.

Fossil corals provide an alternative archive for extending both the ^{14}C calibration (Bard et al., 1990; Cutler et al., 2004; Fairbanks et al., 2005) and atmospheric Δ^{14}C record because both ^{14}C and ^{230}Th/^{234}U/^{238}U ages can be obtained independently from a coral sample with high precision and high accuracy. In this study, we discuss the features and implications of our Δ^{14}C record spanning the past 50,000 years by dating corals from Kiritimati, Barbados, Araki and Santo Islands via ^{230}Th/^{234}U/^{238}U, ^{231}Pa/^{235}U and ^{14}C methods. The original measurements and dates have been reported in Mortlock et al. (2005), Chiu et al. (2005), Fairbanks et al. (2005) and Chiu et al. (2006) (Supplementary Appendix A). Our coral-derived Δ^{14}C record is broadly consistent with the Cariaco Basin Δ^{14}C record, except for the section older than 40,000 years BP, and with published modeled Δ^{14}C based on carbon cycle models using the global ^{14}C production estimates (Beck et al., 2001; Hughen et al., 2004). However, there remain possibly significant short-term departures between the records. In this study, we compare the coral Δ^{14}C record with the very detailed and widely referenced Cariaco Basin Δ^{14}C record (Hughen et al., 2004).

Although it is presumed that paleointensity dominates atmospheric ^{14}C production on longer time scales, model results generally do not reproduce the amplitude of Δ^{14}C observed in various published records without dramatically changing the global carbon budgets and distributions (Beck et al., 2001; Hughen et al., 2004). One explanation for this discrepancy is that the combined uncertainties in the radiocarbon and/or calendar age dating of these archives produce large uncertainties in Δ^{14}C, especially beyond 20,000 years BP. Uncertainties in the absolute values of the paleointensity stacks used in the models and in converting paleointensity to atmospheric Δ^{14}C also lead

to large errors. In addition, we propose that the long-term trend in the $\Delta^{14}C$ record for the past 50,000 years may be biased by the uncertainty of the ^{14}C half-life. For example, an under-estimation of the ^{14}C half-life would produce proportional offsets between the ^{14}C ages and the calendar ages and produce a linear component in $\Delta^{14}C$ record through time. Based on our review of the published data from the 1950s and 1960s used to compute the ^{14}C half-life as well as more recent literature on the measured ^{14}C beta energy spectrum (Selvi and Celiktas, 2002) which challenges assumptions for measurements in the 1950s and 1960s, it is possible that the currently accepted value (''5730 ± 40 years'' accepted in the 1960s) is in error by several percent. If there is a major linear component in the $\Delta^{14}C$ record due to half-life error, then analysis and interpretations of the smaller residual $\Delta^{14}C$ time-series will be significantly different.

2. Material and methods

Coral samples used to reconstruct $\Delta^{14}C$ in this study are from Kiritimati Atoll (2.0°N, 157.8°W) in the central equatorial Pacific, offshore Barbados (13.0°N, 59.5°W) in the western tropical Atlantic, and the uplifted reefs of Araki (15.6°S, 166.9°E) and Santo Islands (15.6°S, 166.8°E), Vanuatu, in the South Pacific (Chiu et al., 2005; Fairbanks et al., 2005).

2.1. A priori sample screening and radiocarbon dating

Secondary calcite, common in fossil corals exposed to vadose fresh water diagenesis, could produce large artifacts in $\Delta^{14}C$ estimates by generally shifting samples' ^{14}C ages to younger values. Thus, coral samples were a priori screened by microscopic observation and by X-ray diffraction (XRD) to avoid diagenetically-altered samples (Burr et al., 1992; Bard et al., 1998; Chiu et al., 2005). Our XRD detection limit of calcite in an aragonite matrix is better than 0.2 wt % (Chiu et al., 2005), and only samples with $<0.2\%$ calcite were included in this study. The complete sample screening criteria are described elsewhere (Fairbanks et al., 2005, 2006).

Radiocarbon dates of coral samples were measured either at the Center of Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory or at the Leibniz Laboratory for Dating and Isotope Analyses, Christian-Albrechts-Universität, Kiel, Germany. Sample pretreatment steps and the target preparation methods are detailed elsewhere (Chiu et al., 2005; Fairbanks et al., 2005).

2.2. $^{230}Th/^{234}U/^{238}U$ dating and a posteriori data screening

All $^{230}Th/^{234}U/^{238}U$ dates of coral samples in this study were obtained by using a multiple-collector ICP-MS (PLASMA 54) at Lamont-Doherty Earth Observatory (LDEO) (Mortlock et al., 2005) (Supplementary Appendix A). Only samples passing the following criteria were included: (1) $\delta^{234}U_{initial}$ of the fossil coral falls within seawater and modern coral range: 138–150 per mil (Edwards, 1988; Hamelin et al., 1991; Henderson et al., 1993; Delanghe et al., 2002; Cutler et al., 2004; Fairbanks et al., 2005). (2) The uranium concentration, [U], falls within the expected range of 2–4 ppm for corals after taking into consideration the coral species (Cross and Cross, 1983). (3) Fossil corals contain only trace amounts of ^{232}Th (no more than several ppb). In addition to these criteria, (4) $^{230}Th/^{234}U/^{238}U$ ages of 10 samples in the age range of 30,000–50,000 years BP were confirmed by redundant $^{231}Pa/^{235}U$ ages (Mortlock et al., 2005; Chiu et al., 2006).

3. Results

3.1. The definition of $\Delta^{14}C$

Past atmospheric ^{14}C concentration can be obtained from the calendar age and ^{14}C age of a sample. $\Delta^{14}C$ (‰) is the notation to represent the departure from modern pre-industrial atmospheric ^{14}C concentration and normalized for mass dependent fractionation (Stuiver and Polach, 1977). By convention, the isotopic value of wood in 1850 is regarded as the pure modern value (i.e. without fossil fuel dilution or thermonuclear bomb ^{14}C enrichment).

$\Delta^{14}C$ (‰) is calculated as followed:

$$\Delta^{14}C\ (‰) = \left(\frac{EXP(\lambda_1 * t_1)}{EXP(\lambda_C * t_C)} - 1\right) 1000(‰). \quad (1)$$

(after Stuiver and Polach, 1977), where λ_1 is the decay constant of the correct ^{14}C half-life, accepted by convention to be 5730 years (Godwin, 1962); t_1 is calendar age ($^{230}Th/^{234}U/^{238}U$ age in this study) (years before 1950); λ_C is ^{14}C decay constant used in conventional ^{14}C age where ''5568 years'' is universally adopted as ^{14}C half-life (Libby, 1955); t_C is the reservoir age-corrected conventional ^{14}C age based on a half-life value of 5568 years (years before 1950).

3.2. Atmospheric $\Delta^{14}C$ record from 0 to 50,000 years BP using fossil corals

Atmospheric $\Delta^{14}C$ values in this study were computed based on Eq. (1) using paired $^{230}Th/^{234}U/^{238}U$ and ^{14}C dates obtained from fossil corals from Kiritimati, Barbados, Araki and Santo Islands (Fairbanks et al., 2005) (Supplementary Appendix A; Fig. 2). Detailed reservoir age determination is described in Fairbanks et al. (2005). The uncertainty of our ^{14}C reservoir correction is not included in the following error analysis of $\Delta^{14}C$, but is speculated to vary by less than ±100 years (see http://radiocarbon.LDEO.columbia.edu for a global map of surface ocean reservoir ages), which is not significant in $\Delta^{14}C$ estimates older than 30,000 years BP.

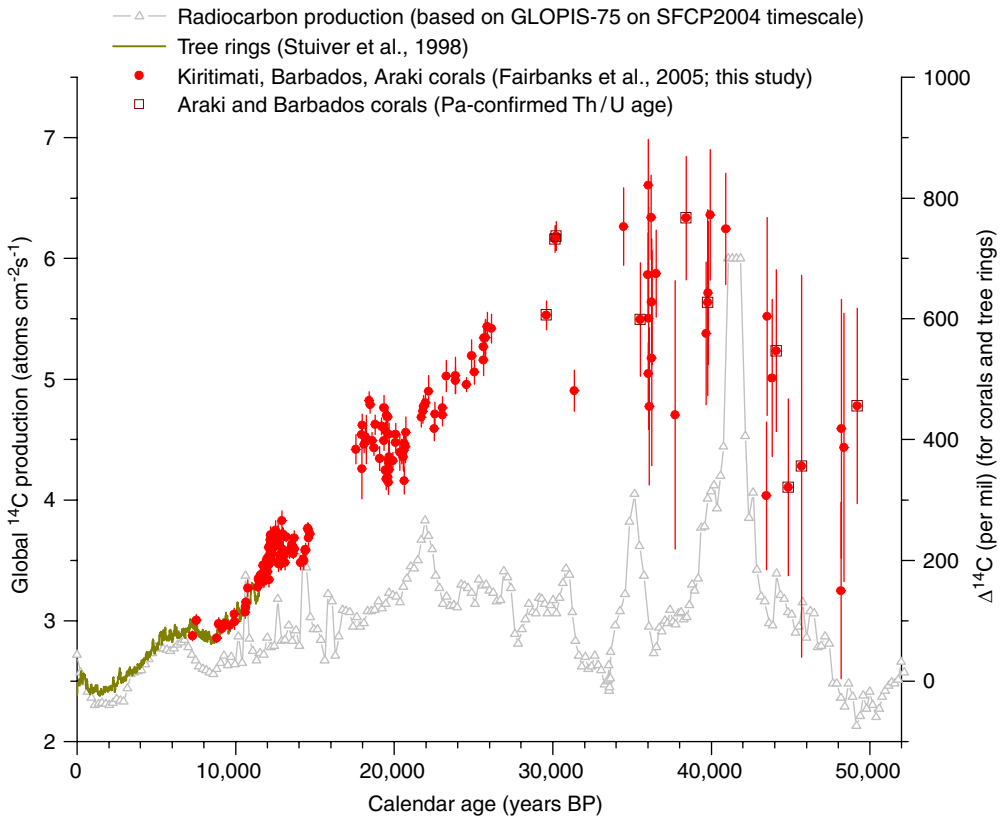

Fig. 2. Atmospheric $\Delta^{14}C$ record for the past 50,000 years based on fossil corals from Kiritimati, Barbados and Araki Islands. The error bars of $\Delta^{14}C$ represent two-sigma uncertainties, which include analytical uncertainties from both ^{14}C and $^{230}Th/^{234}U/^{238}U$ dating. Hollow squares represent ten samples whose U-series ages have been confirmed by redundant $^{231}Pa/^{235}U$ and $^{230}Th/^{234}U/^{238}U$ methods (Mortlock et al., 2005; Chiu et al., 2006). Yellow-green line represents $\Delta^{14}C$ values obtained from tree rings (Stuiver et al., 1998). Gray hollow triangles represent the global ^{14}C productions estimated from the paleointensity stack GLOPIS-75 (Laj et al., 2004), which was adjusted to fit the SFCP2004 time scale (Shackleton et al., 2004) in this figure for comparison purpose, using the approximated relationship between geomagnetic field intensity and the global ^{14}C production (Elsasser et al., 1956; Lal, 1988; Bard, 1998) (see Fig. 1a). The error bars in the global ^{14}C production are ignored for simplicity.

The coral $\Delta^{14}C$ record displays a relatively smooth increase from values of 100 per mil at about 10,000 years BP to ~400 per mil at 20,000 years BP. $\Delta^{14}C$ values reach as high as ~800 per mil during the time period 35,000 to 40,000 years BP and gradually drop to 300–400 per mil between 45,000 and 50,000 years BP (Fig. 2).

Coral $\Delta^{14}C$ values inherit the uncertainties of both $^{230}Th/^{234}U/^{238}U$ and ^{14}C dates. The relative precision of the $^{230}Th/^{234}U/^{238}U$ date, mainly controlled by the precision of ^{230}Th measurement, improves in older samples because more of the daughter product, ^{230}Th, is present. The error estimates of $\Delta^{14}C$ values increase rapidly between 35,000 and 50,000 years BP almost entirely due to the uncertainties in the measured ^{14}C ages. The two-sigma analytical uncertainty in the ^{14}C dates of samples in this age range is typically between 500 and 1200 years and produces a two-sigma uncertainty of about $\pm$100–240 per mil in $\Delta^{14}C$ (Fig. 3). In the younger part of the $\Delta^{14}C$ record (10,000 to 30,000 years BP), the age uncertainty in ^{14}C dating averages less than 100 years (2σ) which corresponds to an uncertainty of less than 30 per mil for $\Delta^{14}C$ (Fig. 3).

4. Discussions

4.1. Small-scale atmospheric $\Delta^{14}C$ anomaly: solar variability and short-term carbon cycle changes

The $\Delta^{14}C$ records obtained from tree-rings provide decadal resolution of $\Delta^{14}C$ variations, and it has been demonstrated that the solar activity minimum corresponds to a positive $\Delta^{14}C$ anomaly of about 10–20 per mil during the Holocene (Stuiver and Quay, 1980). Based on box model calculations (Oeschger et al., 1975), a 50% reduction of deepwater formation produces an anomaly of ~30 per mil in $\Delta^{14}C$. A $\Delta^{14}C$ anomaly of several hundred per mil is unlikely generated by short term carbon cycle changes such as those during the Younger Dryas event (Hughen et al., 1998; Marchal et al., 2001; Delaygue et al., 2003) unless long term variations or extreme conditions of carbon cycle are modeled (models "C" and "D" in Beck et al., 2001; model "d" in Hughen et al., 2004).

Solar variability and the short-term carbon cycle changes, operating at all time scales, modulate ^{14}C production and inventory in the atmosphere, respectively,

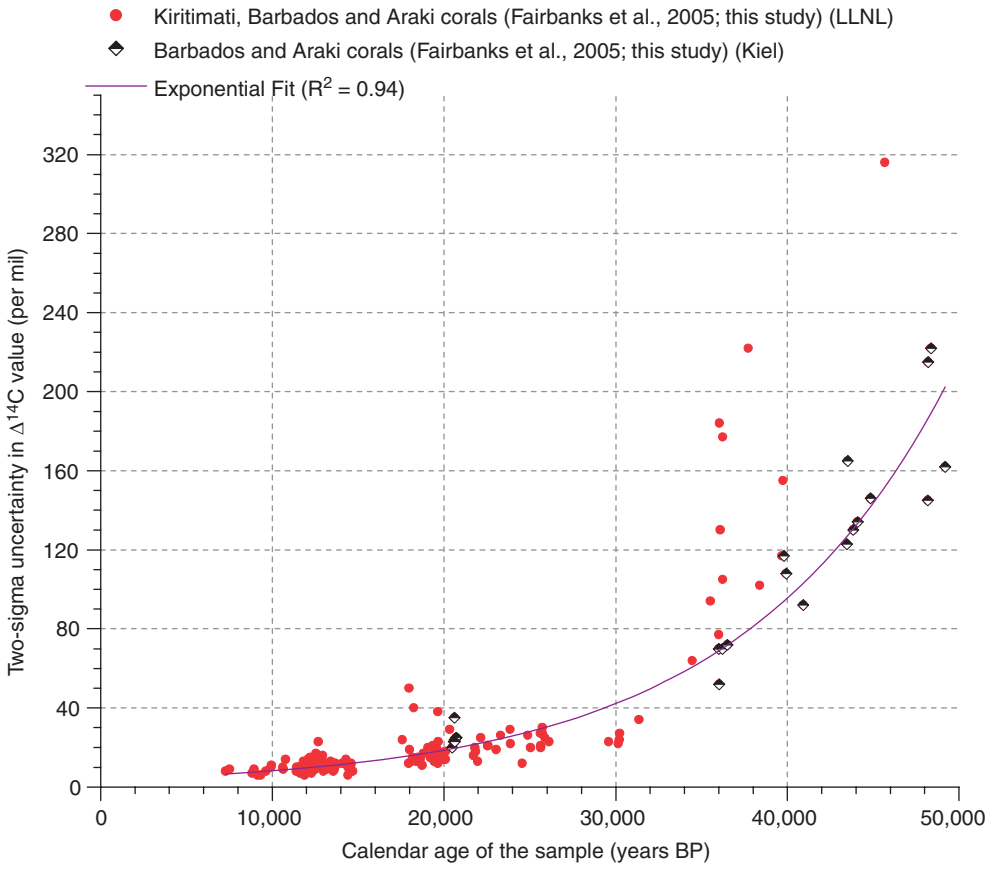

Fig. 3. The calendar age versus the two-sigma uncertainty of the $\Delta^{14}C$ value in our coral record. The uncertainty of $\Delta^{14}C$ inherits the analytical uncertainties from both ^{14}C dating and the determination of calendar age, $^{230}Th/^{234}U/^{238}U$ dating in our case. The curve is an exponential fit of the reported errors in our coral record. For the time period older than 32,000 years BP, only Kiel ^{14}C dates were included in the curve fitting. Although both solar variability and short-term changes in carbon cycle control atmospheric ^{14}C concentration for all time scales, $\Delta^{14}C$ record beyond 30,000 years BP is unlikely to resolve these two influences due to uncertainties in the estimated $\Delta^{14}C$ values.

but measured $\Delta^{14}C$ values in archived samples older than 30,000 years BP are unlikely to resolve their contributions due to the uncertainty in $\Delta^{14}C$ estimates (Fig. 3). Factors other than solar variability and short-term carbon cycle are responsible for at least part of the observed long-term trend in atmospheric $\Delta^{14}C$ for the past 50,000 years and the high $\Delta^{14}C$ values (up to 800 per mil) observed between 30,000 and 50,000 years BP in our record (Fig. 2). Understanding the causes of the $\Delta^{14}C$ trend in the record and overall shape and amplitude of the $\Delta^{14}C$ record are the main objectives of this paper.

4.2. The long-term trend in atmospheric $\Delta^{14}C$

4.2.1. Effect of the geomagnetic field

Atmospheric ^{14}C is produced from the interaction of cosmic rays with ^{14}N. The global ^{14}C production is negatively correlated to the geomagnetic field because the geomagnetic shielding effect reduces the amount of cosmic rays entering the atmosphere. However, the relationship is not linear. For example, when the absolute value of geomagnetic field intensity decreases below 20% of the modern value, any further decrease in the field intensity causes little additional change in global ^{14}C production (Fig. 1a) (Elsasser et al., 1956; Lal, 1988; Bard, 1998).

The atmospheric $\Delta^{14}C$ record beyond 30,000 years BP has been an intriguing topic for the following reasons. Different archives do not exhibit the same $\Delta^{14}C$ variations beyond 30,000 years BP, and there is no commonly accepted explanation for the high atmospheric $\Delta^{14}C$ values (Beck et al., 2001; Hughen et al., 2004) recorded in most archives. Beck et al. (2001) and Hughen et al. (2004) used box models to try to interpret their $\Delta^{14}C$ records from a Bahamian speleothem and sediment cores from the Cariaco Basin, respectively. These authors were unable to generate atmospheric $\Delta^{14}C$ larger than ~400 per mil in model simulations based on paleointensity-calculated ^{14}C production and fixed or modern carbon cycle conditions (see model "A" in Beck et al., 2001 and model "a" in Hughen et al., 2004). Although our coral $\Delta^{14}C$ estimates are based on high-precision and high-accuracy dating methods (Mortlock et al., 2005; Fairbanks et al., 2005), our record also yields $\Delta^{14}C$ values as high as ~800 per mil between 35,000 to 40,000 years BP (Fig. 4). A $\Delta^{14}C$ value of ~800 per mil is much larger than model predictions allow unless the carbon cycle parameters are adjusted to extreme values.

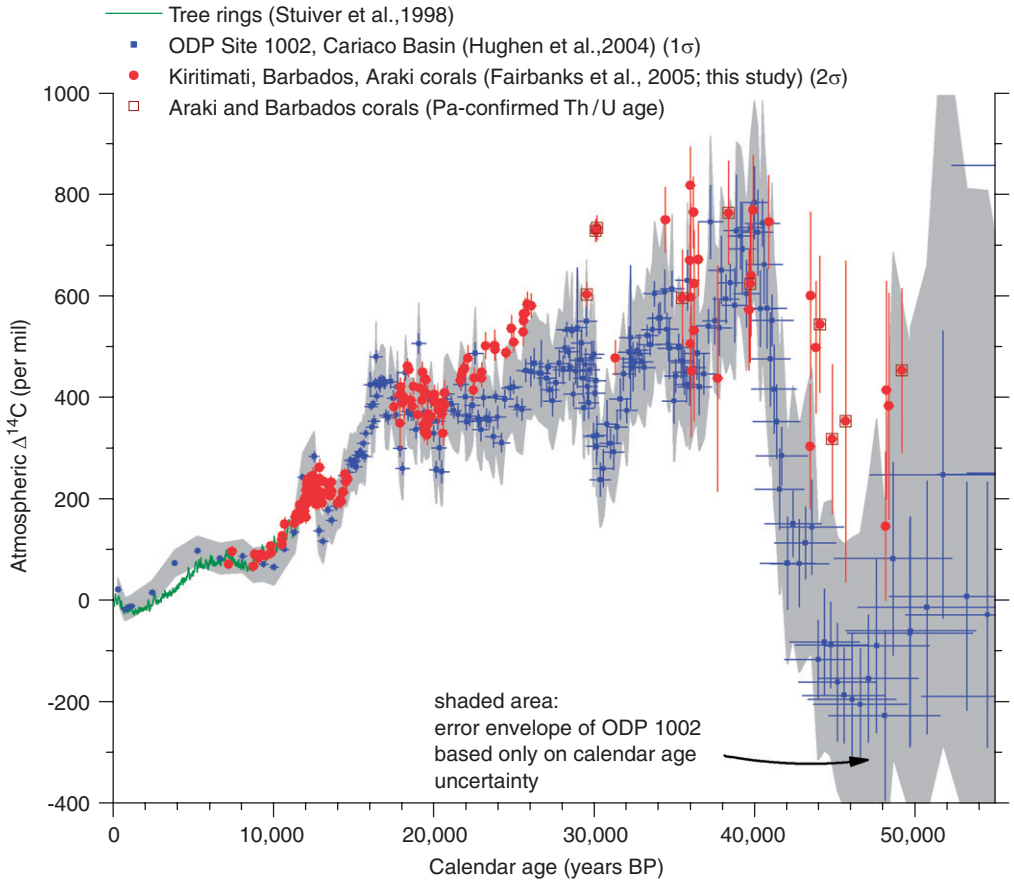

Fig. 4. The comparison of atmospheric $\Delta^{14}C$ for the past 50,000 years from a deep sea core record, ODP Site 1002, in Cariaco Basin (Hughen et al., 2004) with our fossil coral record (Fairbanks et al., 2005). Red solid circles are our coral $\Delta^{14}C$ values with 2σ error, including the analytical uncertainties from both ^{14}C dating and $^{230}Th/^{234}U/^{238}U$ dating. Hughen et al. (2004) did not report the total uncertainties of the $\Delta^{14}C$ values; instead, errors derived from ^{14}C dating and calendar age determination were reported separately. Blue squares are the $\Delta^{14}C$ values from ODP Site 1002 in the Cariaco Basin with "1σ" error of $\Delta^{14}C$ based only on analytical uncertainty from ^{14}C dating (Hughen et al., 2004). The gray envelope represents the range of $\Delta^{14}C$ values of the Cariaco Basin record when only the error of calendar age, based on GISP2 ice core chronology (Meese et al., 1997), is considered (Hughen et al., 2004). Neither the gray envelope nor blue crosses represent the true (total) uncertainties of the $\Delta^{14}C$ values.

For example, Beck et al. (2001) model (C) manages to produce $\Delta^{14}C$ values of about 600–800 per mil during 45,000 to 35,000 years BP, but only when the carbonate sedimentation rate is reduced to 12% of the modern value until 25,000 years BP and allowed to gradually be increased and resumed at 11,000 years BP. None of Hughen et al. (2004)'s model results could produce $\Delta^{14}C$ values of ~800 per mil even after a 50% reduction in surface-deep ocean exchange rate and 90% reduction of carbon flux into shallow marine carbonate sediments. Thus, the discrepancies between measured $\Delta^{14}C$ and modeled $\Delta^{14}C$ remained unresolved.

The "Laschamp event" is the largest and best-documented geomagnetic event recorded during the past 50,000 years (Guyodo and Valet, 1996; Laj et al., 2000). Earlier K–Ar and ^{40}Ar–^{39}Ar dating of the type localities yielded ages of about 46,200 ± 2,500 years old (Hall and York, 1978; Gillot et al., 1979; Guillou et al., 2004); however, recent K–Ar and ^{40}Ar–^{39}Ar dates from type locality lava flows suggest that the most probable age for the Laschamp excursion is 40,400 ± 2,000 years ago (2σ) (Guillou et al., 2004). The geomagnetic anomaly in Lake Lisan sediments dated at ~41,900 years ago, identified as Laschamp event (Marco et al., 1998; Haase-Schramm et al., 2004), is consistent with Guillou et al. (2004) age estimate. Based on the relationship between geomagnetic field intensity and ^{14}C production (Fig. 1a), an atmospheric $\Delta^{14}C$ increase associated with the transition into the Laschamp event would be expected.

Our coral $\Delta^{14}C$ record shows a general increase from 50,000 to 40,000 years BP, which corresponds to the increase in the global ^{14}C production culminating in the Laschamp event (Fig. 2). The "excess ^{14}C" produced during the Laschamp event enters the Earth's reactive carbon cycle and is removed over time primarily through exponential radioactive decay and secondarily via burial (Oeschger et al., 1975). A geomagnetic excursion that occurs subsequent to the Laschamp event would produce a rapid increase of ^{14}C followed by a relatively slow decay that is superimposed on the long-term decay of the early but larger Laschamp event.

Similarly, the Laschamp event has been recognized in the GRIP ice core record using the peak in ^{36}Cl flux dated at ~38,000 years BP (Baumgartner et al., 1998; Muscheler et al., 2005). It can also be identified in high-resolution paleointensity records obtained from deep-sea cores such as NAPIS-75 paleointensity stack (Laj et al., 2000) and its extended version, GLOPIS-75, dated at ~41,000 years BP (Laj et al., 2004). Note, however, that both NAPIS-75 and GLOPIS-75 share the same GISP2-based chronology (Fig. 1b). While ^{36}Cl fluxes determined in ice cores and paleointensity stacks obtained from deep sea cores allow the identification of the Laschamp excursion, limits in the precision and accuracy of ice core chronologies and unresolved differences between them (Johnsen et al., 2001; Southon, 2002; Svensson et al., 2006) do not permit precise absolute dating of this event, evidenced by the discrepancy between ~38,000 and ~41,000 years BP.

4.2.2. *Comparison between coral Δ^{14}C record and the Cariaco Basin Δ^{14}C record*

Sediment cores from the Cariaco Basin ODP Site 1002 provide a remarkably detailed Δ^{14}C record for the past 55,000 years BP (Hughen et al., 2004) (Fig. 4). Cariaco Basin is less than 300 kilometers away from Barbados, and for this reason, we are compelled to compare the similarities and differences between the Cariaco Basin Δ^{14}C record and our coral Δ^{14}C record. There are significant similarities between the Cariaco Basin Δ^{14}C record and our coral Δ^{14}C record. The Cariaco Basin Δ^{14}C record shows an increasing trend from 50,000 to 40,000 years BP and then a gradual decreasing trend to the present, very similar to that obtained from our coral data (Fig. 4). Both records peak at 700 per mil of Δ^{14}C value coinciding with the age of the Laschamp geomagnetic event (Fig. 4). There are fine-scale structures in the Cariaco Basin Δ^{14}C record which are not observed in the coral Δ^{14}C record, especially in the section older than ~25,000 years BP (Fig. 4). In large part, this is due to the sparse coral data compared to the much more detailed Cariaco Basin Δ^{14}C time-series. Although our coral data overlap the Cariaco Basin Δ^{14}C record error envelope over the entire record (Fig. 4), coral Δ^{14}C values are consistently higher than Cariaco Basin Δ^{14}C values in the 44,000 to 50,000 years BP time interval.

The GISP2 calendar ages (Meese et al., 1997) were assigned to the Cariaco Basin core and its ages were linearly interpolated between these tie points (Hughen et al., 2004). The resulting accumulation rates vary between 14 to 88 cm/kyr over short depth intervals (Fig. 5). Importantly, between every pair of tie points, the slope of the Cariaco Basin Δ^{14}C versus age plot changes, sometimes quite significantly (Fig. 5). This is expected if the estimated total number of calendar years for the interval is too few or too many compared to the true number of calendar years. It can be shown that when the estimated number of years is too few (many), the Δ^{14}C will artificially decrease (increase) with increasing age for that particular interval (Fig. 5). One

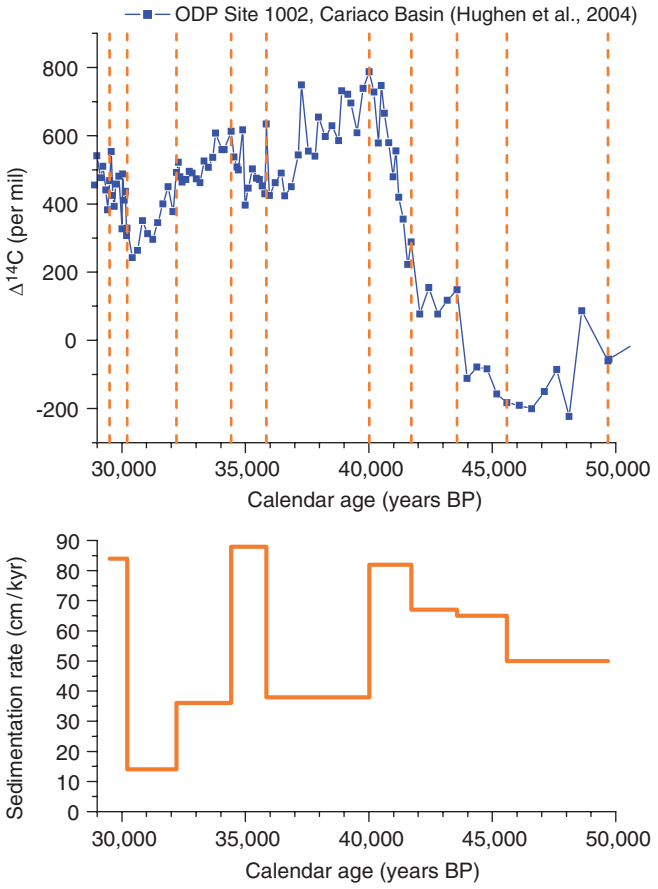

Fig. 5. Comparison between Δ^{14}C record of ODP Site 1002, Cariaco Basin (Hughen et al., 2004) and the sedimentation rates derived from the original GISP2-based calendar age chronology. Dash lines in the upper panel correspond to the ice core chronology tie points identified by changes in sedimentation rates in the original data in Hughen et al. (2004).

way to illustrate the sensitivity of Δ^{14}C to inaccurate tie points is to assign tie point ages using different ice core chronologies (Southon, 2002) or using different tie points from the same ice core, and to note the change in Δ^{14}C anomalies and trends that start and end at the new tie points.

In ODP Site 1002 cores, reported ^{14}C ages were measured on planktonic foraminifera and were corrected by Hughen et al. (2004) assuming a local reservoir age of 420 years. We can now independently estimate the accumulation rates of Cariaco Basin cores by converting the measured ^{14}C ages to calendar ages (listed in Supplementary Appendix B) using Fairbanks et al. (2005)'s radiocarbon calibration program. The results show that the sedimentation rate in ODP 1002 is nearly constant and averages 47 cm/kyr (Fig. 6). In order to illustrate the *potential* effect of inaccurate calendar age estimates on Δ^{14}C values, we selected the Cariaco Basin Δ^{14}C record between 40,000 to ~46,000 years BP and recalculated the Δ^{14}C values during this time period (Fig. 7) using our ^{14}C calibration ages (Supplementary

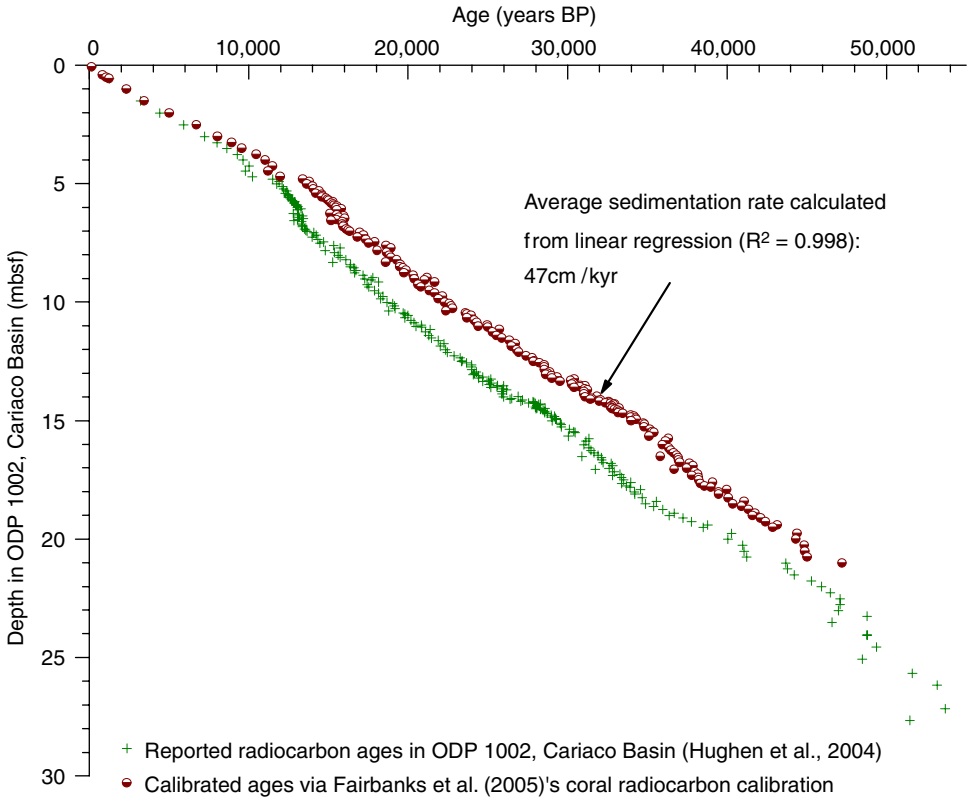

Fig. 6. "Depth versus ^{14}C age (and calibrated age)" plot for the deep sea core at ODP Site 1002, Cariaco Basin. Green crosses are reservoir age-corrected ^{14}C dates of planktonic foraminifera reported in Supplemental Documentation of Hughen et al. (2004). We have calibrated these reported ^{14}C ages to calendar ages (half-filled circles) using Fairbanks et al. (2005)'s coral radiocarbon calibration program. The calibrated ages are listed in Supplementary Appendix B.

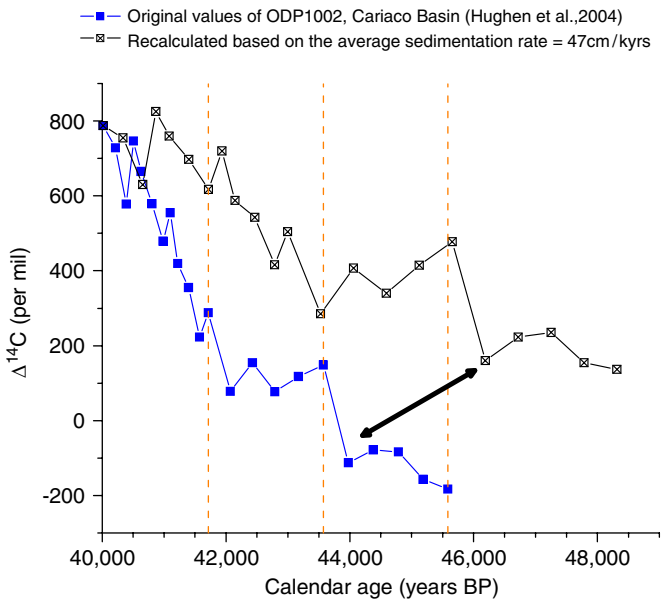

Fig. 7. The effect of changes in sedimentation rates on $\Delta^{14}C$ values in ODP 1002 during 40,000 to ~46,000 years BP. The original data (blue squares) in Hughen et al. (2004) had ice core chronology tie points marking approximately three changes in sedimentation rates (dash lines). The $\Delta^{14}C$ record is significantly different when the calibrated ^{14}C ages, via Fairbanks et al. (2005)'s coral radiocarbon calibration program, are used (cross-filled squares). The changes in "amplitude" and "shape" of the $\Delta^{14}C$ signal cause a shift of this record in a diagonal direction (thick black arrow).

Appendix B) (Fig. 6). Although this age model is a reasonable choice, it is selected only to illustrate the following point. Using this revised age model, the peak amplitude of Cariaco Basin $\Delta^{14}C$ variation is decreased significantly from ~1000 to ~700 per mil (Fig. 7). Importantly, this example also shows that a correction to the calendar age results in a *diagonal shift* in the $\Delta^{14}C$ values indicated by the upward revised Cariaco Basin $\Delta^{14}C$ estimates between 41,000 and 48,000 years BP (Fig. 7).

Analysis of the Cariaco Basin $\Delta^{14}C$ record suggests that some of the differences from our coral record may be generated as a result of the age model adopted for the Cariaco Basin cores, particularly for the 40,000 to 50,000 years BP interval (see Hughen et al., 2004). Application of the latest Greenland ice core chronology by Svensson et al. (2006) would reduce the $\Delta^{14}C$ differences between Cariaco Basin and our coral $\Delta^{14}C$ record. In addition, the miss-assignment of calendar ages, if any, in Cariaco Basin cores could lead to artificial $\Delta^{14}C$ fluctuations, incorrect amplitude of the $\Delta^{14}C$ signal, and shifts in the time-series. For example, substitution of the GRIP or North GRIP ice core age models (Johnsen et al., 2001; Svensson et al., 2006) and/or different tie points leads to different $\Delta^{14}C$ trends between tie points and different $\Delta^{14}C$ amplitudes illustrating the sensitivity of the fine-structure of $\Delta^{14}C$ record to accurate age estimates.

4.3. The uncertainty of ^{14}C half-life

The long-term trend in $\Delta^{14}C$ culminating in extremely high $\Delta^{14}C$ values observed around 40,000 years BP (Fig. 2) (Beck et al., 2001; Hughen et al., 2004; Fairbanks et al., 2005) is difficult to explain by ^{14}C production and various carbon cycle scenarios according to Beck et al. (2001) and Hughen et al. (2004). More intriguingly, the coral radiocarbon calibration curve of Fairbanks et al. (2005) seems strikingly linear—over the entire 50,000 year time span, the differences between the paired coral ^{14}C ages and the $^{230}Th/^{234}U/^{238}U$ ages increase proportionately with time. The "selection" of the ^{14}C half-life value is one parameter that would create a "proportional offset" between the calendar age and the ^{14}C age and leads us to an analysis of the accuracy of the Godwin (1962) ^{14}C half-life, 5730 ± 40 years. In the following section, we review the potential sources of error in computing the Godwin (1962) ^{14}C half-life. We conclude that there is sufficient uncertainty, on the order of several percent, to warrant re-measurement of the ^{14}C half-life using ion counting and other simplified, independent methods such as the calorimetry technique until concordant results are obtained.

4.3.1. The accuracy of ^{14}C half-life measurements

"Conventional ^{14}C age" reported in the literature and from radiocarbon dating laboratories is currently based on the definitions in Stuiver and Polach (1977) using a ^{14}C half-life value of 5568 years (Libby, 1955). The value of 5568 years was later proved inaccurate based on multiple measurements in the 1960s (Godwin, 1962) that indicated that the half-life was several hundred years older (Table 1). After the Fifth Radiocarbon Dating Conference at Cambridge, a consensus value, 5730 ± 40 years, was proposed (Godwin, 1962) based on newly published determinations of the ^{14}C half-life by Mann et al. (1961), Watt et al. (1961) and Olsson et al. (1962). Godwin (1962) stated, "Inasmuch as further experiments may lead to an even more reliable result, we recommend, as a temporary expedient, that radiocarbon age results continue to be reported on the basis of the 'Libby half-life' 5568 yr used heretofore." This statement acknowledged that "5730 years" was considered an improvement, but concerns with the methodologies and the spread in half-life measurements (Table 1) appeared to prevent the new consensus value from being adopted. The latest determination of the ^{14}C half-life was "5660 ± 30 years" (Bella et al., 1968), and to our knowledge no additional measurement was published after that study. Archaeologists and paleoclimatic scientists, among the principle users of radiocarbon dates, may not have considered it crucial to know the half-life with great accuracy because conventional ^{14}C ages are routinely converted to calendar ages using calibration data sets. In principle, as long as radiocarbon calibration curves such as the tree ring/varved sediment/coral-based curve (InCal04; Reimer et al., 2004), the tree ring/coral-based calibration of Fairbanks et al. (2005), and the composite curve CalPal (Jöris and Weninger, 2000; Weninger and Jöris, 2004) are readily available, any conventional ^{14}C age can be converted to an estimated calendar age regardless of what value of ^{14}C half-life is used in the calculation. However, it is essential to know the ^{14}C half-life accurately when interpreting the geochemical and geophysical causes of $\Delta^{14}C$ fluctuations in the past.

A review of the history of the determination of ^{14}C half-life reveals that values anywhere between 4700 to 7200 years have been reported (Fig. 8) (Libby, 1955; Mann et al., 1961; Watt et al., 1961; Olsson et al., 1962; Bella et al., 1968). Earlier gas counter measurements (in the late 1940s and early 1950s) seem to cluster into two groups: ~5600 years and ~6400 years. Each methodology had its own inherent sources of error, and assumptions pertaining to the shape of the beta spectrum, and most were subject to significant instrumental bias or ^{14}C contamination in the gas splitting steps (Miller et al., 1950; Libby, 1955). The most recent measurements of ^{14}C half-life were made in the 1960s using gas counters (Mann et al., 1961; Watt et al., 1961; Olsson et al., 1962; Bella et al., 1968), and a value of "5730 ± 40 years" was proposed based on the first three publications. This consensus value, 5730 ± 40 years, was considerably less than the reported ^{14}C half-life based on the calorimetry technique, 6030 years (Jenks and Sweeton, 1952) (Fig. 8). The calorimetry method of half-life measurement is today a technique favored by some investigators because its simplicity generally leads to accurate results. The main assumption in calorimetry measurements of the ^{14}C half-life is the average energy of β-decay. Clearly, the most convincing result would be the determination of the ^{14}C half-life by various methods that yield the same value, which unfortunately is not the case

Table 1
Measurements of ^{14}C half-life by gas counters in the 1960s

Reference source	Reported ^{14}C half-life (years)	Note
Mann et al. (1961)	5760 ± 50[a]	Mann's regressions for counter wall effect ($R^2 = 0.14-0.25$)
Mann et al. (1961)	~6200	Discarded by Mann et al.
Mann et al. (1961)	5810 ± 62	The average value of Mann's reported data (see Fig. 9)
Watt et al. (1961)	5780 ± 65[a]	
Olsson et al. (1962)	5680 ± 40[a]	
Bella et al. (1968)	5660 ± 30	

[a]Represent the data included in the calculation for the consensus ^{14}C half-life (Godwin, 1962) (also see Fig. 8).

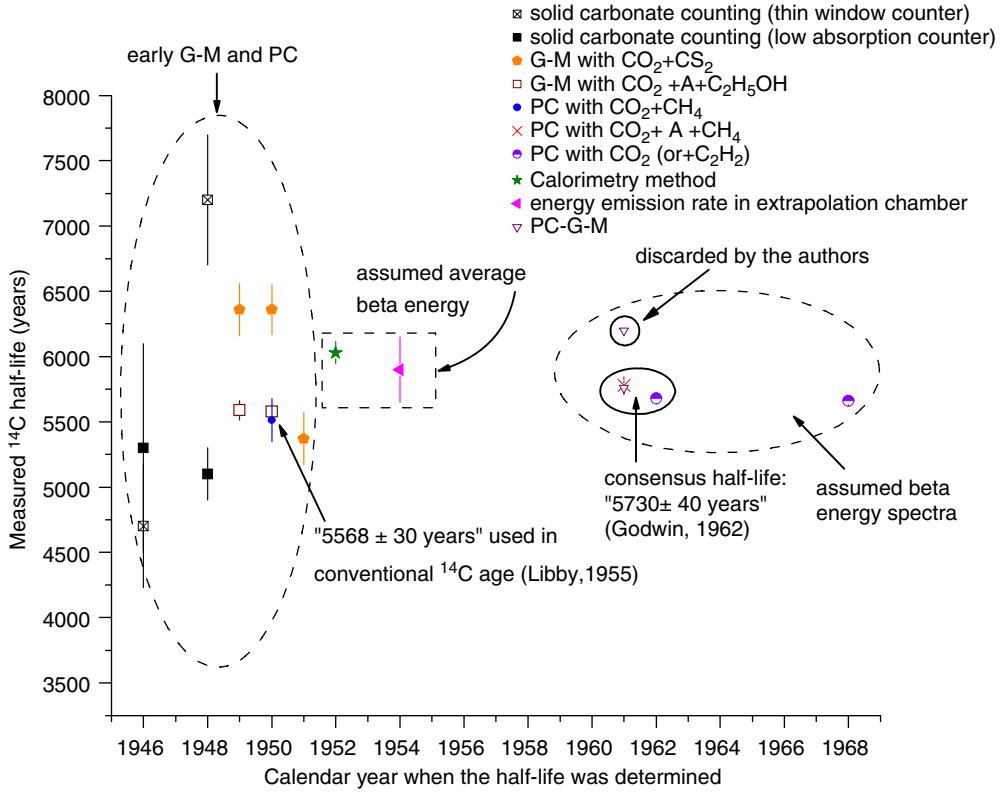

Fig. 8. Summary of the published measurements of the ^{14}C half-life (Jenks and Sweeton, 1952; Caswell et al., 1954; Libby, 1955; Mann et al., 1961; Watt et al., 1961; Olsson et al., 1962; Bella et al., 1968). Data points and error bars were taken or calculated from the original publications or from the summary tables in Libby (1995) and Watt et al. (1961). "PC" denotes proportional counter. "G–M" denotes Geiger-Müller counter. "PC–G-M" denotes measurements made in both proportional and Geiger-Müller regions of the counter (Mann et al., 1961). "A" denotes argon gas. A value of "5730±40" years was determined to be the best estimate based on contemporary measurements (Mann et al., 1961; Watt et al., 1961; Olsson et al., 1962) during the Fifth Radiocarbon Dating Conference in 1960s (Godwin, 1962).

for reported ^{14}C half-life values. This observation alone warrants new measurements of the ^{14}C half-life via multiple techniques.

4.3.2. *Gas-counter measurements of ^{14}C half-life and sources of error*

The accuracy of gas counter measurements made in the 1960s were limited by: (1) the significant adsorption of $^{14}CO_2$ gas during combustion and dilution steps of the highly enriched sample; (2) the counter end effect; and (3) the counter wall effect (Mann et al., 1961; Watt et al., 1961; Olsson et al., 1962; Olsson and Karlén, 1963).

The radioactive source for ^{14}C half-life measurements was usually $^{14}CO_2$ gas generated from barium carbonate. Typically a 10^8 to 1 dilution of the high specific activity CO_2 was required to lower the count rate to the working range of gas proportional counters. Gas splitting proved to be a large source of error due to adsorption in the gas handling system that contaminated subsequent dilution fractions. This "adsorption" problem produced an elevated disintegration rate in the final dilution in a gas counter, and thus potentially biased the ^{14}C half-life towards lower values. Mann et al. (1961) initially obtained two unreasonably low measured values, 4745 and 4595 years, for ^{14}C half-life. They suspected these low values were due to the adsorption of high-specific-activity CO_2 prior to the first dilution, and subsequently conducted a "blank" mixing experiment to test their hypothesis. They found that the background count rate of this testing "blank" was ~20 times more than the normal background. From the blank experiment, Mann et al. (1961) calculated as much as a 30% increase in count rates caused by only a 0.02% of adsorption of the high-specific-activity CO_2. Corrections for the adsorption could raise their measured ^{14}C half-life value from 4600 years to 6570 years. Watt et al. (1961) carried out a blank experiment after each run to assure there was no contamination in the system. Runs with measurable contamination were excluded from their pool data. Olsson et al. (1962) argued that a monomolecular layer corresponded to $\sim 10^{15}$ molecules per cm^2, and adsorption could result in "a sheet of several layers" of molecules. Post analysis, Olsson et al. (1962) applied a back correction term based on their adsorption estimation experiment and theoretical considerations. Although these authors conducted the adsorption check experimentally or made post-measurement corrections, gas adsorption in the gas spitting system remained one of the most challenging problems and the largest source of error in these

measurements (Watt et al., 1961; Olsson et al., 1962), primarily because the corrections were difficult to constrain or the problem was not identified until the experiment was completed.

Two common sources of error specific to the geometries of the counters used are known as the "end effect" and "wall effect." "End effect" is the phenomenon in which the electrical field approaching the end of the counter is so weak that radiations appearing in the gas are not recorded (Libby, 1955). It primarily depends on the length–diameter ratio of the counter and can be estimated without too much difficulty by comparing two counters with different length but the same diameter (Libby, 1955). "Wall effect" is the phenomenon where some radioactive CO_2 molecules disintegrating near the wall of the counter either fail to produce a free electron in the gas or fail to excite one or more from the wall. The "wall effect" contribution is proportional to surface-volume ratio of the counter (Libby, 1955). There were other routine but important parameters such as dead time and discriminator setting of the gas counter which potentially introduced minor sources of error (Mann et al., 1961; Watt et al., 1961).

Since the "wall effect" results from the gas molecules that fail to produce electrons or fail to excite one from the wall of the counter, this problem could be eliminated if there were an infinitely large pressure of gas with sufficient energy in the counter. Thus, one conventional way to correct for the "wall effect" in the 1960s half-life experiments was to project a hypothetical value for infinite pressure based on measurements made over a limited range of pressures. However, projections for corrections due to the "wall effect" were problematic because they were made somewhat subjectively. Figs. 9 and 10 illustrate how values at infinite pressure were estimated in Mann et al. (1961) and Olsson et al. (1962), respectively, during their ^{14}C half-life measurements.

In the case of Mann et al. (1961), both copper and stainless-steel counters and both proportional and Geiger–Müller regions were used to make the measurements in the half-life experiment (Fig. 9). The authors did not separate the measurements from proportional and Geiger–Müller regions for regression purposes, but they did separate results from copper and stainless-steel counters (Fig. 9). Several data points in Fig. 9 were excluded from their regression because of inconsistent results from the samples with copper versus stainless-steel counters and an inappropriate discriminator correction, according to Mann et al. (1961). A complete series of their earlier measurements which led to a half-life value of ~6200 years were also excluded and the data were not reported (Mann et al., 1961). Mann et al. (1961) speculated that possible ethyl ether and/or grease contamination contributed to the "6200 years" half-life value based on new peaks in the mass-spectrometric analyses and a grey film observed on the flask for the condensed CO_2 sample and subsequently reported the ^{14}C half-life as "5760 ± 50 years." We digitized Mann et al. (1961)'s data selection and reconstructed their

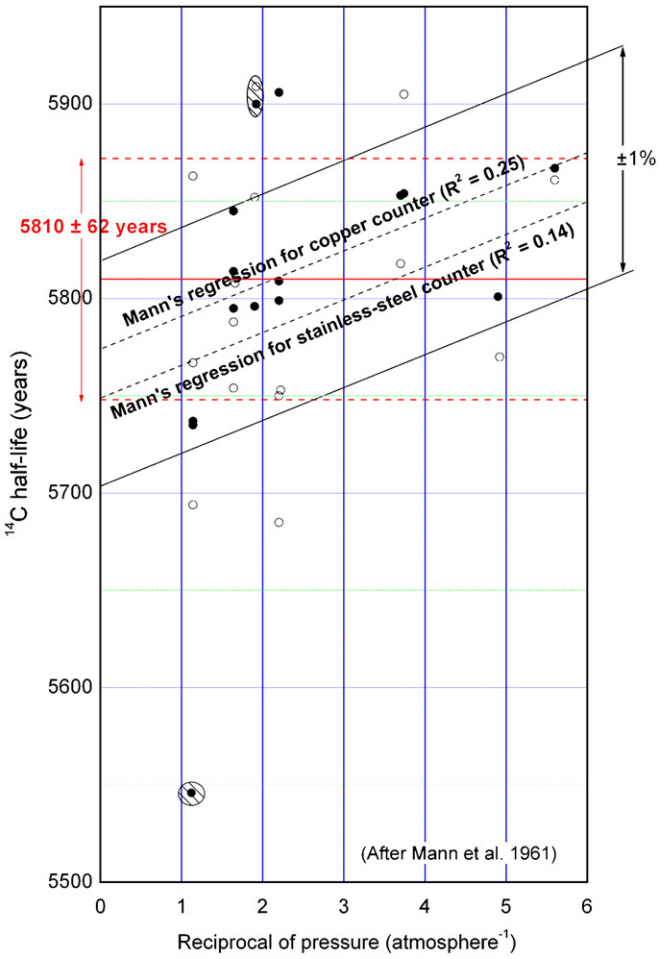

Fig. 9. Measured ^{14}C half-life values versus the reciprocal of pressure, reported in Mann et al. (1961). Solid circles were the data measured in the copper counters, and hollow circles were those measured in the stainless-steel counters. The two black dash lines indicate the least-squares slopes for the two sets of counters; the solid black lines indicate ±1% spread from the average of the two least-squares slopes (Mann et al., 1961). Data points with shades were those discarded from the regression by Mann et al. (1961), and another series of measurements leading to a half-life value of ~6200 years were also discarded (not shown in this figure) by the authors. The ^{14}C half-life was determined to be 5760 ± 50 years in Mann et al. (1961). The red solid and dash lines represent the pooled mean of Mann et al. (1961)'s reported measurements assuming no correction for the "wall effect" such as that in Olsson et al. (1962), shown in Fig. 10. The ^{14}C half-life would be 5810 ± 62 years if the pooled mean were used.

regressions, and found the "*R*-squared values" of the regressions are only ~0.25 for the copper counter measurements and ~0.14 for the stainless-steel counter measurements, respectively (Fig. 9). The poor correlation between the reciprocal of gas pressure and the measured half-life value makes it difficult to justify Mann et al. (1961)'s graphical projection method and half-life estimate (Fig. 9).

Regardless of the validity of Mann et al. (1961)'s arguments about "old" ethyl ether contamination and the inappropriate discrimination correction, the choice of regression itself results in a ±1% uncertainty of ^{14}C

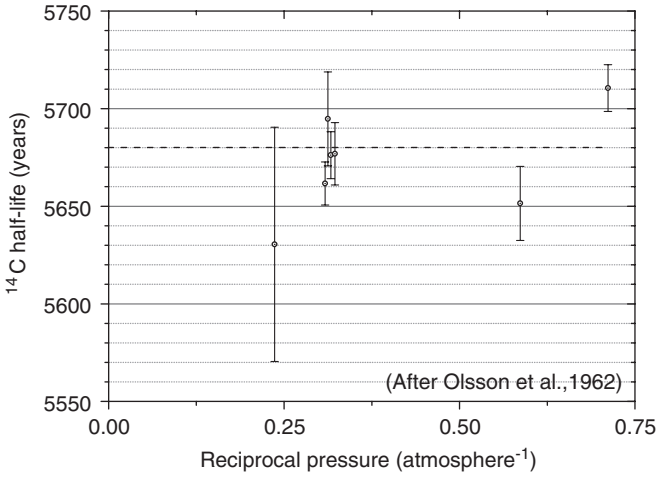

Fig. 10. Measured ^{14}C half-life values versus the reciprocal of pressure, reported in Olsson et al. (1962). This figure is similar to Fig. 9, but uses a different pressure range. In this study, the counter wall effect was not detected, and thus a horizontal line was fitted through the data and projected to infinite pressure. The ^{14}C half-life was determined to be 5680 ± 40 years in this study (Olsson et al., 1962).

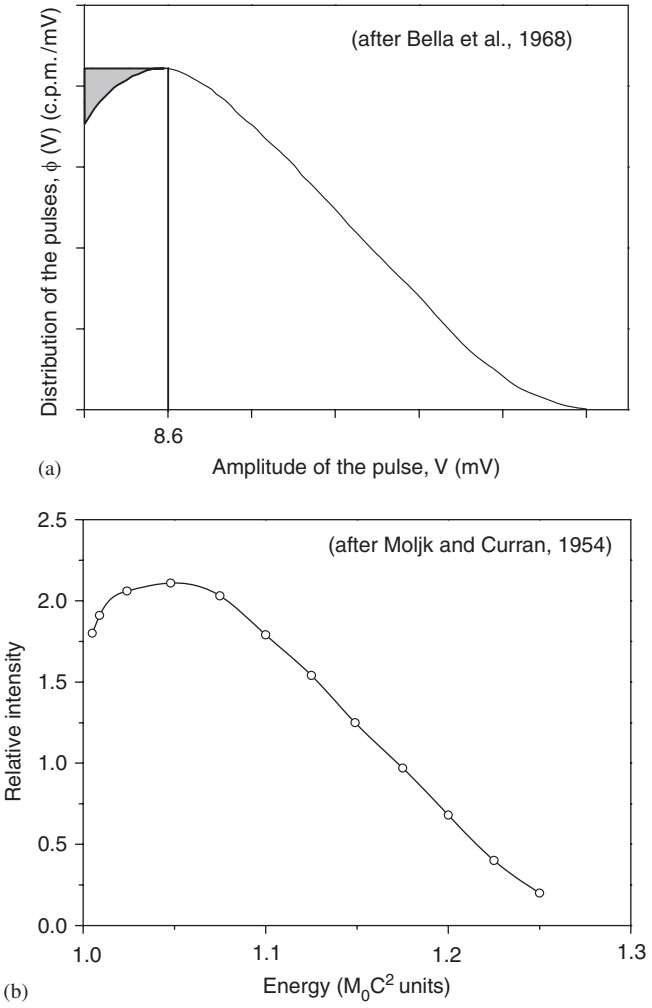

Fig. 11. (a) Distribution of the pulses of the data analyzer in a proportional gas counter (Bella et al., 1968). The shaded area represents the over-estimated counting rate that was subtracted from the raw counting rate in Bella et al. (1968). (b) Theoretical beta spectrum of ^{14}C, assumed "allowed" distribution in energy range above 3 keV (Moljk and Curran, 1954). Hollow circles represent the corrected experimental data (Moljk and Curran, 1954). One energy unit in "M_0C^2" is approximately equal to 510.9 keV (Loevinger, 1957).

half-life value (Fig. 9). More intriguingly, the earlier instrumentation report (Mann et al., 1960) presented different regression slopes of measured data between copper and stainless-steel counters in both proportional region and in Geiger–Müller region. It is apparent that the uncertainty of Mann et al. (1961)'s reported value "5760 ± 50 years" is considerably under-estimated based on the above discussion. If we simply consider all Mann et al. (1961)'s reported data from both copper and stainless-steel counters, excluding the extreme outlier data point (~5570 years), the average of their reported half-life values (analytical uncertainty neglected) is "5810 ± 62 years (1σ)". This value is ~1% larger than Mann et al. (1961)'s reported value ("5760 ± 50 years") based on the gas pressure projection estimate.

In the case of Olsson et al. (1962), different thresholds of discriminator levels were set for various electronics systems, but no wall effect was detected based on Olsson et al. (1962)'s interpretation, and the data were averaged to obtain half-life value at infinite pressure (Fig. 10). According to Olsson et al. (1962), the error bars of data points in Fig. 10 did not include all systematic errors, and thus, the uncertainty of the "horizontal projection" was left unconstrained. The uncertainty of Olsson et al. (1962)'s reported half-life, 5680 ± 40 years, was also considerably under-estimated based on the spread of reported data (Fig. 10). Without correlation with a significant number of data points, any projected regression line, presumably to correct the wall effect, is not robust.

In addition to the uncertainty in the half-life regression projection corrections, gas-counter measurements were also subject to correction of counting rates due to the shape of the ^{14}C beta spectrum (Olsson et al., 1962; Bella et al., 1968). According to Bella et al. (1968), after considering the routine effects of discrimination, dead time, and resolving times of the electronic registration in the channel relative to the counter and also in the channel relative to the photomultipliers, they needed to "adjust" the count rates on the basis of the shape of the distribution spectrum of beta particles. Bella et al. (1968) linked the maximum threshold of the amplitude distribution from their signal analyzer (Fig. 11a) to the maximum intensity of the ^{14}C beta spectrum reported in Moljk and Curran (1954) (Fig. 11b), and subtracted 8 counts/min (c.p.m.) (the shaded area in Fig. 11a) from their discrimination-corrected counting rate (1102 c.p.m.) to approximate the shape of the ^{14}C beta spectrum. The maximum intensity in Moljk and Curran (1954) was ~26 keV and it dropped to ~80% of its maximum value from 26 to 0 keV in the spectrum.

In Bella et al. (1968), the half-life of ^{14}C was calculated based on the following equation:

$$T_{1/2} = \frac{N_a}{\tilde{N}} \times LN2, \quad (2)$$

where N_a = the number of the active atoms contained in the counter, and $\tilde{N}$ = the corrected counting rate. Clearly, the smaller the counting rates the longer the ^{14}C half-life obtained. Olsson et al. (1962) also noted "the shape of the spectrum should be slightly curved near zero". Olsson et al. (1962) bracketed the ranges of their counting rates rather than made corrections based on a specific published ^{14}C beta spectrum. The assumed shape of the ^{14}C beta spectrum, especially in the low-energy range, greatly influences the correction to obtain the "true counting rate", and thus the resulting calculated ^{14}C half-life with this type of instrument. More importantly, any error in estimating the low-energy beta spectrum of ^{14}C would result in reproducible but biased counting rates in the early half-life measurement using similar gas counters. There have been extensive research and continued debate over the shape of ^{14}C beta spectrum especially in the low-energy range (Cook et al., 1948; Angus et al., 1949; Feldman and Wu, 1949; Warshaw, 1950; Wu and Schwarzschild, 1953; Moljk and Curran, 1954; Pohm et al., 1955; Kuzminov and Osetrova, 2000), all of which imply potentially large and poorly constrained errors in ^{14}C half-life values measured using gas counters (Mann et al., 1961; Watt et al., 1961; Olsson et al., 1962; Bella et al., 1968).

Table 1 is a summary of gas-counter measurements of ^{14}C half-life in the 1960s. These values differed by ~2.5% from one another, but were all 3–4% higher than the Libby's ^{14}C half-life, 5568 years. Despite the significant difference from Libby's half-life, these values were still not adopted by the radiocarbon dating community for use in standard radiocarbon age determinations (Stuiver and Polach, 1977). Uncertainties over the true shape of the ^{14}C beta spectrum in low-energy range might have contributed to reluctance in accepting the newer results.

4.3.3. Beta spectrum of ^{14}C and gas-counter measurements

Only in the last of the published gas-counter measurements of ^{14}C half-life (Bella et al., 1968) was a correction of the counting rate based on the shape of beta emission energy distribution explicitly discussed (Fig. 11a and b). The beta spectrum of ^{14}C has been computed, measured, and re-measured by many investigators because of its importance to many fields of radiochemistry (Cook et al., 1948; Angus et al., 1949; Feldman and Wu, 1949; Warshaw, 1950; Wu and Schwarzschild, 1953; Moljk and Curran, 1954; Pohm et al., 1955; Kuzminov and Osetrova, 2000). Most studies agreed on the end-point energy (the maximum energy observed in the spectrum), but many disagreed on the shape of ^{14}C beta spectrum. Some evidence suggested that the ^{14}C beta spectrum deviated from the theoretical "allowed" distribution (Cook et al., 1948; Angus et al., 1949; Warshaw, 1950; Kuzminov and Osetrova, 2000), defined as that predicted by Fermi–Kurie theory (Lieser, 2001); while other data suggested the beta spectrum followed the "allowed" distribution from its end-point energy (~156 keV) to a certain low-energy value (Moljk and Curran, 1954; Pohm et al., 1955; Feldman and Wu, 1949; Wu and Schwarzschild, 1953).

The beta spectrum in the low-energy range presents one of the most challenging measurements due to the extremely low signal to noise ratio, requiring the measured raw signals to be filtered by a noise discriminator. Recently, Selvi and Celiktas (2002) argued a regular noise discriminator distorts the real shape of beta spectrum in the low-energy range and presented a new noise separator technique. By treating the noise as a "pulse" and separating it from the raw beta emission spectrum, Selvi and Celiktas (2002) attempted to filter the noise band in order to reveal a more accurate beta spectrum in the low-energy range. These more recent beta spectrum measurements are motivated by scientific problems unrelated to radiocarbon dating (Selvi and Celiktas, 2002).

Selvi and Celiktas (2002) argued that the ^{14}C beta spectrum is grossly contaminated by electronic noise in the less than 20 keV interval implying that most previous measurements over-estimated the beta energy distribution in the low energy region (Fig. 12). In other words, according to Selvi and Celiktas (2002), there should be less intensity distributed in the low-energy range of ^{14}C beta spectrum than those reported in the early literature (Fig. 11b). Following this argument, it is implied that Bella et al. (1968) over-estimated the true counting rate of the active $^{14}CO_2$ in the gas counter (Fig. 11a). An over-estimation of counting rate of active $^{14}CO_2$ would result in an under-estimation of ^{14}C half-life (see Eq. (2)). The data of Selvi and Celiktas (2002) infer that similar problems were common in gas counting experiments in the 1950s and 1960s since the shape of the ^{14}C beta spectrum in low-energy range was either poorly or not yet resolved at that time. Until a better-constrained ^{14}C beta spectrum is available, gas-counting half-life measurements will be subject to counting bias. This uncertainty in the beta spectrum does not enter routine radiocarbon age determinations because investigators in the radiocarbon community normalize the count rate data according to an international standard that is assigned a specific activity value (Stuiver and Polach, 1977).

4.3.4. Simplified half-life measurements using ^{14}C enriched samples

Rather than directly measuring the disintegration rate to determine the half-life, the energy emission obtained from a known quantity of ^{14}C can be used to calculate the half-life. Jenks and Sweeton (1952) used the calorimetric method to measure the power output of the beta-emission from a known amount of $^{14}CO_2$ in a highly enriched sample. Similarly, Caswell et al. (1954) measured the energy emission rate of ^{14}C samples using an extrapolation

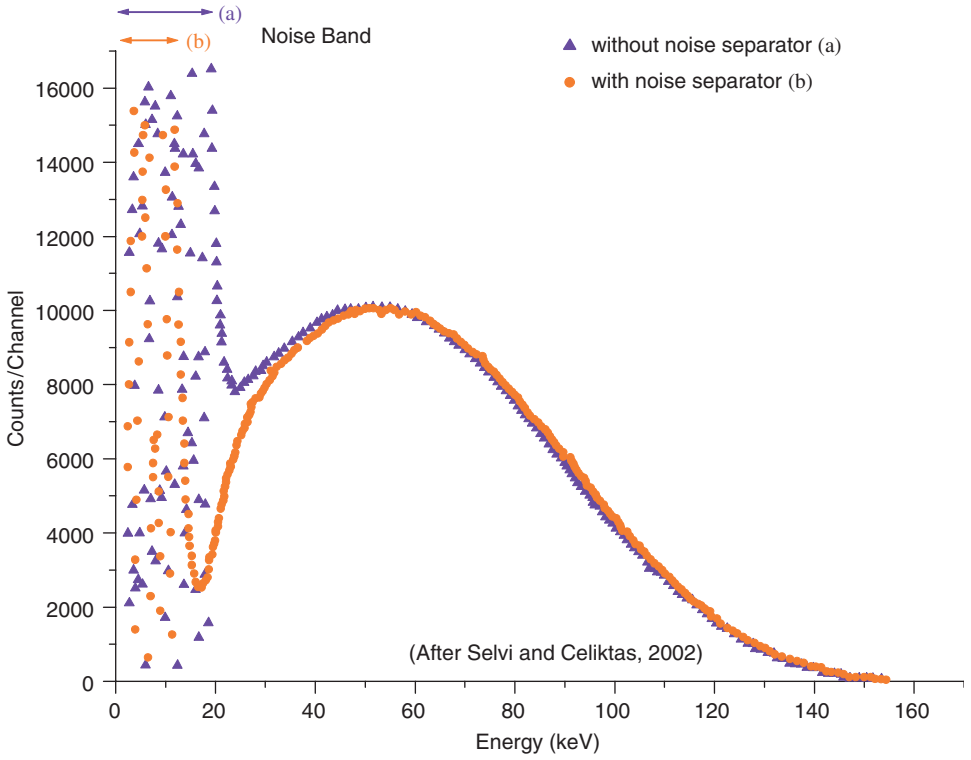

Fig. 12. Pulse-height distributions of beta particles from ^{14}C, reported in Selvi and Celiktas (2002): (a) without the noise separator equipment (solid triangles); and (b) with the noise separator equipment (solid circles).

Table 2
Average beta energy of ^{14}C computed or reported in the literature

Reference source	Average beta enery, $\bar{E}_\beta$ (keV)	Assumed shape of β spectrum for computation
Jenks and Sweeton (1952), computed by B. H. Ketelle	49.0	Allowed
Jenks and Sweeton (1952), computed by B. H. Ketelle	$>49.0^a$	Not-allowed
Caswell et al. (1954)	49.7	Allowed
Loevinger (1957)	49.2 (unlikely to change by more than $\pm 5\%$)	Allowed
Murthy (1971)	49	Allowed
Mantel (1972)	49.3	Composite spectra; allowed
Chu et al. (1999) in Ekström and Firestone (1999)	50.1	Not mentioned

Note: The mean of these reported values is 49.4 ± 0.8 keV (2σ).
[a]Denotes the value excluded from the calculation of the mean value.

ionization chamber, and then calculated the disintegration rates based on average beta energy of ^{14}C.

The calorimetric method is technically simple and only requires an estimate of the average beta energy ($\bar{E}_\beta$) of ^{14}C. The investigators used an equation in which the product of decay constant and the average beta energy of ^{14}C equaled the disintegration power (Jenks and Sweeton, 1952):

$$\text{(Disintegration power per atom of } ^{14}\text{C)} = \text{(decay constant of } ^{14}\text{C)} * \bar{E}_\beta. \quad (3)$$

Since measurements of power and heat flow are straightforward and were precisely measured even in the 1950s, the average beta energy of ^{14}C is the only critical assumption needed in calorimetric methods (Eq. (3)). The average beta energy ($\bar{E}_\beta$) can be computed from an actual, experimental spectrum or from Fermi–Kurie theory assuming the "allowed" distribution (Loevinger, 1957; Mantel, 1972). Most studies estimated $\bar{E}_\beta$ of ^{14}C in the range of 49–50 keV (Jenks and Sweeton, 1952; Caswell et al., 1954; Loevinger, 1957; Murthy, 1971; Mantel, 1972; Chu et al., 1999; Ekström and Firestone, 1999) (Table 2). According to Loevinger (1957), a calculated $\bar{E}_\beta$ would not change by more than 5% if the ^{14}C beta spectrum did not deviate from an "allowed" distribution appreciably. At the time Jenks and Sweeton (1952) determined the ^{14}C half-life to be 6030 years, they assumed an "allowed" shape of the ^{14}C beta spectrum resulting in an average ^{14}C beta energy of 49 keV. Jenks and Sweeton (1952) estimated a total uncertainty of about $\pm 1.4\%$ for the disintegration power

generated by pure ^{14}C. The error analysis included a $\pm 1\%$ error resulting from the uncertainty of the measured fractional $^{14}CO_2$ in the gas mixture ($^{14}CO_2$ + inactive CO_2) used in the calorimetry experiment and a $\pm 1\%$ uncertainty of the disintegration power generated by the gas mixture. Therefore, one might revise the estimate of Jenks and Sweeton (1952) ^{14}C half-life to be "6030 ± 86 years", assuming no uncertainty in the average beta energy of ^{14}C.

Jenks and Sweeton (1952) noted that in order to obtain a ^{14}C half-life value of ~5500 years, like those obtained in gas counting systems in the late 1940s and the early 1950s (Libby, 1955) (see Fig. 8), the average beta energy would have to be reduced to ~45 keV. We now know that this scenario is unlikely, considering the average beta energy of ^{14}C is well constrained despite the uncertainty of the shape of ^{14}C beta spectrum in low-energy range. Table 2 is a summary of published values of average beta energy ($\bar{E}_\beta$) of ^{14}C. The data suggest a mean value of 49.4 ± 0.8 keV (2σ), consistent with the early estimate used by Jenks and Sweeton (1952). If we combine a $\pm 1.4\%$ experimental uncertainty of power generated by pure ^{14}C and the uncertainty ($\pm 1.6\%$) of average beta energy of ^{14}C (Table 2) and assume these errors are independent normal distributions, the total uncertainty of calorimetric measured half-life is about 2%. Thus, a recomputed half-life value based on the measurements reported in Jenks and Sweeton (1952) is "6079 ± 122 years."

The measured ^{14}C half-life value obtained from calorimetric methods ("6030 years") did not attract much attention in most radiocarbon-based literature, perhaps because the value determined by calorimetry (Jenks and Sweeton, 1952) was substantially higher than most published gas counter measurements (Mann et al., 1961; Watt et al., 1961; Olsson et al., 1962; Bella et al., 1968). However, several calorimetry review papers (Gunn, 1964; Gunn, 1970; Ramthun, 1973; Gunn, 1976) emphasized many advantages of calorimetric methods over traditional ionization counting systems. For example, the total power of a fixed quantity of a radioactive source can be directly measured in the calorimeter. If the mass and disintegration energy are known, the half-life can be easily obtained (Eq. (3)). If the half-life is short enough, the change of disintegration power with time alone is sufficient to calculate the half-life (Gunn, 1964). Another advantage of calorimetry is that a large amount of radioactive material may be directly measured without introducing errors resulting from diluting the original material to a lower radioactive level (sometimes by a factor of 10^8; Mann et al., 1961), which is required by the ionization counting system. The elegance of the calorimetry experimental design greatly reduces the introduction of systematic errors, and this is a prime reason why it is widely used for various applications (Rudy et al., 1984; Mann and Unterweger, 1995; Collé and Zimmerman, 2001; Stump et al., 2005). While constant source, counting geometry, dead-time correction and discrimination levels have to be all considered within a gas counting system, the source of calorimetry can be enclosed in the glass or metal container and simply measured by its power output (Ramthun, 1973). The uncertainty of the shape of the beta spectrum in the low energy range (Selvi and Celiktas, 2002) is less critical to the calorimetry technique because of the relatively low energy per ^{14}C disintegration in this part of the spectrum.

Calorimetry ^{14}C half-life value, "6030 years", was consistent with Caswell et al. (1954)'s reported value of ^{14}C half-life, "5900 ± 250 years" (Fig. 8). Caswell et al. (1954) measured the energy emission of ^{14}C samples in an extrapolation ionization chamber and calculated the disintegration rate of the ^{14}C samples based on assumed average beta energy of ^{14}C. The calorimetric method and extrapolation ionization chamber measurement differ in technical designs, but they share the simple assumption of average beta energy of ^{14}C (Jenks and Sweeton 1952; Caswell et al. 1954). Despite the relatively large analytical uncertainty in the reported value of the extrapolation ionization chamber measurement (Caswell et al., 1954), the consistency between the calorimetry and extrapolation ionization chamber half-lives supports the possibility of a longer ^{14}C half-life value than the consensus value (Godwin, 1962).

The value of the half-life of a radionuclide should be confirmed by various methods yielding consistent results, and plutonium-240 (^{240}Pu) is one of the successful examples. The half-life of ^{240}Pu has been reported as "6552.4 ± 1.7 years" by calorimetry (Rudy et al., 1984), "6574 ± 6.2 years" by mass spectrometry (Strohm, 1984), and "6571 ± 17.5 years" (Steinkruger et al., 1984) and "6552.2 ± 13.8 years" (Lucas and Noyce, 1984) by α-particle counting. The estimates suggest no systematic offset observed among different types of instruments, and demonstrate that calorimetry, as well as other methods, can provide very high-precision and high-accuracy measurements. In other words, the counting system is not the only accepted method to measure the half-life of a radionuclide.

4.4. The effect of an inaccurate ^{14}C half-life

It is important to recognize that the absolute values of computed atmospheric $\Delta^{14}C$ are a function of the value of ^{14}C half-life used in the calculation (Eq. (1)) (Stuiver and Polach, 1977). Although "5730 ± 40 years" was accepted as the best available estimate of ^{14}C half-life in 1960s, it was the mean of three published values determined by similar instrumentation procedures and assumptions (Mann et al., 1961; Watt et al., 1961; Olsson et al., 1962). Beck et al. (2001) utilized a 13-box carbon cycle model in order to estimate the atmospheric $\Delta^{14}C$ during the past 50,000 years. In the Beck et al. (2001) model (A), $\Delta^{14}C$ estimates were based on global ^{14}C production from paleointensity stack Sint-200 (Guyodo and Valet, 1996) and an invariant modern balanced carbon cycle. The modeled atmospheric $\Delta^{14}C$ predicts maximum $\Delta^{14}C$ values of 400 per mil during the past 50,000 years (Beck et al., 2001). Our coral

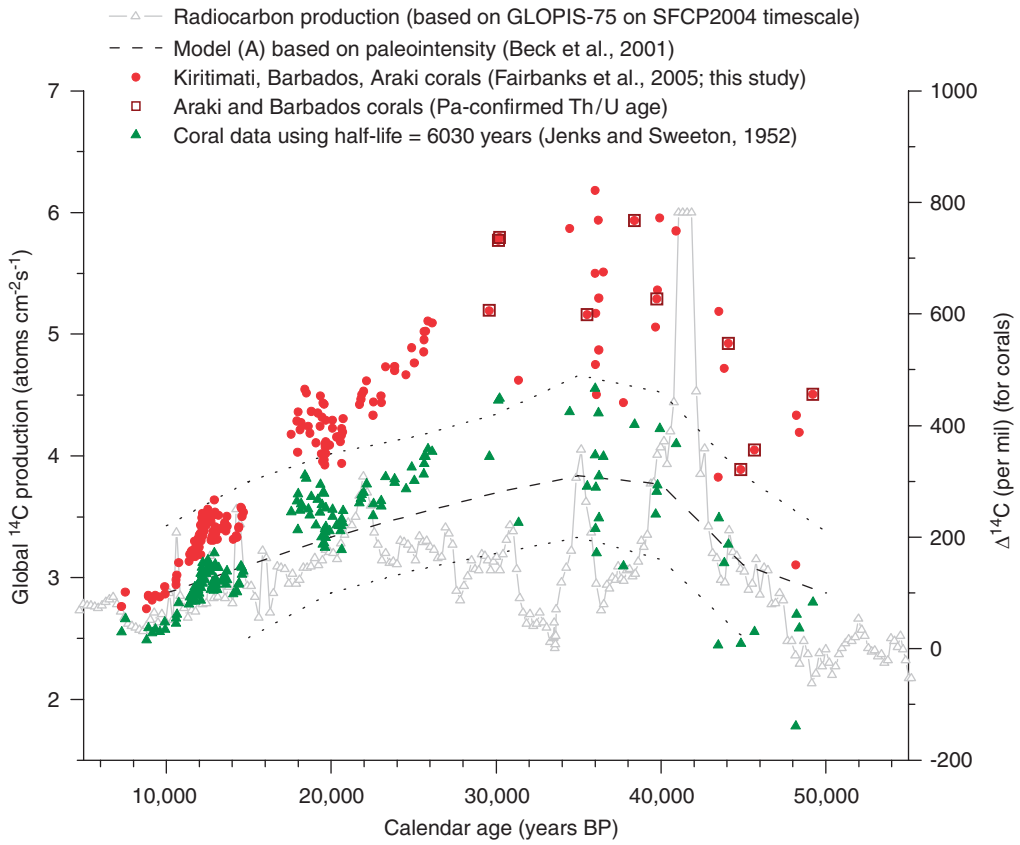

Fig. 13. Atmospheric $\Delta^{14}C$ record for the past 50,000 years based on fossil corals (red circles) using the consensus ^{14}C half-life of 5730 years and recalculated $\Delta^{14}C$ values using the calorimetry estimated half-life of 6030 years (Jenks and Sweeton, 1952) (green triangles). Ten samples have $^{230}Th/^{234}U/^{238}U$ ages confirmed by redundant $^{231}Pa/^{235}U$ ages (hollow squares). Global ^{14}C production (gray hollow triangles) was estimated from paleointensity stack GLOPIS-75 (Laj et al., 2004), which was adjusted to fit the SFCP2004 time scale (Shackleton et al., 2004) in this figure using the approximated relationship between geomagnetic field intensity and global ^{14}C production (Elsasser et al., 1956; Lal, 1988; Bard, 1998). The modeled atmospheric $\Delta^{14}C$, Beck et al. (2001)'s model (A) based on paleointensity stack Sint-200 (Guyodo and Valet, 1996) and an invariant modern carbon cycle condition, and model uncertainty were digitally converted from the original publication (dash and dotted lines). See Fig. 1(b) for the comparison between GLOPIS-75 and Sint-800, which is the extended version of Sint-200. Note the coral $\Delta^{14}C$ values when using a half-life of 6030 years fall within the uncertainty of model prediction. However, carbon box models cannot confirm the accuracy of a ^{14}C half-life of 6030 years because the models are unable to reproduce CO_2 natural variability. We do not endorse adopting a ^{14}C half-life of 6030 years but consider it to be within the range of possible values until efforts to re-measure the ^{14}C half-life are completed.

atmospheric $\Delta^{14}C$ record ("conventional" $\Delta^{14}C$) displays a similar pattern to that of Beck et al. (2001) model (A), but with much higher $\Delta^{14}C$ amplitudes (Fig. 13). Our coral data show that the atmospheric $\Delta^{14}C$ begins to depart from these model-predicted values at 20,000 years BP towards the older part of the record, where the discrepancy becomes more and more significant.

Having now evaluated the methods and related issues relevant to accurate determination of ^{14}C half-life, we test the sensitivity on the calculation of $\Delta^{14}C$ values to the half-life value. If the calorimetry half-life of 6030 years (Jenks and Sweeton, 1952) instead of the consensus half-life of 5730 years (Godwin, 1962) is selected for the computation of our coral $\Delta^{14}C$ values (Eq. (1)), the recalculated $\Delta^{14}C_{6030}$ seem entirely consistent with the Beck et al. (2001) model (A) prediction in which mainly the production controls modeled $\Delta^{14}C$ (Fig. 13). Although a correction of ^{14}C half-life would affect the decay term in carbon box models as well, we have demonstrated the potential to reconcile the discrepancy between modeled $\Delta^{14}C$ values and the coral $\Delta^{14}C$ values using the reported calorimetry determined half-life of 6030 years. However, carbon box models are crude by design and cannot adequately reproduce natural variability of CO_2, and so the models cannot serve as a confirmation for the "6030 years" half-life. New concordant ^{14}C half-life measurements via calorimetry and modern counting techniques are needed.

5. Conclusion

An atmospheric $\Delta^{14}C$ record for the past 50,000 years BP is reconstructed based on stringent screening and robust dating of fossil corals from Kiritimati, Barbados, Araki and Santo Islands. It shares many similarities with the Cariaco Basin $\Delta^{14}C$ record (Hughen et al., 2004) and displays some significant differences. Our $\Delta^{14}C$ record

overall shows an increase from 50,000 years BP to a maximum at about 40,000 years BP marking the Laschamp geomagnetic event. The timing of this $\Delta^{14}C$ increase is expected based on paleomagnetic field intensity records and the estimated global ^{14}C production, but the amplitude of coral $\Delta^{14}C$ is about a factor of two higher than published carbon box model's prediction based on paleointensity only (Beck et al., 2001). The general decline of $\Delta^{14}C$ from 35,000 years BP to the present is consistent with carbon box models that inventory ^{14}C after the large production spikes during the Laschamp and subsequent smaller geomagnetic excursions.

An under-estimate of the ^{14}C half-life is a possible explanation for excessively elevated $\Delta^{14}C$ values. If the calorimetry estimated ^{14}C half-life, 6030 years, is validated by new half-life measurements, it could explain much of the linear component of the radiocarbon calibration curves and the discrepancy between $\Delta^{14}C$ values derived from corals and modeled $\Delta^{14}C$ values based on paleointensity combined with a range of carbon cycle scenarios. We conclude that the variation in paleointensity and a possible offset in the absolute value of ^{14}C half-life together control the overall shape and amplitude in the $\Delta^{14}C$ record for the past 50,000 years. A re-determination of the ^{14}C half-life is urgently needed for radiocarbon-based research. After the ^{14}C half-life is accurately measured and replicated by multiple techniques, our coral data will provide an opportunity to examine subtler carbon cycle influences on the younger half of the $\Delta^{14}C$ record.

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Appendices A and B. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.quascirev.2006.06.015.

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