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The transfer of bomb radiocarbon and anthropogenic Pb to the deep North Atlantic Ocean observed from a deep sea coral

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Abstract

Deep-ocean, $\Delta^{14}C$, Pb concentrations, and Pb isotopes were reconstructed from a deep-sea coral *Enallopsammia rostrata* from 1410 meters depth off of Bermuda. Our high-resolution time series is created from closely spaced radial cross sections, with samples taken from the center of concentric coral growth bands that we show to be oldest portion of the section. Prebomb radiocarbon ages from the coral demonstrate that the vertical growth rate of the coral is linear, and the age of the coral is estimated to be 560-630 years old based on the growth rate. Using this age model to reconstruct $\Delta^{14}C$ in deep seawater, we first detect bomb radiocarbon at the coral growth site around 1980, and show that $\Delta^{14}C$ increased from -80 ± 1‰ (average 1930-1979) to a plateau at -39 ± 3 ‰ (1999-2001). Pb/Ca of the coral ranges between 1.1-4.5 nmol/mol during the 16th and 17th centuries, and Pb isotope ratios ($^{206}Pb/^{207}Pb$ = 1.21, $^{208}Pb/^{207}Pb$ = 2.495) in this period agree with pre-anthropogenic values found in the pelagic sediments of this basin. Coral Pb/Ca is slightly elevated to 6.2 ± 0.9 nmol/mol between the 1740s and the 1850s and then increases to 25.1 ± 0.2 nmol/mol in the 1990s. The increase in coral Pb/Ca is accompanied by a decrease in coral $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$, indicating that that the increase was caused by the infiltration of anthropogenic Pb to the coral growth site. Comparing our data to the surface coral $\Delta^{14}C$ and Pb records from Bermuda reveals time scales of tracer transport from the surface ocean to the coral growth site. Some characteristic features, e.g., the bomb-derived $\Delta^{14}C$ increase, appear in the deep ocean approximately 25 years later than the surface, but the overall increase of $\Delta^{14}C$ and Pb in the deep ocean is smaller and slower than the surface, showing the importance of mixing during the transport of these tracers.

Keywords: deep-sea coral, time-series, lead, lead isotopes, radiocarbon, anthropogenic

1. Introduction

Fluctuations in the atmospheric radiocarbon and Pb over the past century have been dominated by anthropogenic perturbations, radiocarbon mainly by fossil fuel combustion and nuclear weapon testing (Stuiver and Quay, 1981; Nydal and Lovseth, 1983) and Pb by leaded gasoline combustion and high-temperature industrial activities (Wolff and Peel, 1985; Shotyk et al., 1998). As ~~the~~ atmospheric radiocarbon and Pb transfer into the ocean, their oceanic distributions have been altered with time as well. The e~~E~~volution of radiocarbon and Pb in the surface ocean has been documented by many studies through direct analysis of surface seawater samples (Linick, 1980; Schaule and Patterson, 1981; Broecker et al., 1985; Boyle et al., 1986; Wu and Boyle, 1997; Key et al., 2004) or indirectly by analyzing these tracers in annually banded surface corals (Druffel and Linick, 1978; Druffel and Suess, 1983; Druffel, 1989; Shen and Boyle, 1987; Guilderson et al., 1998; Inoue and Tanimizu, 2008; Kelly et al., 2009).

Because of their transient characteristics, monitoring the changes of radiocarbon and Pb in the ocean reservoir provides a large-scale geophysical experiment to understand the time scales of surface water ventilation, inter-basin mixing of water, and dispersal of anthropogenic inputs in the ocean interior. Moreover, knowing their oceanic distribution and evolution is necessary to assess the inventory of bomb radiocarbon and anthropogenic Pb in the modern ocean. Compared to the surface ocean, however, less is known about temporal changes of radiocarbon and Pb in deep ocean. Direct measurements of radiocarbon in the deep ocean began in the late 1950s (Broecker et al., 1960). Ocean-wide-scale surveys like GEOSECS, TTO, WOCE, and GEOTRACES provide deep ocean radiocarbon data with good spatial coverage over discrete time intervals, but high resolution records spanning the gaps in time between the surveys do not yet exist. Deep-ocean Pb data are even scarcer than radiocarbon because reliable

measurement of Pb in deep seawater became available only recently, i.e., Pb concentrations in the late 1970s (Schaule and Patterson, 1981; 1983; Flegal and Patterson, 1983), and Pb isotopes in the mid-1980s (Flegal et al., 1986; Shen and Boyle, 1988a). In the western North Atlantic Ocean, only limited Pb isotope data (Shen and Boyle, 1988b; Reuer, 2002) existed for the waters below 1000m prior to a recent US GEOTRACES survey in 2012 (Noble et al., 2015). The lack of long, continuous data on the changes in deep ocean limits our understanding on the infiltration of bomb radiocarbon and anthropogenic Pb to the ocean interior and associated oceanic processes.

It may be possible to reconstruct changes of radiocarbon and Pb in the deep ocean on decadal to centennial time scales using deep-sea corals. Recently, deep-sea corals have shown to be important archives of past ocean variability. Fossil deep-sea corals have been successfully used to reconstruct changes of the ocean circulation over the last glacial and deglacial times (Adkins et al., 1997; 1998; Goldstein et al., 2001; Schroder-Ritzrau et al., 2003), and their potential use as deep-sea biogeochemical (e.g., nutrient and temperature) proxies are being investigated (Smith et al., 2000; Weinbauer et al., 2000; Shirai et al., 2005; Cohen and Gaetani, 2006). It was shown that dissolved inorganic carbon in the ambient seawater is the primary source of carbon used for skeletogenesis for calcareous deep-sea corals, including *Corallium niobe* (Griffin and Druffel, 1989), *Corallium secundum* (Roark et al., 2006), bamboo corals (Roark et al., 2005), *Desmophyllum cristagalli* (Goldstein et al. 2001; Adkins et al., 2002), and *Lophelia pertusa* (Frank et al., 2004). The source of Pb in deep-sea coral skeletons is unknown, but given that their surface relatives preserve the record of dissolved Pb in the ambient seawater, deep-sea corals might also be able to generate time series of Pb and Pb isotopes in the deep ocean.

In this study we reconstructed deep-ocean, radiocarbon, Pb, and Pb isotope histories at high resolution using a modern deep-sea coral. A coral specimen *Enallopsamia ~~Rostrata~~ rostrata* (Pourtalès, 1878) that was collected alive from the deep North Atlantic Ocean was used for the study. *E. ~~Rostrata~~ rostrata* is regarded as a major structure-forming species and has been found world-wide at depths between ~200m to ~2000m (Freiwald et al., 2004). It has been also found to live longer compared to other deep-sea coral species like *Desmophyllum dianthus* (Adkins et al., 2004), which allows us to attain geochemical records of several hundreds of years. One of the challenges in using deep-sea corals as a paleoceanographic tracer is in estimating growth rate and age of the corals. As the banding of deep-sea corals is not necessarily controlled by the annual cycle for most species, the age of the corals is often estimated by absolute radiometric methods such as radiocarbon (Druffel et al., 1995; Adkins et al., 2002; Roark et al., 2005; 2006), ^{210}Pb (Druffel et al., 1990; Adkins et al., 2004), and ^{234}U-^{230}Th (Adkins et al., 1998; Cheng et al., 2000; Goldstein et al., 2001). In this study, we found that our coral has grown with a constant vertical growth rate. Using this growth rate, the coral was found to be ~560 years old based on a vertical length of the coral, and radiocarbon, Pb/Ca, and Pb isotopes were also measured along the vertical growth axis of the coral to generate time-series. Radiocarbon has been previously measured in modern deep-sea corals in several studies (e.g., Roark et al., 2005; 2006), but these studies used bomb radiocarbon signals to constrain ages of the corals (e.g., assigning a certain year to the peak of Δ^{14}C in the coral) and did not focus on reconstructing the past ocean ^{14}C variability.

2. Sampling and analytical methods

2.1. Coral sampling

An *Enallopsammia rostrata* specimen (ALV-3701-8) was collected alive in September 2001 with the DSV Alvin from a depth of 1410m on the north slope of Bermuda (64°W 32°N) (Fig. 1). After collection, exterior contamination on the coral was mechanically cleaned with a Dremel tool and a diamond abrasion wheel, and sediment trapped inside the coral and the septa was removed with deionized water and a toothbrush (Adkins et al., 2004).

Before cutting the coral, ^{14}C ages were measured in 5 different corallite tips in order to find a branch with the longest history. The result showed that the Tip 1 at the apex of the largest branch is the youngest one (Fig. 2). The excess ^{210}Pb results of Adkins et al. (2004) likewise showed that the corallite tip at the end of the same branch, adjacent to Tip 1, was the most recently precipitated. Based on these results, we focused our time series analysis on the branch that terminates at Tip 1 because it is most likely to contain the deep ocean interval recording bomb radiocarbon and anthropogenic Pb infiltration.

From this branch, radial discs were cut perpendicular to the direction of coral growth in 3-5 mm intervals (Fig. 2). From each radial disc, concentric bands were identified under UV light. The banding in the radial sections was found to be asymmetric with the center of the concentric bands located close to the polyp side of the coral, as previously observed in other *E. Rostrata* specimens (e.g., Houlbrèque et al., 2010). As a preliminary study, we measured ^{14}C ages from transects of three radial sections, from the center to the edge of each section along the longest possible transect (10-16 mm). In all three sections, the maximum ^{14}C age (the oldest age) was found within 1–4mm of the section center, and the ^{14}C age decreased linearly with radial distance outside of the center, corresponding to the linear radial growth rate of 20–30 μm yr^{-1} (Fig. 3). Based on this result, samples used for time series construction were cut from the central part of each radial disc (Fig. 2b). A sample mass of 11-44 mg was first cut from each radial disc

and used for ^{14}C analysis, and the rest was used for Pb and Pb isotope analysis. Radial discs with younger ages often had limited amount of samples as the branch is thinner. The tip of the branch was analyzed for ^{14}C only, and a single Pb and Pb isotope measurement was made for most of these samples. For older samples (thicker branch), 2-3 replicate Pb and Pb isotope measurements were made with a sample mass of ~30 mg for each measurement.

Previous studies on modern deep-sea corals analyzed tracers along the radial section of the coral's thick base (e.g, Roark et al., 2006), while our time series reconstruction is based on the distribution of ^{14}C and Pb along the coral's vertical growth axis. Our sampling strategy provides two advantages over the previous approach. First, as the coral's vertical growth rate is more than an order of magnitude greater than the radial growth rate, it is easier to obtain samples with higher resolution when sampled along the vertical axis. Second, samples taken along the vertical axis are more likely to include recently precipitated coral skeleton given the growth pattern of *E. rostrata*. In the five *E. rostrata* specimens collected from the Central Pacific, Houlbrèque et al. (2010) found that the outermost parts of the coral bases are ~30 to 140 years old, although their ages are expected to be near zero if the corals have been continuously grown to the radial direction. On the other hand, the age of an actively growing polyp at the end of a branch was found to be 6 ±5 years (U/Th age). Thus, Houlbrèque et al. suggested that *E. Rostrata* stops calcifying at the base as the base becomes remote from the polyps (i.e., active areas of calcification), but keeps growing in its upper parts. Their observation also supports the assumption in our age model that the tip of our coral was recently precipitated in the year of coral collection (section 3.1). Such age model cannot be used if the time series reconstruction is made from the radial section of the coral base.

158 2.2. Coral ^{14}C analysis

159 Cut coral samples were cleaned, leached, and graphitized prior to ^{14}C analysis following
160 the method described in Eltgroth et al. (2005). At least 24% of each sample was leached away,
161 sufficient to remove contaminating sources of modern ^{14}C outside of the aragonite lattice
162 (Adkins et al., 2002). Our conventional ^{14}C ages (Stuiver and Polach, 1977) were measured at
163 the UC Irvine Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory using an inorganic
164 calcite blank to account for the background signal from the graphitization and the AMS
165 measurement. Deep-Sea $\Delta^{14}C$ was calculated from these measurements according to:

166 $$\Delta^{14}C = \left(\frac{e^{-\frac{^{14}C\ Age}{Libby\ Mean\ Life}}}{e^{-\frac{Calendar\ Age}{True\ Mean\ Life}}} - 1 \right) x\ 1000‰ \quad (1)$$

167 where the conventional ^{14}C age is a measure of $^{14}C/^{12}C$ of the present day sample, and the
168 calendar age serves to correct the $^{14}C/^{12}C$ for radiocarbon decay back to the original
169 concentration at the time of coral skeleton precipitation. The calendar age of each coral sample
170 was determined from a coral age model derived from the preindustrial, prenuclear ^{14}C results for
171 our coral specimen with the youngest tip of the coral fixed at the date of coral collection. The
172 details of our age model are discussed in section 3.1.

173

174 2.3. Coral Pb/Ca and Pb isotopes analysis

175 Cut samples were crushed to 2-4 mm size and cleaned using a method described in Reuer
176 (2002) and Shen and Boyle (1988b), which includes cleaning using distilled water, H_2O_2-NaOH,
177 and HNO_3. Then the samples were further crushed to 280-700μm size and divided into 1-3
178 subsamples so that each sample has approximately 30 mg of coral mass. These samples went

through another round of cleaning using distilled water, H_2O_2-NaOH, HNO_3, and a reducing agent that is a mixture of ammonia, hydrazine, and citric acid.

Cleaned corals were dissolved in strong HNO_3, and the Pb/Ca ratio was analyzed from an small aliquot withdrawn from that ~~of the~~ solution. The Pb concentration was analyzed on this aliquot by isotope dilution quadrupole ICP-MS (VG PlasmaQuad 2+) after spiking the aliquots ~~samples~~ with a ^{204}Pb enriched spike (Oak Ridge National Laboratory; calibrated with a gravimetric Pb concentration standard). The Ca concentration was measured by flame AAS (Perkin-Elmer 403) for Pb/Ca ratios. The a~~A~~verage standard deviation for the coral Pb/Ca replicates was 0.9 nmol/mol for the samples with Pb/Ca lower than 15 nmol/mol, and 2.7 nmol/mol for samples with Pb/Ca higher than 15 nmol/mol. These deviations are ~~mainly~~ considered as natural variability of Pb/Ca within subsamples rather than analytical uncertainties. A coral disc cut in 3-5 mm vertical interval contains coral skeletons that grew for a few years, which can result in variability in Pb/Ca ratios among its subsamples. Moreover, if a sample cut from the radial disc erroneously includes an area outside of the growth center, the age variance within its subsamples will be greater. Indeed, a larger standard deviation among the replicates are often found in the samples from curved areas of the branch, where it is likely that our sample cutting does not follow the exact growth axis.

The rest of the dissolved coral samples were used to determine Pb isotope ratios. Samples were first purified by HBr-HCl anion exchange chromatography, and the sample solutions ran through columns were dried down on a clean hot plate and re-dissolved in dilute HNO_3. After spiking the samples with Tl, stable Pb isotopes (^{206}Pb, ^{207}Pb, and ^{208}Pb) in the samples were determined by multiple collector ICP-MS (Micromass/GV IsoProbe). Pb isotope measurement standards (NBS SRM-981 and an independent internal lab standard) were also prepared by

adding Tl, and were measured at the beginning and the end of each session. Data were processed and corrected as in Boyle et al. (2012), which is modified from Reuer et al. (2003). This includes exponential "beta" mass fractionation correction normalized with a $^{205}Tl/^{203}Tl$ spike, tailing correction derived from a curve fit to ^{209}Bi at half-mass interval, on-peak-zero corrections for instrumental hardware blanks using HNO_3 (for Tl isotopes) and Tl-spiked HNO_3 (for Hg and Pb isotopes), and final renormalization to the absolute values reported for NBS SRM-981 (Galer and Abouchami, 1998; Thirlwall, 2002; Baker et al., 2004). Procedural column blanks were determined by analyzing 1-2 column blanks every 18-25 samples. The isotope ratio of the column blanks could not be accurately determined due to low signal intensity (10^{-3}-10^{-4} V). Thus, we assumed that if any Pb was added to the sample during the column procedure, the Pb would have the isotope ratio of Pb typically used in U.S., which is approximated by our internal lab standard BAB3deg ($^{206}Pb/^{207}Pb$ = 1.1910 ± 0.0003; $^{208}Pb/^{207}Pb$ = 2.4743±0.0005), and subtracted the averaged values from the sample data based on the ^{208}Pb signal intensity of the column blanks. These column blanks averaged 6.5 pg of Pb, and correction for these procedural column blanks made only slight differences to the final data relative to the raw data. External reproducibility of a Pb standard that has Pb signal intensities comparable to samples was 0.2 per mil for $^{206}Pb/^{207}Pb$ and 0.3 per mil for $^{208}Pb/^{207}Pb$ (1σ, n=25, measured on 6 different days). The samples were not measured repeatedly, but reproducibility of the samples should be on the same magnitude as those of the standard, although samples with lower signal intensities may have higher errors due to the resistor Johnson noise and uncertainties in the blank correction.

3. Results

3.1. ^{14}C time series and age model

Our ^{14}C results show 2 different regions of behaviour: the results from the lower part of the coral (0-52.6 cm) trace a straight line, but the results from the upper part of the coral (53.1-55 cm) show a rapid decrease in ^{14}C age that is independent of the growth curve (Fig. 4). This is consistent with a linear growth rate of the coral that is obscured by the invasion of radiocarbon-enriched water to the coral growth site at the 53.1 cm mark. These results may also be used to estimate the vertical growth rate of the coral. Using a linear least-squares fit to the data up through 52.6 cm, the vertical growth rate is 0.87 mm yr^{-1}, which we consider as the lower bound for the vertical growth rate (Fig. 4). If we exclude the scattered data in 45-52.6cm and use the lowest (oldest) 7 points, the best-fit growth rate is estimated to be 0.98 mm yr^{-1}. Based on these growth rates, the coral lived for 560-630 yr given its length (55.3 cm). This estimate agrees with the result of ^{226}Ra-^{210}Pb study on our deep sea coral (Adkins et al., 2004), where they suggested a vertical growth rate slower than 5 mm yr^{-1} and a coral longevity of at least 110 years. Our vertical growth rate is also in agreement with those established for the five different *E. rostrata* specimens from the Equatorial Pacific based on U-series dating (ranging 0.6-1.9 mm yr^{-1}) (Houlbrèque et al., 2010) and for other deep-sea coral species, which range from 0.1 to 9.4 mm yr^{-1} (Druffel et al., 1990; Cheng et al., 2000; Mortensen et al., 2001; Risk et al., 2002).

We set the age at the top end of the Tip 1 to September 2001, the known date of coral collection, and calculated the calendar ages of the other coral samples based on the distance of each sample from the top end of the branch and the estimated growth rate. We used the 0.98 mm yr^{-1} growth rate for time series reconstruction in this paper, considering that the lowest (oldest) part of the coral is least affected by anthropogenic radiocarbon and is likely to reflect the true growth rate of the coral. The calendar age estimate based on the lower (0.87 mm yr^{-1}) growth rate is also shown in Tables 1 and 2.

There might be uncertainties in the age estimate associated with sample preparation. Despite our effort to cut samples as much as possible from the center of the coral discs, the cut samples may include an area wider than the center of growth, incorporating a younger part of the coral than what was estimated by the age model. This should not be a problem for the samples without replicates, including all ^{14}C samples, and their age estimates. However, such errors may have occurred to the Pb samples that were measured in triplicate~~s~~ because larger (~100mg) size of the samples was cut out from the disc. Pb samples that have higher relative standard deviation within their triplicate Pb/Ca results possibly have these errors because coral skeletons with younger ages likely have different Pb contents as well. Uncertainties in the age estimates of these samples are difficult to quantify, however, because exact size of the cut coral pieces and width of the central area were not monitored for each coral sample. If a coral sample was cut within 4 mm from the center of a radial disc where its true central part was 3 mm wide, this sample would be ~18 years younger than its estimated age given the radial growth rate (20–30 μm yr^{-1}) of this coral, but this should be taken as a high end of the uncertainties in the age estimates. These uncertainties could be better estimated and corrected if ^{14}C ages of these samples were known. However, in this study, ^{14}C and Pb were not both measured in all samples, and although they were from the same position in the coral, their ages may not be exactly identical as samples for ^{14}C and Pb were taken separately (i.e., from different subsamples). For Pb/Ca and Pb isotopes, we made replicate or triplicate measurements in order to monitor possible Pb contamination during analytical procedure. However, a single measurement may be more appropriate for deep-sea corals, which have low growth rates in general, to decrease the potential errors derived from sampling. These should be considered for any deep-ocean time series reconstructions using deep-sea corals in the future.

3.2. Pb/Ca and Pb isotope ratios

Pb/Ca and Pb isotope ratios analyzed from the deep-sea coral are presented in Fig. 5. Low Pb/Ca ranging from 1.1-4.5 nmol/mol are found between the 1500s and mid-1700s, and during this time period, relatively high $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios appear between 1.207-1.210 and 2.495-2.508, respectively. These Pb isotope ratios fall in the range of those found in the Quaternary marine sediments and ferromanganese nodules in this basin (average of 16 samples excluding one anomalous sample are $^{206}Pb/^{207}Pb = 1.210 \pm 0.072$, $^{208}Pb/^{207}Pb = 2.509 \pm 0.014$; Chow and Patterson, 1962), and thus, we consider the Pb in this period as pre-anthropogenic (natural). A slightly increased Pb/Ca is found in the mid-1700s, and the Pb/Ca around 6 nmol/mol remains relatively constant until 1854-1858. Coral Pb/Ca increases rapidly from 1854-1858 until it reaches a peak (28.7 nmol/mol) around 1980, and then decreases slightly afterward. Lower $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios compared to the pre-anthropogenic values are found in the mid-1700s, and as the Pb/Ca ratio increases, the isotope ratios further decrease to $^{206}Pb/^{207}Pb = 1.19$, $^{208}Pb/^{207}Pb = 2.46$ in ~1914. The Pb isotope ratios remain rather constant for a few decades until the late 1970s, and then rapidly drop to $^{206}Pb/^{207}Pb = 1.185$ and $^{208}Pb/^{207}Pb = 2.450$ in 1995.

No seawater Pb isotopes were measured from the coral growth site during the period that the coral lived, but the Pb isotope ratios of a seawater ($^{206}Pb/^{207}Pb = 1.184 \pm 0.002$, $^{208}Pb/^{207}Pb = 2.451 \pm 0.005$) collected at ~600 km east of the coral site in 1998 (1490m, 33º42'N, 57º49'W) (Reuer, 2002) agrees with the coral Pb isotope ratios found in 1997. Along with the fact that the coral Pb isotopic ratios prior to the mid-1700s agree with the pre-anthropogenic Pb isotope values, this result implies that the Pb in this deep sea coral was precipitated from the ambient

seawater without significant isotope fractionation, and thus the observed variance in the coral Pb isotopes reflects the changes in deep ocean Pb isotope ratios.

4. Discussion

4.1. Deep-sea $\Delta^{14}C$ time series

The reconstructed $\Delta^{14}C$ in deep seawater shows a stable $\Delta^{14}C$ up to the early 1970s with a value of -80 ± 1 ‰ (Fig. 6). We detect the first influence of bomb radiocarbon with the slight rise in $\Delta^{14}C$ starting around 1980. $\Delta^{14}C$ then increases by 41‰ to plateau at -39 ± 3 ‰ (1999-2001). At first glance, the nearest isopycnal (σ_θ) matched GEOSECS, TTO, and WOCE station $\Delta^{14}C$ data appear to disagree with the coral results, but a close look reveals that the prebomb $\Delta^{14}C$ in the southern stations agree with our pre-bomb record and the more northern stations in the late 1990s agree with the end of our $\Delta^{14}C$ record. Comparing to the GEOSECS data of the North Atlantic from 1972-1973, the more southern station (-76 ± 4 ‰) agrees with our prebomb value of -80 ± 1 ‰. The four stations from TTO in 1981 show that the bomb pool has reached the more northern stations (–45 ± 4‰, –51 ± 4‰), but $\Delta^{14}C$ in our record (approx. –75 ± 4‰) is just beginning to rise and is in line with the $\Delta^{14}C$ observations from the more southern stations (–69 ± 4‰, –79 ± 4‰). Because the more northern WOCE stations from the late 1990s (–34 ± 4‰, –33 ± 4‰) agree with our coral result (–39 ± 3‰), we conclude that this deep ocean site was fully engulfed in the bomb radiocarbon pool by the late 1990s and that the $\Delta^{14}C$ of this site began to level off from then. In contrast, the WOCE station that is just south of Bermuda (from 1997) has a lower $\Delta^{14}C$ value than our coral result, showing this site had not yet been nearly engulfed in the bomb radiocarbon pool yet.

4.2. Deep-sea Pb and Pb isotopes time series

Pb/Ca of the deep-sea coral starts to rise clearly from the 1860s (Fig. 5). This is consistent with the increase in Pb concentrations in the Bermuda surface coral around 1850-1860 (Kelly et al., 2009) and river sediments from the northeastern United States around 1830 (Lima et al., 2005), which was caused by the increased coal combustion and Upper Mississippi Valley ore smelting in the United States. This trend also agrees with the increased anthropogenic Pb emission from the western Europe around the 1840s (Shotyk et al., 1998). The decrease in coral $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios occurring in accordance with the Pb/Ca increase (Fig. 5) supports that this increase is the result of the penetration of anthropogenic Pb into the coral growth site. The anthropogenic Pb found in the surface of the western North Atlantic Ocean in the past two centuries show lower $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios than the natural values ($^{206}Pb/^{207}Pb = 1.210 \pm 0.072$, $^{208}Pb/^{207}Pb = 2.509 \pm 0.014$) (see Fig. 7, for example) (Shen and Boyle, 1988a; Veron et al., 1994; Hamelin et al., 1997; Kelly et al., 2009). The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of the anthropogenic Pb found in the surface of the eastern North Atlantic Ocean are even lower than the western North Atlantic Ocean because of the low isotope ratios (e.g., $^{206}Pb/^{207}Pb$ ranging 1.06-1.16) of the Pb emitted from western Europe (Veron et al., 1994; Weiss et al., 2003).

The ~~Seawater~~ Pb concentration of seawater at 1430m depth in 1984 at 32°12'N, 64°30'W (near the coral growth site) was ~~measured to be~~ 53 pmol kg^{-1} ~~at 1430m depth close to the coral growth site (32°12'N, 64°30'W) in 1984~~ (Boyle et al., 1986). Comparing this seawater value to the coral Pb/Ca from 1984 (26.85 nmol/mol), the partition coefficient of Pb (D_p = $(Pb/Ca)_{coral}/(Pb/Ca)_{seawater}$) for this coral is ~~calculated~~ estimated as ~~to be~~ 5.2. Two other Pb measurements were made from the northwest (34°15'N, 66°17'W; 77 pmol kg^{-1} at 1470m)

(Schaule and Patterson, 1981) and the east (33°42'N, 57°49'W; 57.3 pmol kg^{-1} at1490m) (Reuer, 2002) of the coral growth site in 1979 and 1998, respectively, and D_p of Pb derived from these concentrations are 3.5 and 4.5. These D_p estimates (ranging 3.5-5.2) all fall in the range of D_p in other deep-sea corals derived from ^{210}Pb, e.g., 3-20 in *Desmophyllum cristagalli* (Adkins et al., 2004) and a maximum of ~8 in *Corrallium niobe* (Druffel et al., 1990).

One should note that these D_p estimates have intrinsic errors because they are calculated based on a single seawater Pb datum that does not represent a long-term averaged Pb value, whereas the Pb/Ca ratio measured from a few-mm thick coral discs is an average of the Pb values of several years. Moreover, for surface growing corals, it was found that D_p of some minor elements can be variable in a single coral due to kinetic artifacts (Devilliers et al., 1994; 1995; Cohen et al., 2001), and fine-scale fluctuations have been found within a skeletal structure both in surface and deep-sea corals (Cohen and McConnaughey, 2003; Sinclair, 2005; Robinson et al., 2006; Gagnon et al., 2007). These errors are expected to be small in our data because 1) the deep-sea coral used in this study is considered to have grown at a constant rate, and 2) we tried to collect coral samples from the same location (near the centre of growth) in the coral discs. More importantly, the fractional kinetic and structural artifacts should be smaller than the order of magnitude range of Pb/Ca variations~~nce~~ caused by anthropogenic Pb inputs.

Considering the spatial variability of Pb in the ocean, we used D_p = 5.2 for seawater Pb reconstruction in this paper, as this is based on the seawater data collected most closely to the coral growth site. Applying D_p =5.2 to the coral Pb/Ca ratios earlier than 1700s assuming D_p was constant during the growth of coral, pre-anthropogenic seawater Pb concentrations in deep sea is estimated to be approximately 3-11 pmol kg^{-1} (Fig. 5). This value is similar to or lower than the pre-anthropogenic Pb concentration estimated for the western North Atlantic surface waters (15

pmol kg^{-1}) based on Bermuda coral Pb/Ca (Kelly et al., 2009). This might be the result of sinking particle scavenging of Pb at depth, which is often observed in Pb and ^{210}Pb vertical profiles in the modern ocean (Craig et al., 1973; Bacon et al., 1976; Cochran et al., 1990; Schaule and Patterson, 1981). The deep-sea Pb concentration gradually increases from the 1860s, and the maximum Pb concentrations at 54 pmol kg^{-1} appear in 1980-1987.

4.3. Comparison to surface $\Delta^{14}C$ and Pb time series

A comparison of the deep-ocean $\Delta^{14}C$ record to the coral record from the surface ocean near Bermuda (Druffel, 1989) and the atmospheric record (Manning and Melhuish, 1994; Nydal and Lovseth, 1996; Stuiver et al., 1998) shows the movement of atmospheric $\Delta^{14}C$ to the surface and deep ocean reservoirs (Fig. 6). The atmosphere and the surface ocean $\Delta^{14}C$ begin to increase at nearly the same time (1955–1958), but $\Delta^{14}C$ in the deep ocean begins to rise 22-25 years later, around 1980. The northern hemisphere atmosphere peaks at 1000‰ in 1963 and the surface ocean at Bermuda plateaus at 150‰ 10 years later in 1973-1974. The maximum $\Delta^{14}C$ in the deep ocean is also reached in ~25 years later than the surface ocean, which implies 22-25 years of transit time from the surface to the coral growth site.

A similar result is observed when we compared our deep-sea coral Pb isotope record to the surface-ocean Pb isotope record reconstructed from Bermuda corals (Kelly et al., 2009). The most noticeable similarity in the two records is the decrease in $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios that occurs in 1951-1952 in surface water and around 1976 in the deep ocean (Fig. 7) and relatively constant Pb isotope ratios ($^{206}Pb/^{207}Pb$ = 1.19 and $^{208}Pb/^{207}Pb$ = 2.46) that are maintained for a few decades before the decrease occurs. Other Pb isotope features appeared in the surface water prior to the 1950s, e.g. a peak in Pb isotope ratios around 1880 and the

following decrease, are not shown clearly in the deep sea record because of the relatively low surface-ocean Pb concentrations during that period, as the surface features are easily erased during transport by mixing. Surface water Pb concentrations increase rapidly after ~1950, and thus the surface Pb isotope feature (decreasing $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) in 1951-1952 probably has resulted in the decrease in deep-sea Pb isotope ratios observed around 1976. The ~25 years of delay in the appearance of Pb isotopic features between the surface and deep sea is consistent with the observation from $\Delta^{14}C$, and based on these results, one may conclude that it takes approximately 25 years for ^{14}C and Pb to be transported from surface to the deep ocean north of Bermuda.

Another difference between the surface and deep-sea coral records is that the increases in deep-sea $\Delta^{14}C$ and Pb are much smaller and slower than those at the surface. Bomb radiocarbon causes ~100‰ increase of $\Delta^{14}C$ in the surface ocean (Druffel, 1989), whereas deep-sea $\Delta^{14}C$ increases by ~40‰ by the intrusion of bomb radiocarbon (Fig. 6). Similarly, the Pb concentration in the surface ocean near Bermuda increases ~12.5 fold from 1850-1860 to ~1976 (Kelly et al., 2009) (Fig. 7), while the Pb concentration in deep sea increases approximately 5 fold during the same period. The smaller increase of $\Delta^{14}C$ and Pb in deep sea indicates that during their transport these tracers were rigorously mixed with the waters with less $\Delta^{14}C$ and Pb contents, i.e., less contaminated waters, that is probably older than the surface seawater. For Pb, particle scavenging at depth may also have played a role in decreasing the impact of anthropogenic Pb in the deep sea.

To construct a simple model of this penetration and mixing, w~~W~~e assume that the radiocarbon at the surface ocean that evolves as in the Bermuda coral is pushed down to the deep-sea coral site along a pipe that has no thickness, with a speed of u =3000 km/25 yr. The

3000km is an approximate distance from the winter outcropping region of the σ_θ = 27.6 isopycnal to the deep-sea coral site, and 25 yr is the time scale of the radiocarbon transfer when the flow is assumed to be dominated by advection. We further assume that during the transfer, ~~the~~ surface radiocarbon is mixed with ambient seawater that is characterized by a constant ^{14}C concentration (C_B), and ~~the~~ mixing is represented by a mixing time scale, τ (yr). The "mixing" is used as a general term here, describing any process that allows exchange of ^{14}C between the tube and the ambient seawater. Then, the governing equation for the evolution of radiocarbon in the flow is

$$\frac{dC}{dt} = -u\frac{\partial C}{\partial x} - \frac{C - C_B}{\tau} \quad (2)$$

where C(x, t) = ^{14}C concentration in the tube and C_B is the ^{14}C concentration in the ocean interior. R~~The r~~adioactive decay is ignored in this equation because ~~the radioactive decay flux~~it is small compared to the ~~others~~ other terms over an ~50 yr time scale. We assume C_B as the ^{14}C concentration equivalent to $\Delta^{14}C$ = -80‰ as this is the best fit to the pre-bomb $\Delta^{14}C$ estimates from the old deep-sea coral data and water column measurements. For the surface $\Delta^{14}C$ time series, we subtracted 33‰ from the Bermuda coral $\Delta^{14}C$ record to make the pre-bomb surface coral $\Delta^{14}C$ (-47±4; average of the data in 1950.8-1957.8) overlap with the older deep-sea coral data. The offset between the pre-bomb $\Delta^{14}C$ between the surface and deep ocean is the result of surface-deep exchange and water mass mixing (e.g., contribution of AAIW), but we assume these processes were constant in time. Then, using the equation above, we modeled the evolution of $\Delta^{14}C$ at the deep-sea coral site with a wide range of τ and found the τ that best fits the observed coral data. The mixing time scale that best reproduces the deep-sea coral $\Delta^{14}C$ data is 17 yr (Figure 6), which yields a Peclet number (P*e*=u*τ/L; L is the length scale of the system) around 0.7. This means that mixing is more important than advection in the transport of

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radiocarbon in this system. Jenkins (1988) showed the distribution of tritium-^{3}He in the upper thermocline of the subtropical North Atlantic was found to be most comparable to the Peclet number of 1 or less using a one-dimensional advection-diffusion model. Similar results (P*e* around 1) were inferred from the tracer distributions in the upper 500m of the BATS site (Stanley et al., 2012) and the subpolar North Atlantic Ocean (Waugh et al., 2004) using a different modelling approach. The Peclet number obtained from our model is comparable to these results, although it is noteworthy that our estimate is derived from a decadal-scale time-series of a tracer at one location, whereas these estimates are based on tracer distribution in the water column at a certain time, so they represent integration of different time and space scales.

Our model assumes that radiocarbon is transported by constant u and τ , which is probably unrealistic in the ocean where advective-diffusive mixing is prevalent (Haine et al., 1998; Haine and Hall, 2002). Recent studies have pointed out that water in the ocean interior have a continuous distribution of transit times since its last contact with a surface (Holzer and Hall, 2000; Khatiwala et al., 2001; Haine and Hall, 2002). This distribution is a fundamental property of the water and thus is independent of any characteristics of a particular tracer. In this scenario, a deep ocean tracer at a given location is ~~a~~ the sum of the ~~tracers~~ tracer concentrations in the surface source waters that have mixed into that location, whose relative proportions are set by the distribution of transit times. Thus, in order to interpret our joint tracer data, a more sophisticated approach such as Transit Time distributions (TTD) model (e.g., Waugh et al., 2004) may be required. Such attempt will need a more careful set up of the surface boundary conditions for the tracers, especially for Pb and Pb isotopes. Because of a shorter residence time of Pb in the atmosphere and the surface ocean, the distribution of Pb and Pb isotopes in the surface North Atlantic Ocean exhibit a larger spatial variance than radiocarbon, depending on prevailing winds,

distance from main sources, and surface ocean currents (Hamelin et al., 1997; Helmers and v~~V~~an der L~~l~~oeff, 1993; Veron et al., 1994; Weiss et al., 2003). Moreover, the spatial variance itself has changed greatly as the dominant Pb emitting sources change over time (e.g., Weiss et al., 2003). Thus, the surface boundary condition for Pb and Pb isotopes that evolves both in time and space will be necessary to model the evolution of deep-sea Pb and Pb isotopes.

5. Conclusion

We used a modern deep-sea coral collected from ~1400m deep off Bermuda to reconstruct time series of radiocarbon, Pb, and Pb isotopes. By analyzing these tracers along the coral's vertical growth axis, we were able to ~~show~~ derive high-resolution (sub-centennial) ^{14}C and Pb records for the last 560-650 years. The reconstructed time series shows the intrusion of bomb radiocarbon and anthropogenic Pb into the deep North Atlantic Ocean. The d~~D~~eep-ocean $\Delta^{14}C$ time series shows ~~the~~ bomb radiocarbon first moving to the coral growth site in ~1980, and $\Delta^{14}C$ increases from -80 ± 1‰ (average 1930-1979) to -39 ± 3 ‰ (average 1999-2001). The c~~C~~oral Pb/Ca ratio starts to increase rapidly from the mid-1850s until 1980 due to the intrusion of anthropogenic Pb into the deep sea, which is accompanied by a decrease in $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios. A transit time of ~25 years is estimated when comparing the timing of bomb-derived $\Delta^{14}C$ increase and Pb-isotope-ratio decrease between the deep-sea and surface coral records, assuming advection-dominated transport of these tracers. However, the increase of $\Delta^{14}C$ and Pb in the deep sea is lower than the surface, representing these tracers were mixed with seawater with low $\Delta^{14}C$ and Pb during the transport. Indeed, a simple advection-mixing model using the radiocarbon data shows that mixing may be more important than advection in the transport of radiocarbon from the surface to the deep-sea coral site. Overall, this study shows the

potential of using deep-sea corals as a recorder of radiocarbon, Pb, and Pb isotope variability in deep sea on a decadal to centurial time scale, which is the time scale that cannot be studied by direct seawater observation or by using other deep-ocean proxy archives like sediment cores. The time series obtained from the deep-sea coral provides useful information on the processes delivering the tracers from the surface to the ocean interior.

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Commented [EB1]: Presumably Jess will also have a grant number to add.

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