



RESEARCH ARTICLE

10.1002/2016GC006578

Key Points:

- We ^{14}C date highly detrital sediment from the Antarctic margin containing very little autochthonous carbon
- We employ composite and isotope dilution Ramped PyrOx ^{14}C dating, considering blank contamination for each
- Both approaches sacrifice analytical precision for gains in accuracy; application to other detrital systems depends on uncertainty limits

Supporting Information:

- Supporting Information S1

Correspondence to:

C. Subt,
csubt@mail.usf.edu

Citation:

Subt, C., H. I. Yoon, K. C. Yoo, J. I. Lee, A. Leventer, E. W. Domack, and B. E. Rosenheim (2017), Sub-ice shelf sediment geochronology utilizing novel radiocarbon methodology for highly detrital sediments, *Geochem. Geophys. Geosyst.*, 18, 1404–1418, doi:10.1002/2016GC006578.

Received 5 AUG 2016

Accepted 2 MAR 2017

Accepted article online 7 MAR 2017

Published online 7 APR 2017

Sub-ice shelf sediment geochronology utilizing novel radiocarbon methodology for highly detrital sediments

C. Subt¹ , H. I. Yoon², K. C. Yoo² , J. I. Lee² , A. Leventer³ , E. W. Domack¹, and B. E. Rosenheim¹

¹College of Marine Science, University of South Florida, St Petersburg, Florida, USA, ²Korea Polar Research Institute, Incheon, South Korea, ³Department of Geology, Colgate University, Hamilton, New York, USA

Abstract Sub-ice shelf sediments near Larsen C ice shelf (LIS-C) show fine-scale rhythmic laminations that could provide a near-continuous seasonal-resolution record of regional ice mass changes. Despite the great potential of these sediments, a dependable Late Quaternary chronology is difficult to generate, rendering the record incomplete. As with many marginal Antarctic sediments, in the absence of preserved carbonate microfossils, the reliability of radiocarbon chronologies depends on presence of high proportions of autochthonous organic carbon with minimized detrital organic carbon. Consequently, acid insoluble organic (AIO) ^{14}C dating works best where high productivity drives high sediment accumulation rates, but can be problematic in condensed sequences with high proportions of detrital organic carbon. Ramped PyrOx ^{14}C dating has progressively been shown to improve upon AIO ^{14}C dates, to the point of matching foraminiferal carbonate ^{14}C dates, through differential thermochemical degradation of organic components within samples. But in highly detrital sediments, proportions of contemporaneously deposited material are too low to fully separate autochthonous organic carbon from detrital carbon in samples large enough to ^{14}C date. We introduce two modifications of the Ramped PyrOx ^{14}C approach applied to highly detrital sediments near LIS-C to maximize accuracy by utilizing ultra-small fractions of the highly detrital AIO material. With minimization of the uncertainty cost, these techniques allow us to generate chronologies for cores that would otherwise go undated, pushing the limits of radiocarbon dating to regions and facies with high proportions of pre-aged detritus. Wider use of these techniques will enable more coordinated *a priori* coring efforts to constrain regional glacial responses to rapid warming where sediments had previously been thought too difficult to date.

1. Introduction

An accurate reconstruction of past Earth conditions requires an archive that is not only datable, but that offers the ability to compile dates into a meaningful chronology that can be regionally correlated to preexisting age models. Sedimentary archives are fundamentally detrital in nature, and in sediments where high proportions of detritus include the material from which ages are sought, dating can become ambiguous. Antarctic glacial marine sediments have long been considered among the most problematic to date due to a lack of preserved foraminifera [Domack *et al.*, 1989; Licht *et al.*, 1998; Andrews *et al.*, 1999; Mackintosh *et al.*, 2014]. Hence, acid insoluble organic (AIO) radiocarbon (^{14}C) is often used for Antarctic sediments with the hope that authigenic algal-derived organic matter from the water column above (henceforth referred to as “syndepositionally-aged”) dilutes any pre-aged detritus transported from continental rocks or sediments that would be dated in conjunction with the authigenic material. But AIO ^{14}C ages have often been found to incorporate pre-aged reworked carbon [Andrews *et al.*, 1999; Leventer *et al.*, 2006; Rosenheim *et al.*, 2008; Mackintosh *et al.*, 2011; Rosenheim *et al.*, 2013; Subt *et al.*, 2016]. In “highly detrital” sediments, the portion of syndepositionally-aged carbon is exceedingly small, creating further difficulties in achieving accurate ages. The potential of sedimentary research in Antarctica is maximized if the effects of detrital organic carbon in AIO are reduced, increasing accuracy of AIO dates. Doing so can expand Antarctic research not only into improved deglacial chronology, but also into broadened exploration of regions where typical dating methods have been impractical or ineffectual.

Although dating AIO material can be problematic, proper application to well-understood stratigraphy and depositional settings has improved our understanding of Antarctic deglaciation. Advances in using

stratigraphic information to ensure more accurate ^{14}C using the AIO carbon have expanded our ability to date sediments without carbonate material [Domack *et al.*, 1989, 1999]. AIO ^{14}C dating has allowed for advancements such as an unsurpassed chronology of 43 dates in ~ 44 m of Holocene sediment in the Palmer Deep [Domack *et al.*, 2001], constraints on Antarctic Peninsula and Ross Sea Ice Sheet retreat during the Last Glacial Maximum (LGM) [Heroy and Anderson, 2007; McKay *et al.*, 2008], and can provide limiting ages for grounding line retreat [e.g., Domack *et al.*, 2005; Leventer *et al.*, 2006; Mackintosh *et al.*, 2011; Rebesco *et al.*, 2014]. Traditionally, AIO material in sediments has been used in conjunction with constant age offsets, whereby a core-top age is subtracted from all subsequent downcore ages, as an alternative to the more trusted carbonate ^{14}C ages [Andrews *et al.*, 1999; Domack *et al.*, 1999; Mackintosh *et al.*, 2011]. The subtraction of a constant ^{14}C age downcore, however, can result in nonlinear isotopic bias, and is dependent on the constancy of the proportions of ancient carbon and syndepositionally-aged carbon, which is unlikely given the ephemeral nature of ice flows [Pudsey *et al.*, 1994; Andrews *et al.*, 1999; Michalchuk *et al.*, 2009; Rosenheim *et al.*, 2013; Subt *et al.*, 2016], and on the uncertain assumption that the reservoir age has remained the same through time [Stuiver *et al.*, 1986; Carlson and Clark, 2012]. Thus, despite refinements in ^{14}C dating, Antarctic sediment cores can often lack accurate chronologies.

Methodological improvements in separating pools of organic carbon within the sediment have been made by employing compound-specific/compound-class diatom-bound ^{14}C dating [Eglinton *et al.*, 1996, 1997; Pearson *et al.*, 1998; Ohkouchi *et al.*, 2003; Ingalls *et al.*, 2004; Ohkouchi and Eglinton, 2006, 2008; Yamane *et al.*, 2014]. This technique involves the chemical extraction of specific compounds (biomarkers) associated with organism-specific processes. Early work utilizing this technique had difficulties with the large amounts of material required for ^{14}C analysis [Ingalls and Pearson, 2005]. Compound-specific ^{14}C dating has since been developed more recently for sediments that contain greater quantities of the necessary pools of carbon. However, recent work in the Ross Sea [Yokoyama *et al.*, 2016] and the Wilkes Land Coast [Yamane *et al.*, 2014] illustrates large uncertainties that result from applying compound-specific ^{14}C dating to hemipelagic sediments. Moreover, this approach requires large amounts of sediment for extraction to produce an accurate chronology.

Ramped PyrOx ^{14}C dating has also offered recent advances in separating of pools of organic carbon through thermochemical degradation [Rosenheim *et al.*, 2008, 2013; Subt *et al.*, 2016]. In Ramped PyrOx, the least diagenetically stable component of the sediment is related to the least thermochemically stable (lowest temperature) and is thus concentrated in the first aliquot of CO_2 to be collected when temperature is increased linearly. Early work shows that high-resolution temperature intervals approached foraminiferal ages, but lower-resolution intervals did not offer as much an improvement [Rosenheim *et al.*, 2008]. Results suggested that contributions from different pools changed downcore and that constant age offsets were potentially erroneous [Rosenheim *et al.*, 2013]. Further advancements have been made by using smaller aliquots at the beginning of the reaction to reduce the amount of older CO_2 incorporated into the aliquot [Subt *et al.*, 2016]. Smaller first aliquots have also been shown to improve the age to match the ^{14}C age from carbonate material [Subt *et al.*, 2016]. Ramped PyrOx dating is not without complication, especially for highly detrital sediments. If the amount of autochthonous, syndepositionally-aged carbon in a sample is too small, it may be overwhelmed by blank contamination [Santos *et al.*, 2010; Fernandez *et al.*, 2014] or overwritten by older, pre-aged carbon in larger thermochemically separated samples. It should also be noted that both compound-specific and Ramped PyrOx dating may still yield an average age from a mixture of components.

Although many incremental advances have been made to improve the accuracy and precision of dates from highly detrital samples, much of the research conducted in Antarctic marine sediments is still highly dependent on the ability to retrieve high-resolution sediment cores with sufficient carbonate material for dating. Alternative ^{14}C dating approaches are needed to reduce uncertainty of more accurate ^{14}C dates from highly detrital sub-ice shelf sediments. We generate a reliable and meaningful chronology for a sediment core proximal to the grounding line of the Larsen C ice shelf (LIS-C, Figure 1), offering a major advance involving a manipulation of the Ramped PyrOx approach to minimize precision costs of previous incremental advances [Rosenheim *et al.*, 2008, 2013; Subt *et al.*, 2016]. We present two innovations to the Ramped PyrOx approach that allow us to look beyond the last deglaciation and to address more condensed sediment sequences over the Holocene that are difficult to date due to a greater mixture of detrital material (Figures 1 and 2). In one technique, we apply multiple identical Ramped PyrOx analyses and combine ultra-small low-temperature aliquots of CO_2 of the same sample (Composite technique). In the other, we combine

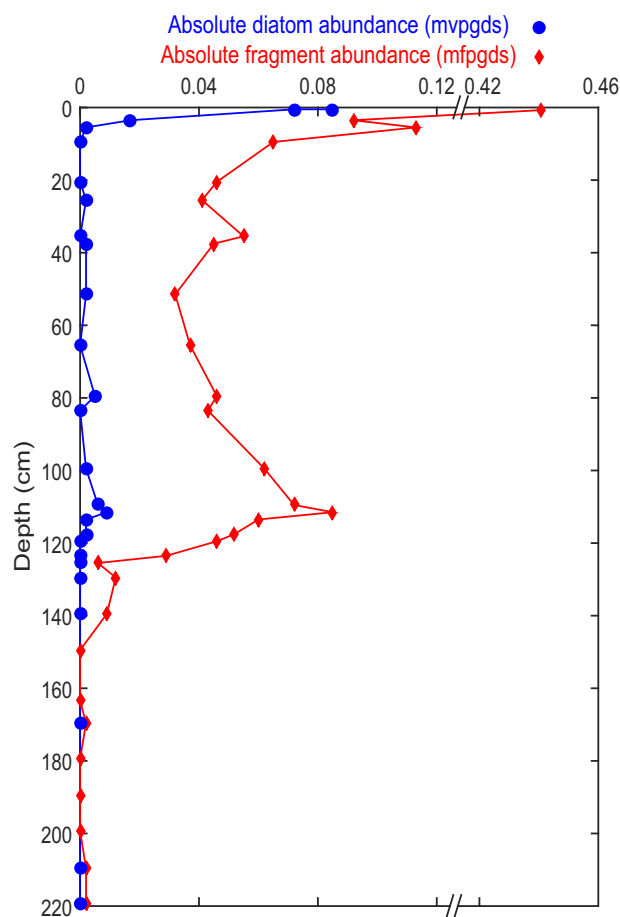


Figure 1. Diatom valve counts in core EAP13 GC16B show nearly barren assemblage downcore except for samples within the top 5 cm, establishing the highly detrital nature of this core.

ultra-small low-temperature CO₂ aliquots with a surrogate of known age and quantity (Isotope Dilution technique). By developing these alternate techniques and improving AIO ¹⁴C dating, future research may be able to delve deeper into regions, time periods and lithofacies that have precluded dating and adequate understanding.

2. Methods

2.1. Site Locations

This study examines marine sediments from near the LIS-C in the Antarctic Peninsula (Figure 3). It is one of the most sensitive regions to recent climate change [Vaughan *et al.*, 2001]. Thus, it is important to determine whether the strong climate sensitivity of the LIS-C is purely the result of anthropogenic warming, or if past climate variability has shown similar trends. Other parts of the Larsen Ice Sheet (LIS-B in 2002 and LIS-A in 1992) have disintegrated rapidly in recent years, garnering public attention and spurring advancement of research concerning Antarctic glacial advance and retreat [Brachfeld *et al.*, 2003]. LIS-C is the largest and most stable ice shelf of this system, and ice conditions in 2013 allowed a close approach of the R/V Araon to the ice shelf edge. Sediment cores were taken that were largely considered sub ice shelf in nature (see below). Interpretation of sediment transport process and bio-

geochemistry in these setting is not only interesting from the standpoint of modern ice shelf environments, but also may relate, as an analog environment, to ocean sedimentation from the Cryogenian.

2.2. Core Description

Several cores were taken along the East Antarctic Peninsula in 2013 on-board the R/V Araon by the Korea Polar Research Institute (KOPRI). Gravity core 16B (EAP13 GC16B: 66° 3.89832' S, 60° 27.69212' W) was taken near the northern region of the LIS-C (Figure 3). It was taken from a water depth of 324 m and is 238 cm long. This location is rather unique in that it has remained under a disintegrating ice sheet adjacent to the LIS-C, which retreated from this site in the past century [Ferrigno *et al.*, 2008]. Figure 4 describes this core graphically, but we offer this brief textual description for reference. This core consists of four lithologic units: the upper 21 cm of the core is characterized by sandy diamicton, rich in calcareous microfauna. The interval from 21 to 90 cm is characterized by finely laminated, sandy-clayey silt. From 90 to 194 cm, the mud consists of slightly sandy, silty clay. Below 194 cm, a structureless diamicton constitutes the basal unit of the stratigraphy. The mud intervals (from 21 to 194) are characterized by a systematic bundling of fine laminations that consist of alternating (rhythmic) intervals of thick and thin couplets (of silt and clay). Generally, intervals of thinner couplets are thicker and more variable than the thicker couplet intervals. Horizontal laminations dominate the lower third of the mud interval, but then are interspersed with inclined bedding, likely indicative of migrating bed forms with amplitudes of approximately 20–30 cm. Reversals in the direction of inclined bedding are evident in several intervals. There are finer-scale higher-frequency alternations within the lamination bundles but these are deserving of a much more detailed analysis than appropriate to

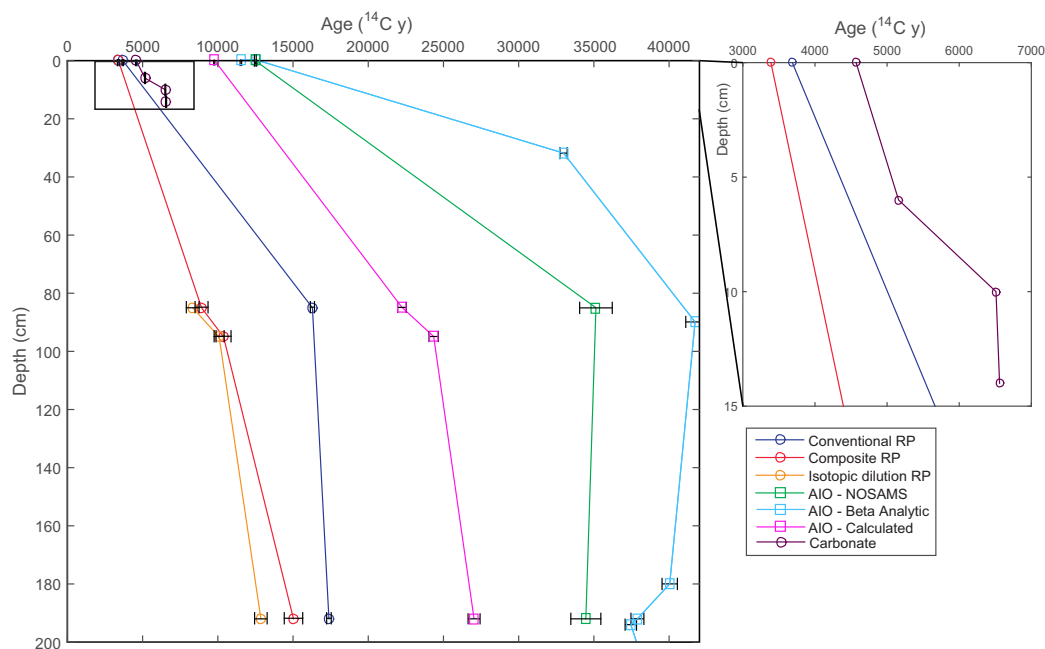


Figure 2. Comparison of Larsen C age models using conventional, composite, and isotope dilution Ramped PyrOx techniques as well as measured and calculated AIO ages. Note an additional Beta Analytic data point extends beyond the depth range shown in this figure. The complete data can be found in Tables 1 and 2.

this paper and will be discussed in a subsequent publication. Notably lacking within the mud facies are any signs of unsorted, coarse sand, or gravel. Also of note are five disconformable horizons whereby the inclined laminations are abruptly truncated, but notable without any coarse lag or irregular erosive surface (these are indicated as surfaces D-1 through D-5 in Figure 4). Hence this core is unique in that most sub-ice shelf muds consist of non-rhythmic laminations typically interspersed with coarse grains of ice-rafted origin [Domack *et al.*, 2005; Rebesco *et al.*, 2014]. The fine-scale systematic (rhythmic) laminations in this core could provide annual and even seasonal (varved) time increments on a near-continuous basis. Therefore, core EAP13 GC16B has great potential as a precise and accurate chronometer for ice mass changes associated with the LIS-C. Yet, due to its overwhelming detrital nature, there is a challenge in developing a fixed absolute time for what is now a “floating record” of potential glacial marine varves.

Twelve sediment samples were taken from this core for ^{14}C analysis (Figure 4). Only four samples near the top of the core contained sufficient well-preserved foraminiferal tests for carbonate ^{14}C analysis.

2.3. Carbonate ^{14}C Analysis

Four samples were taken within the top 14 cm of the core from which sufficient foraminifera were retrievable for ^{14}C analysis. All samples were benthic, monospecific *Globacassidulina biora* in pristine condition, but the assemblage in general was diverse, well-preserved, and abundant.

2.4. AIO ^{14}C Chronologies

Preliminary AIO ^{14}C measurements were analyzed by Beta Analytic Radiocarbon Dating Laboratory. To remove carbonate components prior to AMS dating, freeze-dried bulk sediments were dispersed and subjected to 2.5 N HCl at 90°C for a minimum of 1.5 h and rinsed in deionized water at 70°C until neutrality was reached. These analyses were pursued to inform the best approach to apply the alternative techniques of Ramped PyrOx, as described below. All Ramped PyrOx aliquots analyzed by the three techniques were sent to the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility for $^{14}\text{C}/^{12}\text{C}$ ratio determination. High precision measurements were applied for ages from RP1 (the first temperature interval of Ramped PyrOx dates). As preliminary AIO ages were analyzed by Beta Analytic, a second set of AIO sediment samples were also analyzed at NOSAMS to avoid interlaboratory differences and to match the core depths with those used for Ramped PyrOx analyses. For comparison, AIO ^{14}C ages were also calculated from the weighted arithmetic mean of the spectrum of Ramped PyrOx ages, as they have previously been

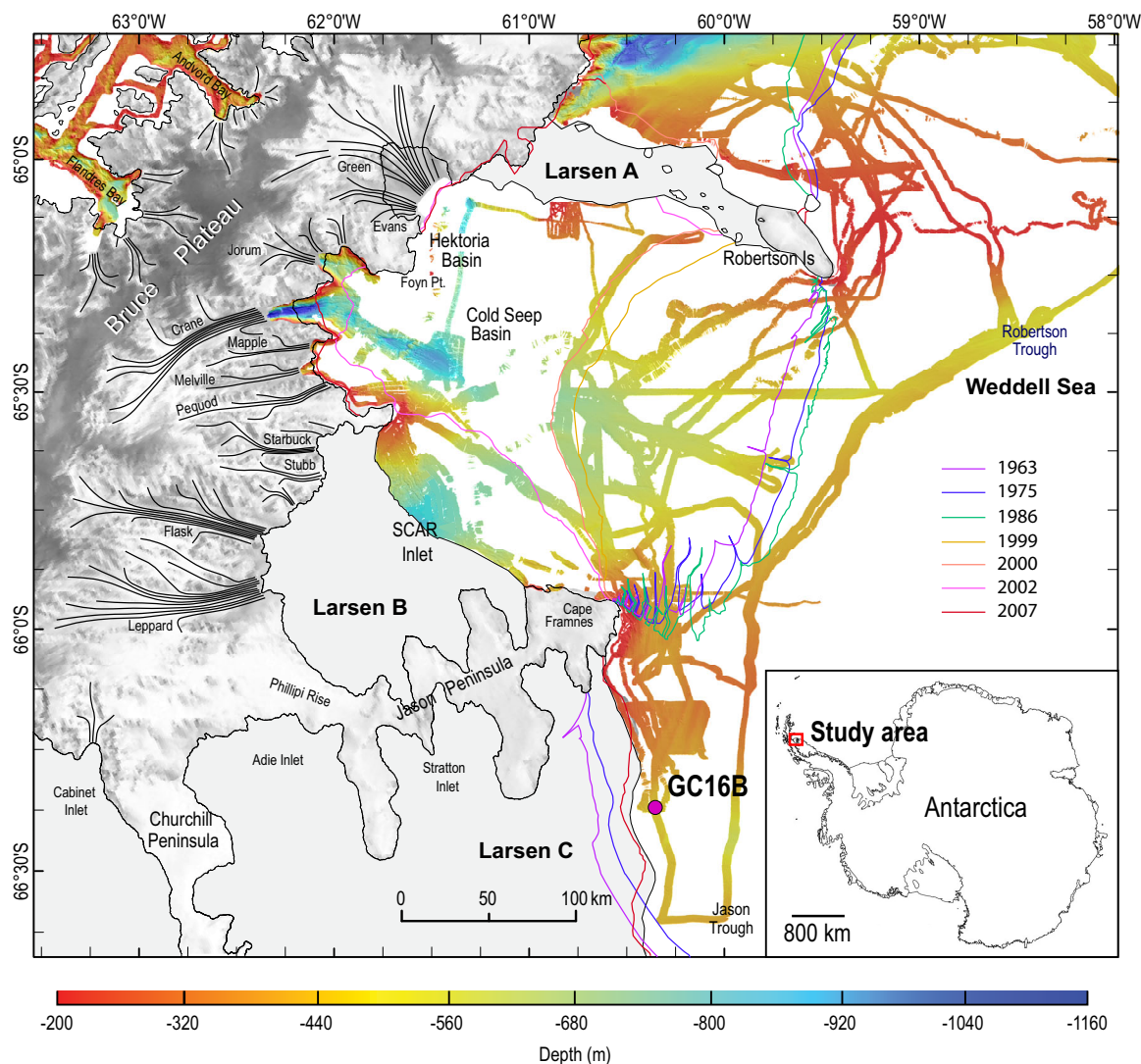


Figure 3. Map of the study region near the Larsen C on the eastern Antarctic Peninsula with swath bathymetry data. The purple circle indicates the location of core EAP13 GC16B and its accompanying box core, EAP13 BC16A (modified from Lavoie *et al.* [2015]). LGM extent of Larsen Ice Shelf surpasses the scope of this map.

found to coincide with measured AIO ^{14}C ages [Rosenheim *et al.*, 2013]. Pretreatment protocols vary widely between laboratories, and have the potential to affect sediment ^{14}C measurements. The acid treatment performed by Beta Analytic (described above) is the most rigorous. Samples analyzed using Ramped PyrOx and used to calculate AIO ^{14}C dates underwent a much gentler approach described below. NOSAMS pretreatment protocols are very similar to that used for Ramped PyrOx, with the exception of applying a lengthier acid-treatment period.

2.4.1. Conventional Ramped PyrOx ^{14}C Analysis

All sediment samples were processed at the University of South Florida—College of Marine Science. Each sample was dried and homogenized, then pretreated with 1N HCl for ~ 2 h to remove carbonate material. The samples were centrifuged and rinsed in deionized water until the pH of the supernatant was normalized at 7.0. The samples were dried and stored in pre-combusted (525°C , 2 h) glass vials until analysis. Individual Ramped PyrOx analyses were based on the methods described by Rosenheim *et al.* [2008], wherein sediment was weighed out (~ 100 μmol C based on %TOC measurements) into pre-combusted (900°C , 2 h) quartz flow-through reactor inserts in between plugs of pre-combusted (525°C , 2 h) quartz wool. The quartz reactor was inserted into the top portion of the combustion chamber, and was continuously purged with 35 mL/min of ultra-high purity (UHP) He, while the combustion chamber was continuously purged with 4 mL/min of (UHP) O_2 in 7 mL/min of (UHP) He to prevent back-flow of O_2

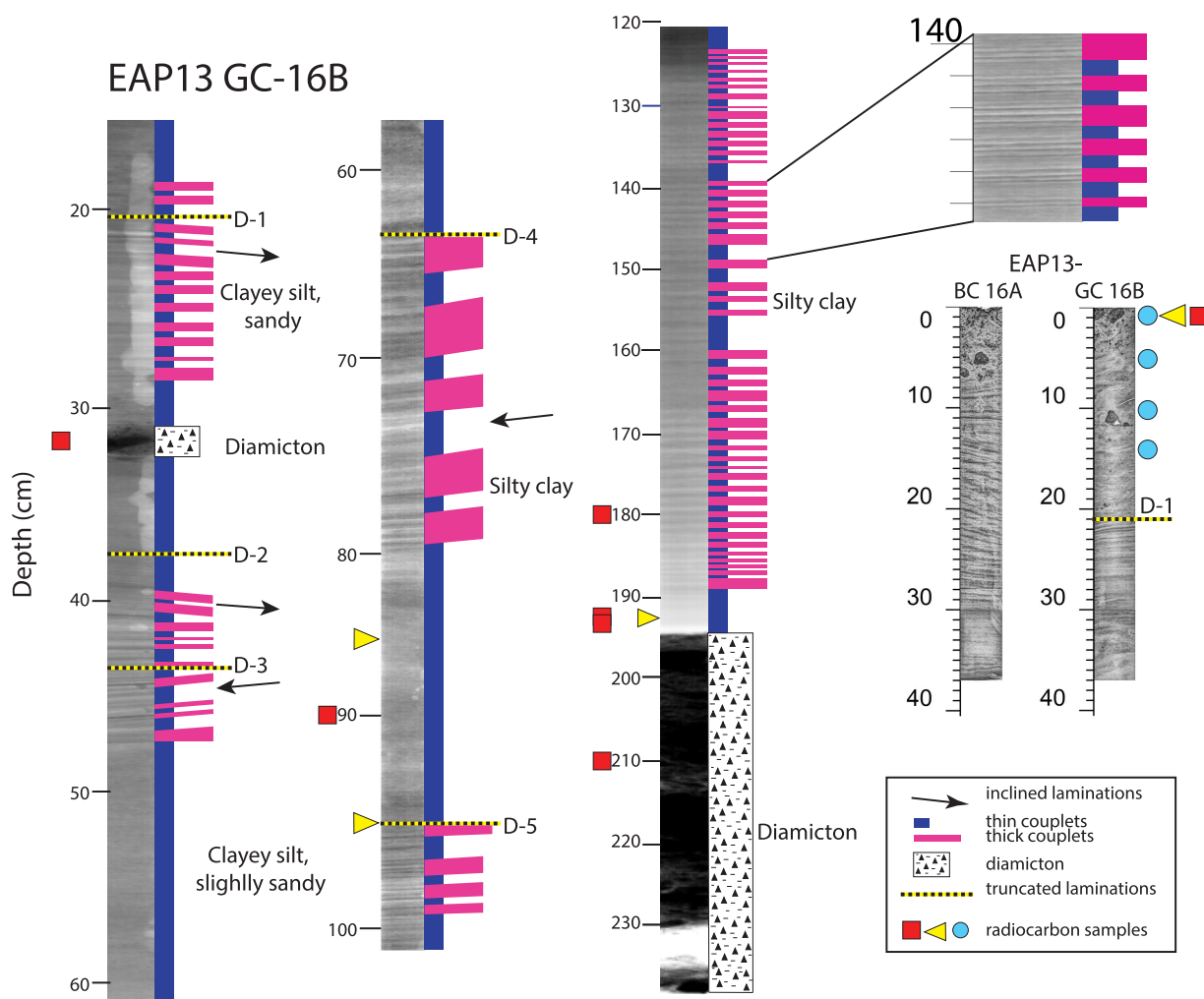


Figure 4. Stratigraphic column for EAP13 GC16B. Blue circles indicate carbonate, red squares indicate preliminary AIO measurements, and yellow triangles indicate RP radiocarbon dates.

into the reactor (Figure 5). The reactor resides within two tubular furnaces, where the top furnace (pyrolysis furnace) is ramped up in temperature by 5°C/min and the bottom furnace (oxidation furnace) is kept at a constant temperature of 800°C throughout the pyrolysis reaction. Pyrolysates entrained in He and flowing downstream were converted to CO₂ in the combustion furnace on CuO wire. An infrared CO₂ detector (Sable Systems Ca-10) measured the CO₂ concentration in the mixture of gases as it flowed to one of two 8-loop borosilicate glass cryogenic traps partially immersed in liquid N₂. Remotely controlled pneumatic valves (Luwers) toggled in a way that enabled one trap to accumulate incoming condensable products from the He carrier gas at atmospheric pressure while the other was connected to allow expansion into a vacuum separations line for cryogenic purification of CO₂ with liquid nitrogen and n-propanol cooled to solid-liquid phase transition with liquid nitrogen. Purified CO₂ aliquots were collected and flame-sealed into evacuated pre-combusted (525°C, 2 h) Pyrex tubes with pre-combusted copper oxide and silver wire (Figure 5).

To provide a baseline by which two novel techniques could be compared, Ramped PyrOx analyses were performed with little change to the originally established approach [Rosenheim *et al.*, 2008]. Subsequent work by Rosenheim *et al.* [2013] and Subt *et al.* [2016] showed that smaller low-temperature aliquots could improve the dates considerably. Thus for this study, we collected the two lowest-temperature aliquots (RP1 and RP2) at sizes of 10–15 μmol, and the subsequent three CO₂ aliquots (RP3, RP4, and RP5; supporting information Table S1) at approximately 23–27 μmol, roughly equally splitting the remaining carbon.

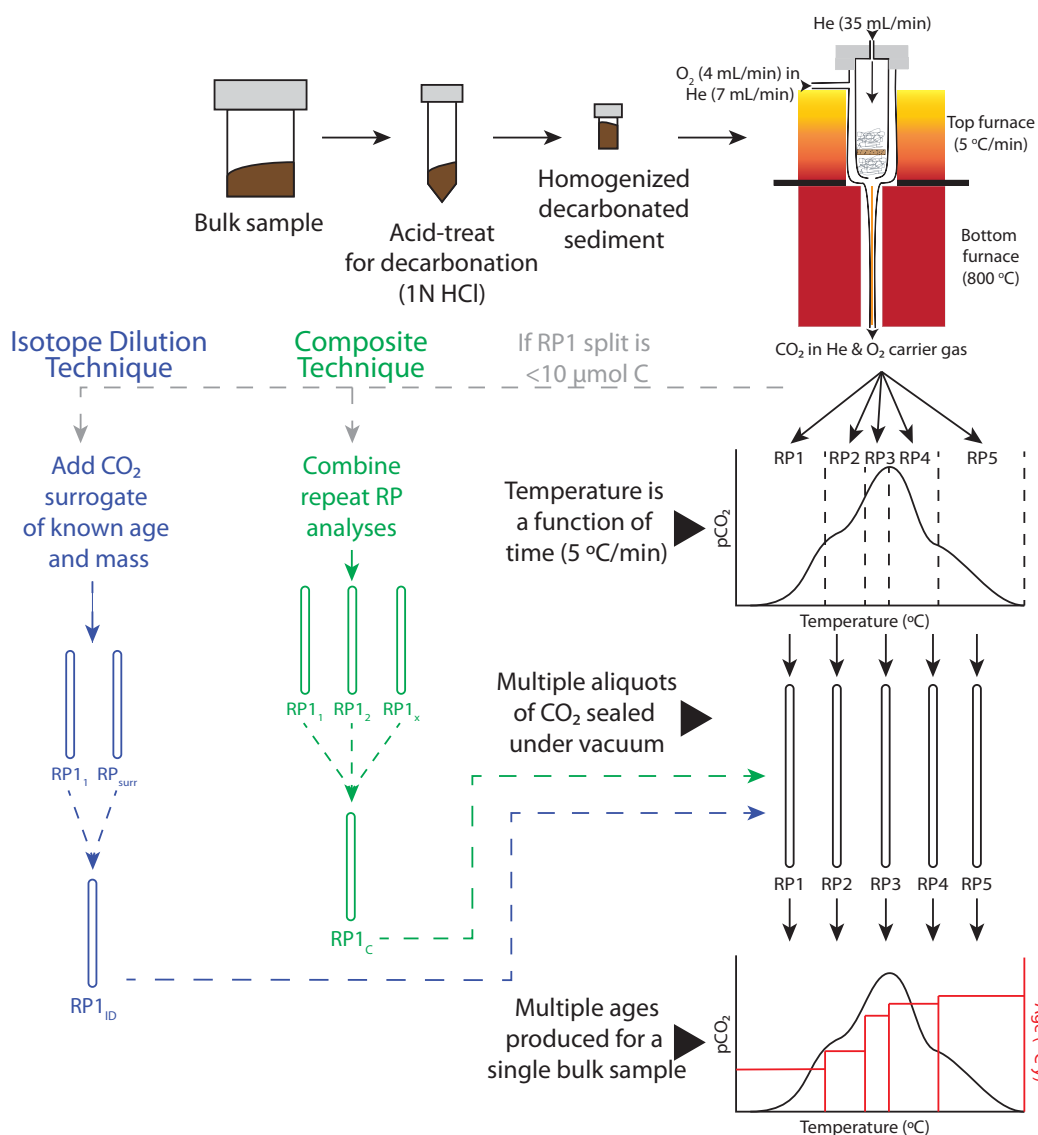


Figure 5. Schematic demonstrating steps involved in pretreatment and Ramped Pyrolysis Oxidation (^{14}C) analysis. Samples are homogenized and treated with 1N HCl for ~2 h for decarbonation. Samples are pyrolyzed at a rate of 5°C/min in the top furnace of the combustion chamber and carried by He to the bottom furnace, which is held constant at 800°C, and combined with O_2 gas where products of the pyrolysis reaction are subsequently oxidized. CO_2 resulting from this process accumulates gradually and separated at selected time intervals. Subsamples are purified in a vacuum line before being collected and flame-sealed in individual pyrex tubes where aliquots are numbered sequentially based on T_1 (e.g., RP1 is lowest-temperature aliquot and Ramped Pyrolysis Oxidation is highest-temperature). Each CO_2 aliquot is individually analyzed for Ramped Pyrolysis Oxidation. In conventional Ramped Pyrolysis Oxidation analyses (black), lowest-temperature aliquots contain between 10 and 15 μmol of CO_2 . If $<10 \mu\text{mol}$ are desired, then alternate techniques may be appropriate: Composite Ramped Pyrolysis Oxidation (green) analyses consist of combining the lowest-temperature aliquots from multiple identical analyses of the same sample. Isotope dilution Ramped Pyrolysis Oxidation (blue) analyses consist of combining the lowest-temperature aliquot with a CO_2 surrogate of known age and mass.

It is important to note that blank contamination (unavoidable admixture of contaminant CO_2 into the sample during any analysis) from Ramped Pyrolysis Oxidation analysis should be accounted for in all samples analyzed. The blank contamination for each sample was calculated using equations based on the derivation of blank correction by Santos *et al.* [2007]:

$$\delta_U = \delta_M + \delta_M \left(\frac{m_{\text{dead}}}{m_U} \right) + \delta_M \left(\frac{m_{\text{mod}}}{m_U} \right) - \delta_{\text{mod}} \left(\frac{m_{\text{mod}}}{m_U} \right) \quad (1)$$

$$\sigma_{\delta_U}^2 = \sigma_{\delta_M}^2 \left(1 + \frac{m_{dead} + m_{mod}}{m_U} \right)^2 + \sigma_{m_{dead}}^2 \left(\frac{\delta_M}{m_U} \right)^2 + \sigma_{m_{mod}}^2 \left(\frac{\delta_M - \delta_{mod}}{m_U} \right)^2 + \sigma_{m_U}^2 \left(\frac{\delta_{mod} m_{mod} - \delta_M m_{dead} - \delta_M m_{mod}}{m_U^2} \right) \quad (2)$$

where δ is the fraction modern (Fm) value, as described by *Stuiver and Polach [1977]*, σ is uncertainty, m is the mass, and subscripts U and M are the unknown and the measured values of the sample, respectively, and subscripts *dead* and *mod* are ^{14}C -free blank and modern blank, respectively (supporting information Text S1). Recent studies on modern and dead blank contamination in the Ramped PyrOx system suggests m_{mod} is time-dependent, while the m_{dead} remains the same over time and is independent of the pyrolysis system [*Fernandez et al., 2014*]. The total modern carbon in one Ramped PyrOx analysis is $2.8 \pm 0.6 \mu\text{g}$ (all errors reported are 1σ). A proportion of this amount was assigned as the modern blank contamination for each temperature interval based on the collection time of each aliquot. m_{dead} has a constant mass of $1.4 \pm 0.8 \mu\text{g}$ and is not time-integrated, thus all $1.4 \mu\text{g}$ must be applied to each aliquot from a Ramped PyrOx run.

To surpass the limitations of the Ramped PyrOx method in analyzing ultra-small fractions of young material in highly detrital sediments (Figure 6), we have developed two techniques to minimize the costs in precision while improving accuracy. For both techniques, the preexisting AIO ^{14}C ages were used to estimate the proportion of material assumed to be syndepositionally-aged (f_{SA} , as shown in Figure 6) by assuming a two end-member mixing model and a linear accumulation rate (supporting information Text S2). Initial sample Ramped PyrOx analyses were also conducted to determine the CO_2 evolution as well as the percent of total organic carbon (%TOC) in each sample (Table 1). Decomposition rates of organic carbon and preliminary AIO ^{14}C dates were used to calculate the temperature at which the estimated amount of syndepositionally-aged material combusts (T_i ; supporting information Text S2). We inherently assume in this approach that no pre-aged organic carbon would decompose until all autochthonous organic carbon had pyrolyzed—this is a necessary oversimplification that enables our preliminary estimate of the sampling temperature.

2.4.2. Composite Ramped PyrOx ^{14}C Analysis

Of the four LIS-C samples collected for Ramped PyrOx ^{14}C dating, three (85, 95, and 192 cm core depths) had very small f_{SA} ; thus the “conventional” $10 \mu\text{mol}$ RP1 would have incorporated too much pre-aged detrital material. For these samples, a composite of analyses was performed where equivalent masses were analyzed each time ($100 \mu\text{mol C}$, as determined by %TOC). RP1 was collected at the same temperature (T_i ;

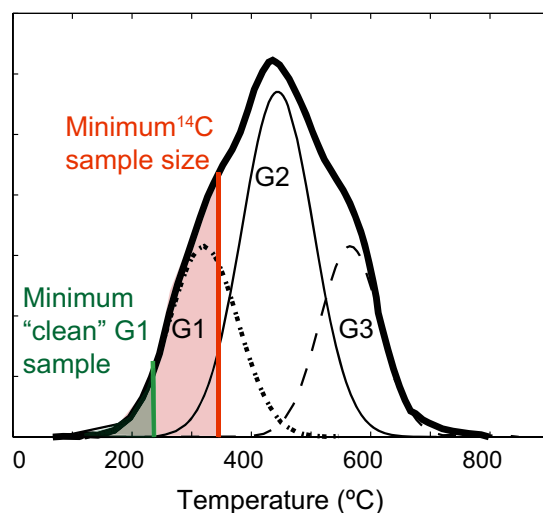


Figure 6. Idealized thermograph illustrating the evolution of pCO_2 as temperature is raised at a constant rate in a situation where the amount of autochthonous OC may be smaller than a measurable ^{14}C sample. Gaussian modeling has been implemented (G1–G3) to represent the mixture of multiple organic components incorporated in the bulk organic sample [*Rosenheim et al., 2013*]. The minimum “clean” sample denotes where the lowest-temperature aliquot can be taken to collect G1 component without a mixture of the G2 component.

Table 1) each time, and the number of analyses was determined by f_{SA} (Figure 5). An additional two aliquots were collected for a portion of the analyses, where RP2 was $\sim 10\text{--}15 \mu\text{mol}$ and RP3 included the remaining material. To reduce analytical error associated with AMS measurements of small samples, RP1 aliquots of the same sample were combined (RP1_C, Figure 5); $10 \mu\text{mol}$ was decided to be a sufficiently large sample to produce an acceptably small analytical uncertainty ($<10\%$) based on previous analyses made with the Ramped PyrOx approach (Figure 6) and minimize the number of composite runs that needed to be combined (each with its own blank contamination). Because the amount of carbon in each sample is collected in a relatively short amount of time, the time-dependent modern blank contamination is not very large [*Fernandez et al., 2014*]. However, the resulting modern blank contamination from mixing multiple aliquots becomes cumulative. In the case of composite aliquots, m_{mod} was calculated by taking into account the cumulative, time-integrated proportion of each individual CO_2 aliquot.

Table 1. Sample Preliminary Data for Core EAP13 GC16B, Including AIO Ages Analyzed at Beta Analytic

Depth (cm)	%TOC	AIO Age (¹⁴ C y)	±	f _{SA} ^a	T ₁ ^b (°C)
0	0.315	12,500	50	0.2575	288
0		11,470	50		
32		32,960	240		
85	0.675			0.0132	270
90		41,720	620		
95	0.420			0.0141	279
180		40,030	510		
192	0.795	37,880	430	0.0400	338
194		37,440	380		
210		39,460	440		

^af_{SA} refers to the calculated fraction of estimated syndepositionally-aged carbon in the sample and was calculated using preliminary AIO ¹⁴C measurements and assuming a two-endmember mixing model.

^bT₁ is the temperature at which syndepositionally-aged material was estimated to combust.

Additionally, *m_{dead}* was used as determined by *Fernandez et al.* [2014] because only the composite sample was recombusted and subject to the likely source of ¹⁴C-free blank contaminants.

2.4.3. Isotope Dilution Ramped PyrOx ¹⁴C Analysis

An isotope dilution technique was applied to equal-sized low-temperature aliquots of the same samples as the composite technique for comparison of an independent technique using the Ramped PyrOx approach. Multiple analyses (composite analyses) were also required for this technique, but the number was reduced by adding an amount of a diluent, which may be any substance of well-constrained radiocarbon content. We used NBS Oxalic

Acid I (Ox-I) as the surrogate for this technique because it is a modern standard that generally decomposes at lower temperatures than the estimated T₁ for each sample. Multiple analyses were conducted using the same parameters as those in the composite technique and were combined with individual samples of Ox-I to create a single ~10 μmol aliquot (RP1_{ID}, Figure 5). For each isotope dilution, resulting ages needed to be corrected for the addition of a diluent to calculate the age of the sample using the following equations:

$$\delta_{U-ID} = \frac{\delta_S - \delta_U - f\delta_S}{-f} \quad (3)$$

$$\sigma_{\delta_{U-ID}}^2 = \sigma_f^2 \left(\frac{\delta_S - \delta_U}{f^2} \right)^2 + \sigma_{\delta_S}^2 \left(1 - \frac{1}{f} \right)^2 + \sigma_{\delta_U}^2 \left(\frac{1}{f} \right)^2 \quad (4)$$

where subscripts *U-ID* and *S* are the isotope dilution-corrected unknown and the diluent respectively, and *f* is the proportion of the unknown relative to the mixture of diluent and unknown (supporting information Text S3). It should be noted that these equations utilize the blank-corrected unknown (δ_U , σ_{δ_U}), thus the blank correction must be applied first before correcting for the addition of a surrogate. This blank correction was applied in the same manner as was done for the composite technique.

In this study, the diluent was prepared using Ramped PyrOx analyses in the same manner as the samples for consistency. Doing so adds slightly to the blank contamination previously described, but the time of decomposition of Ox-I is only minutes and not much blank will accumulate over that time. In the future, this blank contamination could be reduced by using closed-tube combustion to extract CO₂ from the diluent.

Determining how much isotopic diluent to add to composite Ramped PyrOx samples involves minimizing the number of times that the sample needs to be composited while maximizing precision. By reducing the number of analyses per sample, we also reduced the amount of time spent on the technique (preparing and compositing multiple runs), thereby decreasing the mass of sample required. However, reducing the number of analyses increases the amount of Ox-I relative to the sample and incurs an increased cost in precision.

3. Results

The CO₂ evolution (thermographs) of all four samples shows interesting trends that relate to diagenetic and thermochemical stability of each sample (Figure 7). Thermographs in Figure 7 have undergone a simple temperature offset to match maximum temperature peaks. This is to correct for potential technical issues independent of sediment properties, such as movements of the thermocouples from sample loading between analyses, causing the thermographs to shift along the temperature ramp. Because the targeted temperature intervals are so small, these shifts on the order of magnitude of a few degrees are significant

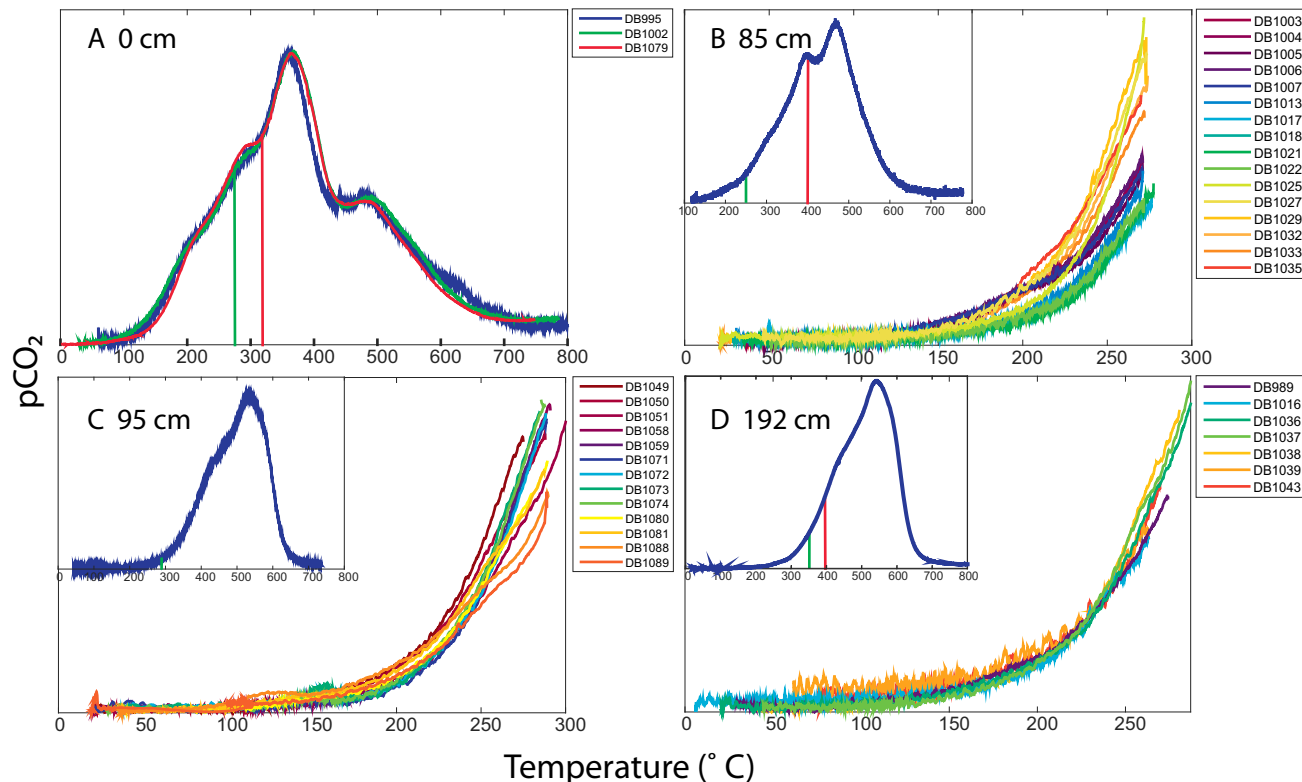


Figure 7. pCO₂ evolution along the temperature ramp for individual sample analyses (indicated in legends by laboratory run number) at core depths of (a) 0 cm, (b) 85 cm, (c) 95 cm, and (d) 192 cm. Insets in Figures 7b, 7c, and 7d are representative of a single full run and vertical lines show average temperatures where first aliquots were collected for Composite and Isotope Dilution (green) and Conventional (red) techniques.

relative to the slopes of the thermographs over these short intervals. Samples from 85, 95, and 192 cm depth intervals possess similar shapes, with only small variations in the height of main peaks. The first distinct peak occurs at ~390–400°C, and a second main peak occurs between ~480 and 500°C. In the core-top sample, the main peak occurs at ~370°C, the second smaller peak at ~500°C and they shift in relative proportion. CO₂ thermographs also showed some variability between analyses of the same sample (Figure 7). In samples at 85, 95, and 192 cm core depths, the combination of multiple runs provides us with the opportunity to visualize the replicability of thermograph shapes when the same sample is analyzed by Ramped PyrOx multiple times in the same manner [Williams *et al.*, 2014]. Each run was normalized and integrated onto the same temperature scale for statistical comparison.

All ages are reported in Table 2 in both blank-corrected ¹⁴C years and calibrated years BP (supporting information Table S2). All following discussion refers to ages in uncalibrated ¹⁴C years. However, the calibration of these ages does not change the overall findings. The Ramped PyrOx ¹⁴C ages derived using composite and isotope dilution demonstrate a nearly constant sedimentation rate downcore (~69 yr/cm). The composite technique yielded ages between 8,900 and 15,000 ¹⁴C years. The isotope dilution technique yields ages from 8,300 to 12,900 ¹⁴C years. The offset between these ages increases downcore. The core-top sample required no alternate technique to yield an age of acceptable precision, but was dated twice using the conventional Ramped PyrOx technique and yielded ages of 3390 ± 50 (~12 μmol CO₂) and 3685 ± 40 (~15 μmol CO₂) ¹⁴C years. The analytical uncertainty of these ages increased downcore for all techniques used. The conventional Ramped PyrOx technique yields the lowest uncertainty, but oldest ages. The isotope dilution technique yields lower uncertainty for the samples analyzed (330–420 ¹⁴C y) than the composite technique (430–610 ¹⁴C y). Carbonates were only available to date within the first 15 cm of the core, so only the core-top sample can be compared to carbonate ages. Nevertheless, the Ramped PyrOx ages are younger by ~1050–1440 ¹⁴C years than the corresponding carbonate ages (Table 2 and Figure 2).

Table 2. Radiocarbon Dates and Calendar Year Corrected Values for EAP13 GC16B with All Analysis Techniques, as Explained in the Text^a

Depth (cm)	Type	Mass (μmol of C)	δ ¹³ C (‰)	Fm	± (1σ)	Age (¹⁴ C yrs BP)	± (1σ)	Calibrated Age (yrs BP)	± (1σ)
0	AIO Sediment ^c		-25.93	0.2112	0.0016	12,490	50	N/A	
85	AIO Sediment ^c		-25.06	0.0126	0.0017	35,000	1100	N/A	
192	AIO Sediment ^c		-25.46	0.0137	0.0017	34,500	1000	N/A	
0	AIO Calculated			0.2990	0.0012	9,695	35	N/A	
85	AIO Calculated			0.0631	0.0023	22,200	290	N/A	
95	AIO Calculated			0.0485	0.0019	24,310	310	N/A	
192	AIO Calculated			0.0348	0.0017	27,000	400	N/A	
0	Conventional RP1	14.820	-25.64	0.6320	0.0035	3,685	40	620	90
0	Conventional RP1	12.315	-24.86	0.6558	0.0043	3,390	50	250	80
0	Conventional RP5	6.882	-20.78	0.0173	0.0048	33,000	2200	N/A	
85	Conventional RP1	11.982	-27.11	0.1316	0.0023	16,300	140	16,300	180
85	Conventional RP5	18.318	-23.63	0.0060	0.0016	41,000	2100	N/A	
192	Conventional RP1	13.011	-27.22	0.1148	0.0022	17,387	150	17,500	200
192	Conventional RP5	11.996	-23.45	0.0114	0.0024	36,000	1700	N/A	
85	Composite RP1	9.870	-24.75	0.3295	0.0177	8,900	430	6,600	490
95	Composite RP1	11.370	-25.6	0.2747	0.0171	10,400	500	8,400	650
192	Composite RP1	8.520	-29.08	0.1540	0.0118	15,000	610	14,700	860
85	Isotope Dilution RP1	10.190	-21.95	0.3546 ^b	0.0187	8,300 ^b	420	6,000	420
95	Isotope Dilution RP1	9.790	-24.43	0.2849 ^b	0.0118	10,000 ^b	330	8,000	410
192	Isotope Dilution RP1	11.850	-24.77	0.2017 ^b	0.0105	12,900 ^b	420	11,500	470
0	Foraminiferal Carbonate			0.5661	0.0028	4,570	40	1,660	70
6	Foraminiferal Carbonate			0.5261	0.0023	5,160	35	2,460	70
10	Foraminiferal Carbonate			0.4447	0.0017	6,510	30	4,080	70
14	Foraminiferal Carbonate			0.4419	0.0019	6,560	35	4,140	70

^aAges are reported in blank-corrected ¹⁴C years BP and have been calibrated to calendar years BP using Calib 7.1 Marine13 calibration curve with ΔR = 880 ± 30 based on living foraminifera obtained from the Larsen B embayment [Domack et al., 2005]. Total masses of carbon used for ¹⁴C analysis are included for all Ramped PyrOx analyses.

^bValues have been corrected for the addition of a surrogate using equations (3) and (4).

^cAIO Sediment refers to treated samples analyzed by NOSAMS.

4. Discussion

The results of our AIO ¹⁴C dates measured by two different techniques and calculated from Ramped PyrOx determinations illustrate the ambiguity associated with dating a mixture of different-aged material. Acid insoluble organic matter was treated differently to remove carbonates prior to AIO dating due to the fact samples were originally sent to a commercial laboratory with a different protocol for removal of carbonates. Although only a ~10-¹⁴C year difference was observed between core-top AIO ages, an offset of >3000 years was observed at 192 cm depth (Table 2). Previous research has found that calculated AIO ¹⁴C dates based on the weighted arithmetic mean of Ramped PyrOx ¹⁴C dates are similar to measured ¹⁴C analyses of the measured AIO dates [Rosenheim et al., 2013]. Yet in this study, calculated AIO dates are consistently younger than measured values (Figure 2). The disparity between measured values can be attributed to interlaboratory differences, primarily in differing acid-treatment protocols. Moreover, in samples where the ¹⁴C date is very old, such as AIO in these samples, small differences in the ¹⁴C/¹²C ratio measured by AMS, caused by process or sample heterogeneity, can cause large differences in the ¹⁴C dates (supporting information Figure S5). The more rigorous pretreatment protocols used at Beta Analytic may have removed more AIO material, thus resulting in older preliminary AIO ¹⁴C dates. By contrast, samples that underwent Ramped PyrOx analyses and used to calculate AIO ¹⁴C dates were treated with a more dilute acid for a minimal amount of time. Thus, these analyses showed the best preservation of the most labile component. Such differences, illustrative of highly detrital sediment and brought forth by different acid treatments, are prominent in this study due to the age and detrital nature of the sediments.

Like AIO ¹⁴C dates, thermographs can also be impacted by small differences in processing and analysis. We examined the replicability in the initiation of pyrolysis decomposition in the Ramped PyrOx system and found strong similarities between all samples, suggesting good low-temperature replicability (Figure 7). However, small differences are evident in all cases, which is most likely explained by sample heterogeneity. It is important to note that the data from pyrolysis initiation (Figures 7b–7d) are highly amplified compared to Figure 7a and previous publications showing reproducibility [Rosenheim and Galy, 2012; Rosenheim

et al., 2013; *Williams et al.*, 2014; *Bianchi et al.*, 2015]. Thus, very small differences in the proportions of different components within a sample may result in visible thermograph variations. Other possible causes for thermograph variability, including movement of the thermocouples and changes in sample size, were avoided by, offsetting the temperature as described in the results and by analyzing equal masses of individual samples, respectively.

All three Ramped PyrOx techniques discussed in this study (conventional, composite, and isotope dilution) result in significantly younger dates than their associated AIO ^{14}C dates and thus offer substantial improvement on the AIO ^{14}C dating approach. Conventional Ramped PyrOx ^{14}C dates are also significantly younger than carbonate dates at core-top samples by >1000 ^{14}C years. But this is likely caused by reworking and lag processes which serve to concentrate foraminifera of various dates across surfaces of little or no sedimentation [i.e., *Domack et al.*, 1999, 2005; *Rebesco et al.*, 2014]. These processes seemingly acted without leaving any visual clues (broken tests, opacity) that the tests had been reworked. The offset may also be influenced by inherent chemical differences between planktic algal material and benthic foraminifera. For example, *Ohkouchi et al.* [2002] and *Uchida et al.* [2005] demonstrated temporal offsets between the two proxies, despite large differences in study sites, water depth and sedimentation rates. In this study, there was no carbonate material further downcore with which to compare the AIO chronology, but a previous study by *Subt et al.* [2016] shows that the use of a smaller RP1 aliquot for a Ramped PyrOx analysis can yield similar dates to those derived from carbonate material. Here we demonstrate that in highly detrital sediments, the use of ultra-small aliquots of the most labile material in the composite Ramped PyrOx technique improves chronologies at depths where AIO ^{14}C is overwhelmed by pre-aged detrital material that produces dates clearly too old to be realistic (Figure 2).

Ramped PyrOx ^{14}C dates derived using alternate techniques (composite and isotope dilution Ramped PyrOx) showed significantly younger dates than not only AIO, but also conventional Ramped PyrOx ^{14}C dates. Nevertheless, there are relatively small differences between the composite and isotope dilution Ramped PyrOx ^{14}C dates. Although, in order to estimate how much CO_2 to sample in the beginning of the pyrolysis decomposition, we assumed that no pre-aged carbon would decompose until all autochthonous OC decomposed, we have no clear way to rule out the possibility that the material within each single aliquot is likely still a mixture incorporating some degree of pre-aged OC. By assuming a ^{14}C free endmember, we minimize the sample size from the beginning of the decomposition reaction, thereby minimizing the potential for admixture of pre-aged OC. The fact that these two independent techniques produce relatively equal chronologies emphasizes their utility in approaching the true date of the sample by demonstrating that the fraction of pre-aged material sampled in each aliquot, if greater than zero, is likely not variable.

Interpretation of our determinations of the ^{14}C content of the extreme low-temperature end of our thermographs as calibrated radiocarbon ages depends upon our consideration of these aliquots as mixtures of autochthonous and pre-aged carbon. It is not meaningful to calibrate ages of mixtures of autochthonous and detrital OC, although we have learned quite a bit about Antarctic deglaciation from calibrated AIO ages [e.g., *Domack et al.*, 2001]. Considering the potential pitfalls of calibrating radiocarbon ages from samples that we cannot rule out as mixtures along with our goal to chronicle the unique sediments from the LIS-C, we only apply radiocarbon calibration to carbonate and RP1 (Table 2). We calibrate the RP1 ages from our two alternative techniques of the Ramped PyrOx approach because the improvement of ages of independent ages strongly suggests minimization of the pre-aged OC. In other words, the improvement in ages demonstrates that the mixture of pre-aged detrital material in RP1 is substantially diluted. By comparison, carbonate ^{14}C ages show older core-top ages than Ramped PyrOx ^{14}C ages of equivalent depth, indicating that even carbonate ^{14}C ages can be either mixed with older forams or biased to some degree. Furthermore, it is important to note that dating of chemical separations of individual compounds [*Ohkouchi and Eglinton*, 2006; *Ohkouchi and Eglinton*, 2008; *Yokoyama et al.*, 2016] does not guarantee zero admixture of older members of that compound class.

Given that both Ramped PyrOx techniques reported herein result in consistently improved chronologies, it becomes necessary to choose between them. Such a choice should aim to minimize labor and to maximize accuracy. Consideration of the AIO ^{14}C age of the sample and the hypothesized age or stratigraphic control of the deposit in question is important in informing this decision (supporting information Text S4). If the difference between AIO ^{14}C ages and the stratigraphic control is large, then the target for dating becomes smaller. In such cases, a larger number of composited runs are required to accumulate sufficient CO_2 for ^{14}C

analysis (supporting information Figure S2). This number of runs, as well as the %TOC dictates the amount of sample required to accumulate sufficient ultra-small first aliquots from identical runs to minimize analytical error, as well as the amount of time needed to complete these runs (supporting information Figure S3). Moreover, if considering the isotope dilution Ramped PyrOx technique, the availability of a well-measured surrogate of a known age is, of course, very important (supporting information Figure S4).

One of the most important considerations for using these alternate techniques, and a guiding factor in deciding whether any one of them is even appropriate for a set of given samples, is the blank contamination associated with combining aliquots from multiple runs (supporting information Text S4). Modern blank contamination from Ramped PyrOx is time-dependent [Fernandez *et al.*, 2014], thus an aliquot collected over a short amount of time has less modern blank than an aliquot collected over a longer period. ^{14}C dead blank contamination results from recombustion reagents (Ag and CuO), and is therefore applied equally to each aliquot that is recombusted [Fernandez *et al.*, 2014]. This means that the overall blank contamination is more significant for an ultra-small aliquot than a larger aliquot. When multiple ultra-small aliquots are mixed as in the alternate techniques, the combined blank contamination can lead to much greater uncertainty. Recent improvements made on the Ramped PyrOx system have reduced the blank contamination to $2.8 \pm 0.6 \mu\text{g}$ modern C and $1.4 \pm 0.8 \mu\text{g}$ dead C (supporting information Figure S6). This is a significant improvement over the amounts of blank contamination reported by Fernandez *et al.* [2014], and consequently also provides an improvement on the precision of our Ramped PyrOx ^{14}C ages. By reducing the uncertainty from blank contamination, we are also able to combine a significantly larger sum of ultra-small aliquots required for our new techniques.

Assuming both composite and isotope dilution Ramped PyrOx can produce equally accurate ^{14}C ages and that the necessary resources are available for either technique, the main deciding factor becomes the precision, or the overall uncertainty resulting from either technique. Uncertainties from both techniques increase with age of sample and with the number of runs composited. Both uncertainties are also subject to change depending on the difference between the ^{14}C age of the surrogate and the age of the lowest-temperature dated material. However, by using the isotope dilution technique, we effectively reduce the number of runs required to accumulate the necessary amount of CO_2 , reducing the blank contamination and the analytical error. Nevertheless, the isotope dilution technique also requires the addition of a surrogate of known age and mass, which propagates additional uncertainty. When small proportions of the total OC are targeted, necessitating many composites, isotope dilution should likely be favored over composite Ramped PyrOx. Conversely, when the number of runs required is low (targeted proportion of initial OC is higher), the isotope dilution technique has higher uncertainty because of additional uncertainty propagation from isotope dilution and composite Ramped PyrOx should be chosen. This is particularly true for older samples (Figure 8). The position of the uncertainty crossover between composite or isotope dilution techniques depends on

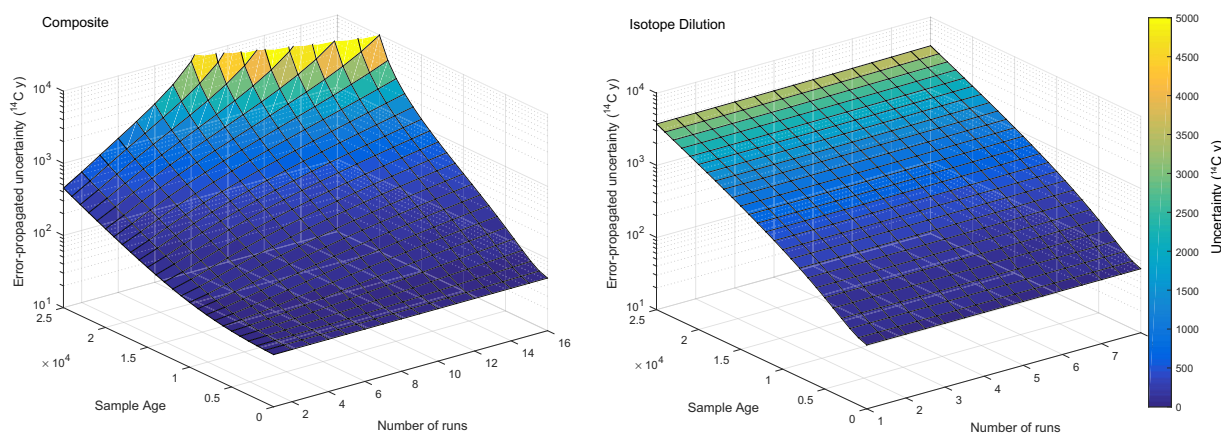


Figure 8. Uncertainty as a function of the number of runs required to accumulate sufficient CO_2 for precise ^{14}C dating and the fully corrected age of the sample is variable depending on the technique used for Ramped PyrOx. Above uncertainties are based on the assumption of $f = 0.7$, $\delta_S = 1.039$, and $m_U = 120 \text{ mg C}$. Values for blank contamination are as reported in Methods section. For simplicity, an analytical uncertainty of 0.002. Note the z axis is shown in logarithmic scale.

the number of runs required and how the age of the sample and shape of the thermograph confer to dictate the amount of surrogate used (Table 1).

It is important to note that the composite and isotope dilution techniques of Ramped PyrOx are for highly detrital sediment; not every sample analyzed using Ramped PyrOx may require these techniques. Many samples may not require multiple runs to accumulate sufficient CO₂ for ¹⁴C dating, as in the case of the core-top sample in this suite of samples or previous work [Subt *et al.*, 2016]. Just as conventional Ramped PyrOx is an alternative when carbonates are not available and AIO ¹⁴C dating may be problematic, the composite and isotope dilution techniques are an alternative when the projected amount of syndepositionally-aged material is too small to be captured in a conventional Ramped PyrOx aliquot (~10–15 μmol CO₂) without influence from the mixture of the age of ancient detritus.

The techniques developed for this study have greatly improved our ability to date highly detrital samples. Techniques such as isotope dilution are not new and unique to this work, and it is conceivable that we can use isotope dilution, for instance, at core intervals where there is some, but not enough, foramiferal carbonate for a single date. However, similar calculations and logic to that found in Figure 8 would need to be carried out independently to assess the cost in precision of isotopic dilution for foraminiferal carbonate dates. By using these techniques, we may ultimately become capable of retrieving more accurate dates for Antarctic marginal marine sediments not only within periods of high productivity and reduced glacial deposition, but within the glacial deposits where dating has so often been precluded. These techniques would also be applicable to a wide range of problematic sediments in regions outside of Antarctica with a highly detrital nature.

5. Conclusions

We have provided two new alternative techniques for the Ramped PyrOx ¹⁴C approach which have improved our ability to date sediments with very low proportions of syndepositionally-aged material. Both techniques we have described show a large improvement in the separation of pre-aged detritus from the much smaller syndepositionally-aged fraction not only for AIO ¹⁴C dating, but on conventional Ramped PyrOx analyses as well. Differences in composite and isotope dilution Ramped PyrOx ¹⁴C dates may occur due to sample heterogeneity, blank contamination, and error propagation. Nevertheless, the differences between the two new techniques are small to negligible relative to the overall improvement in ages compared to AIO. Careful consideration must be taken when deciding which technique is most appropriate for a set of samples. The availability of techniques like those described herein remove limitations on geoscientists working in sediments from the Antarctic margin. Ultimately, this may allow accurate dating of sediments under ice shelves, glacial tills, or siliceous muds and oozes buried prior to the LGM. Sub-ice shelf sediments, for example, could serve as a modern analog for Cryogenian research [e.g., Vincent *et al.*, 2000; Hoffman *et al.*, 2012]. It would also allow researchers to study ice sheet behavior not only during the deglacial period, but into the glacial period as well. Thus, by using these alternative techniques, we can not only date Antarctic marine sediments from the LGM to the present, but we can also provide chronologies beyond these horizons, where highly detrital material has precluded radiocarbon dating in the past.

References

- Andrews, J. T., E. W. Domack, W. L. Cunningham, A. Leventer, K. J. Licht, A. Jull, D. J. Demaster, and A. E. Jennings (1999), Problems and possible solutions concerning radiocarbon dating of surface marine sediments, Ross Sea, Antarctica, *Quat. Res.*, 52(2), 206–216.
- Bianchi, T. S., V. Galy, B. E. Rosenheim, M. Shields, X. Cui, and P. Van Metre (2015), Paleoreconstruction of organic carbon inputs to an oxbow lake in the Mississippi River watershed: Effects of dam construction and land use change on regional inputs, *Geophys. Res. Lett.*, 42, 7983–7991, doi:10.1002/2015GL065595.
- Brachfeld, S., E. Domack, C. Kissel, C. Laj, A. Leventer, S. Ishman, R. Gilbert, A. Camerlenghi, and L. B. Eglinton (2003), Holocene history of the Larsen-A Ice Shelf constrained by geomagnetic paleointensity dating, *Geology*, 31(9), 749–752.
- Carlson, A. E., and P. U. Clark (2012), Ice sheet sources of sea level rise and freshwater discharge during the last deglaciation, *Rev. Geophys.*, 50, RG4007, doi:10.1029/2011RG000371.
- Domack, E. W., A. J. T. Jull, J. B. Anderson, T. W. Linick, and C. R. Williams (1989), Application of tandem accelerator mass-spectrometer dating to late Pleistocene-Holocene sediments of the East Antarctic continental shelf, *Quat. Res.*, 31(2), 277–287.
- Domack, E. W., S. Ship, and J. Anderson (1999), Late Pleistocene–Holocene retreat of the West Antarctic Ice-Sheet system in the Ross Sea: Part 1—geophysical results, *Geol. Soc. Am. Bull.*, 111(10), 1486–1516.
- Domack, E. W., A. Leventer, R. Dunbar, F. Taylor, S. Brachfeld, and C. Sjunneskog (2001), Chronology of the Palmer Deep site, Antarctic Peninsula: A Holocene palaeoenvironmental reference for the circum-Antarctic, *Holocene*, 11(1), 1–9.

Acknowledgments

Most of the analyses reported herein were supported by funds from the Dean of the College of Marine Science, the Office of the Provost, and the Office of the Senior Vice President for Research at the University of South Florida through BER's laboratory start-up package. Samples were collected and initially dated as part of the project titled "KIFES (KOPRI, PM 16060)," funded by the Ministry of Oceans and Fisheries, Korea, and the KOPRI project PE17030. Sedimentological work on this core was supported by grants NSF PLR 0732625 to A.L. and NSF OPP-0732467 to E.W.D. C.S. was supported by the USF Florida Georgia Louis Stokes Alliance for Minority Participation (FGLSAMP) Bridge to the Doctorate Fellowship Award (HRD # 1400837). For additional information and data, please see the supporting information.

- Domack, E. W., D. Duran, A. Leventer, S. Ishman, S. Doane, S. McCallum, D. Amblas, J. Ring, R. Gilbert, and M. Prentice (2005), Stability of the Larsen B ice shelf on the Antarctic Peninsula during the Holocene epoch, *Nature*, *436*(7051), 681–685.
- Eglinton, T. I., L. I. Aluwihare, J. E. Bauer, E. R. M. Druffel, and A. P. Mcnichol (1996), Gas chromatographic isolation of individual compounds from complex matrices for radiocarbon dating, *Anal. Chem.*, *68*(5), 904–912.
- Eglinton, T. I., B. C. Benitez-Nelson, A. Pearson, A. P. Mcnichol, J. E. Bauer, and E. R. M. Druffel (1997), Variability in radiocarbon ages of individual organic compounds from marine sediments, *Science*, *277*(5327), 796–799.
- Fernandez, A., G. M. Santos, E. K. Williams, M. A. Pendergraft, L. Vetter, and B. E. Rosenheim (2014), Blank corrections for ramped pyrolysis radiocarbon dating of sedimentary and soil organic carbon, *Anal. Chem.*, *86*(24), 12,085–12,092.
- Ferrigno, J., A. Cook, A. Mathie, R. Williams, C. Swithinbank, K. Foley, A. Fox, J. Thomson, and J. Sievers (2008), *Coastal-Change and Glaciological Map of the Larsen Ice Shelf Area, Antarctica: 1940–2005*, 28 pp., U.S. Geol. Surv., Reston, Va.
- Heroy, D. C., and J. B. Anderson (2007), Radiocarbon constraints on Antarctic Peninsula ice sheet retreat following the Last Glacial Maximum (LGM), *Quat. Sci. Rev.*, *26*(25), 3286–3297.
- Hoffman, P. F., G. P. Halverson, E. W. Domack, A. C. Maloof, N. L. Swanson-Hysell, and G. M. Cox (2012), Cryogenian glaciations on the southern tropical paleomargin of Laurentia (NE Svalbard and East Greenland), and a primary origin for the upper Russøya (Islay) carbon isotope excursion, *Precambrian Res.*, *206–207*, 137–158.
- Ingalls, A. E., and A. Pearson (2005), Ten years of compound-specific radiocarbon analysis, *Oceanography*, *18*(3), 18–31.
- Ingalls, A. E., R. F. Anderson, and A. Pearson (2004), Radiocarbon dating of diatom-bound organic compounds, *Mar. Chem.*, *92*(1–4), 91–105.
- Lavoie, C., et al. (2015), Configuration of the Northern Antarctic Peninsula Ice Sheet at LGM based on a new synthesis of seabed imagery, *The Cryosphere*, *9*(2), 613–629.
- Leventer, A., E. Domack, R. Dunbar, J. Pike, C. Stickley, E. Maddison, S. Brachfeld, P. Manley, and C. McClennen (2006), Marine sediment record from the East Antarctic margin reveals dynamics of ice sheet recession, *GSA Today*, *16*(12), 4–10.
- Licht, K. J., W. L. Cunningham, J. T. Andrews, E. W. Domack, and A. E. Jennings (1998), Establishing chronologies from acid-insoluble organic ¹⁴C dates on Antarctic (Ross Sea) and arctic (North Atlantic) marine sediments, *Polar Res.*, *17*(2), 203–216.
- Mackintosh, A., N. Golledge, E. Domack, R. Dunbar, A. Leventer, D. White, D. Pollard, R. Deconto, D. Fink, and D. Zwartz (2011), Retreat of the East Antarctic ice sheet during the last glacial termination, *Nat. Geosci.*, *4*(3), 195–202.
- Mackintosh, A. N., et al. (2014), Retreat history of the east Antarctic Ice sheet since the last glacial maximum, *Quat. Sci. Rev.*, *100*, 10–30.
- McKay, R. M., G. B. Dunbar, T. R. Naish, P. J. Barrett, L. Carter, and M. Harper (2008), Retreat history of the Ross Ice Sheet (Shelf) since the Last Glacial Maximum from deep-basin sediment cores around Ross Island, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *260*(1–2), 245–261.
- Michalchuk, B. R., J. B. Anderson, J. S. Wellner, P. L. Manley, W. Majewski, and S. Bohaty (2009), Holocene climate and glacial history of the northeastern Antarctic Peninsula: The marine sedimentary record from a long SHALDRIL core, *Quat. Sci. Rev.*, *28*(27–28), 3049–3065.
- Ohkouchi, N., and T. I. Eglinton (2006), Radiocarbon constraint on relict organic carbon contributions to Ross Sea sediments, *Geochem. Geophys. Geosyst.*, *7*, Q04012, doi:10.1029/2005GC001097.
- Ohkouchi, N., and T. I. Eglinton (2008), Compound-specific radiocarbon dating of Ross Sea sediments: A prospect for constructing chronologies in high-latitude oceanic sediments, *Quat. Geochronol.*, *3*(3), 235–243.
- Ohkouchi, N., T. I. Eglinton, L. D. Keigwin, and J. M. Hayes (2002), Spatial and temporal offsets between proxy records in a sediment drift, *Science*, *298*(5596), 1224–1227.
- Ohkouchi, N., T. I. Eglinton, and J. M. Hayes (2003), Radiocarbon dating of individual fatty acids as a tool for refining Antarctic margin sediment chronologies, *Radiocarbon*, *45*(1), 17–24.
- Pearson, A., A. P. Mcnichol, R. J. Schneider, K. F. Von Reden, and Y. Zheng (1998), Microscale AMS ¹⁴C measurement at NOSAMS, *Radiocarbon*, *40*(1), 61–75.
- Pudsey, C., P. Barker, and R. Larter (1994), Ice sheet retreat from the Antarctic Peninsula shelf, *Cont. Shelf Res.*, *14*(15), 1647–1675.
- Rebesco, M., et al. (2014), Boundary condition of grounding lines prior to collapse, Larsen-B Ice Shelf, Antarctica, *Science*, *345*(6202), 1354–1358.
- Rosenheim, B. E., and V. Galy (2012), Direct measurement of riverine particulate organic carbon age structure, *Geophys. Res. Lett.*, *39*, L19703, doi:10.1029/2012GL052883.
- Rosenheim, B. E., M. B. Day, E. Domack, H. Schrum, A. Benthien, and J. M. Hayes (2008), Antarctic sediment chronology by programmed-temperature pyrolysis: Methodology and data treatment, *Geochem. Geophys. Geosyst.*, *9*, Q04005, doi:10.1029/2007GC001816.
- Rosenheim, B. E., J. A. Santoro, M. Gunter, and E. W. Domack (2013), Improving Antarctic sediment ¹⁴C dating using ramped pyrolysis: An example from the Hugo Island Trough, *Radiocarbon*, *55*(1), 115–126.
- Santos, G. M., J. R. Southon, S. Griffin, S. R. Beaupre, and E. R. M. Druffel (2007), Ultra small-mass AMS ¹⁴C sample preparation and analyses at KCCAMS/UCI Facility, *Nucl. Instrum. Methods Phys. Res., Sect. B*, *259*(1), 293–302.
- Santos, G. M., J. R. Southon, N. J. Drenzek, L. A. Ziolkowski, E. Druffel, X. Xu, D. Zhang, S. Trumbore, T. I. Eglinton, and K. A. Hughen (2010), Blank assessment for ultra-small radiocarbon samples: Chemical extraction and separation versus AMS, *Radiocarbon*, *52*(2–3), 1322–1335.
- Stuiver, M., and H. A. Polach (1977), Discussion; Reporting of C-14 data, *Radiocarbon*, *19*(3), 355–363.
- Stuiver, M. P., G. W. Pearson, and T. Braziunas (1986), Radiocarbon age calibration of marine samples back to 9000 cal yr BP, *Radiocarbon*, *28*(2), 980–1021.
- Subt, C., K. A. Fangman, J. S. Wellner, and B. E. Rosenheim (2016), Sediment chronology in Antarctic deglacial sediments: Reconciling organic carbon ¹⁴C ages to carbonate ¹⁴C ages using Ramped PyrOx, *Holocene*, *26*(2), 265–273.
- Uchida, M., Y. Shibata, K. I. Ohkushi, M. Yoneda, K. Kawamura, and M. Morita (2005), Age discrepancy between molecular biomarkers and calcareous foraminifera isolated from the same horizons of Northwest Pacific sediments, *Chem. Geol.*, *218*(1–2), 73–89.
- Vaughan, D. G., G. J. Marshall, W. M. Connolley, J. C. King, and R. Mulvaney (2001), Devil in the Detail, *Science*, *293*(5536), 1777–1779.
- Vincent, F. W., E. J. A. Gibson, R. Pienitz, V. Villeneuve, A. P. Broady, B. P. Hamilton, and C. Howard-Williams (2000), Ice shelf microbial ecosystems in the high arctic and implications for life on snowball earth, *Naturwissenschaften*, *87*(3), 137–141.
- Williams, E. K., B. E. Rosenheim, A. P. Mcnichol, and C. A. Masiello (2014), Charring and non-additive chemical reactions during ramped pyrolysis: Applications to the characterization of sedimentary and soil organic material, *Org. Geochem.*, *77*(0), 106–114.
- Yamane, M., Y. Yokoyama, Y. Miyairi, H. Suga, H. Matsuzaki, R. B. Dunbar, and N. Ohkouchi (2014), Compound-specific ¹⁴C dating of IODP Expedition 318 Core U1357A obtained off the Wilkes Land Coast, Antarctica, *Radiocarbon*, *56*(3), 1009–1017.
- Yokoyama, Y., et al. (2016), Widespread collapse of the ross ice shelf during the late Holocene, *Proc. Natl. Acad. Sci. U. S. A.*, *113*(9), 2354–2359.