






ADVANCING ANTARCTIC SEDIMENT CHRONOLOGY THROUGH COMBINED RAMPED PYROLYSIS OXIDATION AND PYROLYSIS-GC-MS

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ABSTRACT. Radiocarbon (^{14}C) dating of sediment deposition around Antarctica is often challenging due to heterogeneity in sources and ages of organic carbon in the sediment. Chemical and thermochemical techniques have been used to separate organic carbon when microfossils are not present. These techniques generally improve on bulk sediment dates, but they necessitate assumptions about the age spectra of specific molecules or compound classes and about the chemical heterogeneity of thermochemical separations. To address this, the Rafter Radiocarbon Laboratory has established parallel ramped pyrolysis oxidation (RPO) and ramped pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) systems to thermochemically separate distinct carbon fractions, diagnose the chemical composition of each fraction, and target suitable RPO fractions for radiocarbon dating. Three case studies of sediment taken from locations around Antarctica are presented to demonstrate the implementation of combined RPO-AMS and Py-GC-MS to provide more robust age determination in detrital sediment stratigraphy. These three depositional environments are good examples of analytical and interpretive challenges related to oceanographic conditions, carbon sources, and other factors. Using parallel RPO-AMS and Py-GC-MS analyses, we reduce the number of radiocarbon measurements required, minimize run times, provide context for unexpected ^{14}C ages, and better support interpretations of radiocarbon measurements in the context of environmental reconstruction.

KEYWORDS: Antarctica, instrumentation, radiocarbon AMS dating, ramped pyrolysis, sediments.

INTRODUCTION

Chronology of sediment stratigraphy is a key application of radiocarbon (^{14}C) dating. Improved chronology increases our ability to correlate sedimentary records to nearby marine-derived paleoclimate proxy records and/or high-resolution ice core records (e.g., Bracegirdle et al. 2019; Ashley et al. 2021). In marine sediments, carbonate microfossils such as foraminifera are an ideal ^{14}C dating target (e.g., McKay et al. 2016), but are rarely preserved in Antarctic sediments (Ohkouchi et al. 2003; Ohkouchi and Eglinton 2006, 2008; Rosenheim et al. 2008; Yamane et al. 2014; Berg et al. 2020). In the absence of microfossils, extraction of organic carbon from acid-insoluble organic matter (AIOM) is often the only option (Andrews et al. 1999; McGeehin et al. 2001; Ohkouchi et al. 2003; Leventer et al. 2006; Ohkouchi and Eglinton 2008; Rosenheim et al. 2008; Mackintosh et al. 2011; Rosenheim et al. 2013a, 2013b; Subt et al. 2016). However, the application of conventional bulk combustion of AIOM has resulted in ages older than the time of deposition because the bulk measurement represents an average of the multiple carbon pools that comprise the sediment mixture (Eglinton et al. 1997; Subt et al. 2016; Berg et al. 2020). Older, reworked organic carbon in detrital sediment acts as a

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contaminant, obscuring the depositional age, a phenomenon particularly problematic around Antarctica (Eglinton et al. 1996; Ohkouchi et al. 2003; Ohkouchi and Eglinton 2006, 2008; Rosenheim et al. 2013b; Subt et al. 2016; Berg et al. 2020). Accurate chronologies therefore require the isolation of syndepositional organic carbon from reworked or pre-aged organic carbon. Methods for both chemical and thermochemical separation of organic carbon have been developed to improve accuracy of radiocarbon dating of sediment deposition (Eglinton et al. 1996; Rosenheim et al. 2008).

Compound-specific radiocarbon analysis (CSRA) has been applied to different compounds and compound classes, increasing accuracy of depositional age in most cases but also elucidating limitations to the approach. Specific chemical compounds that can be confidently expected to represent the depositional age can be separated and dated using CSRA (Eglinton et al. 1996, 1997; Mollenhauer et al. 2005; Ohkouchi and Eglinton 2008; Ohkouchi et al. 2003, 2005; Yamane et al. 2014; Berg et al. 2020). Although it is a powerful technique, a major CSRA limitation is the difficulty of collecting sufficient source-specific material from cores to accurately measure radiocarbon over a stratigraphically useful interval (Eglinton et al. 1996; Ohkouchi et al. 2005; Mollenhauer and Rethemeyer 2009; Ohkouchi and Eglinton 2008). Small sample sizes of isolated, purified compounds complicate graphitization and radiocarbon measurement resulting in larger uncertainties and increased contamination issues (Eglinton et al. 1996). If derivatization is required, additional carbon may be introduced which needs to be corrected for in the data interpretation (Eglinton et al. 1996). There are also challenges in measuring realistic processing blanks (Eglinton et al. 1996; Ohkouchi and Eglinton 2008). An isolated and purified compound may also still be a mixture of carbon sources, either before or after deposition, or a result of heterotrophic incorporation of multiple sources of variably-aged carbon (Ohkouchi and Eglinton 2008). Considering these difficulties, there is scope for complementary methods that can separate sediment carbon into broad compound classes while avoiding some of the technical challenges of CSRA.

Ramped Pyrolysis Oxidation-Accelerator Mass Spectrometry (RPO-AMS)

Thermochemical separation of organic matter pools for radiocarbon dating can be achieved with the ramped pyrolysis oxidation (RPO) approach, leveraging thermochemical stability of molecules, but sacrificing knowledge of the chemical structures being dated (Rosenheim et al. 2008; Berg et al. 2020). RPO-AMS has been applied to study degradation of oil contamination of sediments (Pendergraft et al. 2013; Pendergraft and Rosenheim 2014; Rogers et al. 2019), soil residence time and turnover rates (Plante et al. 2013; Zhang et al. 2017; Grant et al. 2019; Hemingway et al. 2019; Sanderman and Grandy 2020), and riverine, marine, and subglacial sediment carbon cycle (Rosenheim and Galy 2012; Zhang et al. 2017; Bao et al. 2019; Hemingway et al. 2019; Venturelli et al. 2020, 2023; Venturelli 2021).

RPO-AMS is particularly valuable in high latitude (Arctic and Antarctic) chronology applications (e.g., Rosenheim et al. 2008, 2013b; Subt et al. 2016, 2017; Venturelli et al. 2020, 2023; Smith et al. 2021; Suzuki et al. 2021; Venturelli 2021; Cui et al. 2022; Roseby et al. 2022; Truax 2023). RPO separates syndepositional carbon, generally found in low-temperature pyrolysis fractions, from older reworked carbon in the higher temperature fractions that would bias a traditional bulk radiocarbon date toward an older and thus inaccurate date of deposition (Rosenheim et al. 2008, 2013b; Subt et al. 2016, 2017; Venturelli et al. 2020, 2023). RPO-AMS has achieved significant improvement in sediment chronology compared to bulk sediment

(Subt et al. 2016, 2017; Venturelli et al. 2020, 2023; Venturelli 2021; Truax 2023) with fewer technical challenges than CSRA, yet limitations remain. Thermal fractions contain a mixture of chemical compound groups which may incorporate multiple sources. Charring can also occur during pyrolysis, resulting in molecular alteration particularly in higher temperature fractions, but does not generally impact sediment chronology (Williams et al. 2014). Typically, five to seven temperature fractions are measured for ^{14}C content, attempting to establish a plateau of younger ages at the low temperature range that best represent the age of deposition (Rosenheim et al. 2008). The large number of radiocarbon measurements can be cost prohibitive, and it has become common to measure only the lowest temperature fraction(s) (e.g., Smith et al. 2021; Roseby et al. 2022). Further, in the absence of an age plateau at low temperatures, even the lowest temperature fraction may contain some older, reworked material, thus yielding only a maximum age for timing of deposition (Subt et al. 2016, 2017). Finer temperature resolution can help, but to obtain a sufficiently large sample requires aggregation of the ultra-low temperature fraction from repeated RPO runs or isotope dilution (Subt et al. 2017).

Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS)

Py-GC-MS can support RPO-AMS by identifying the chemical composition of each temperature fraction, thus approaching the chemical specificity of CSRA. Interpretation of Py-GC-MS is not as straightforward as other chemical fingerprinting techniques because the original source compounds must be inferred from pyrolysates (Carr et al. 2010). However, by using a thermal desorption mode rather than flash pyrolysis, a ramped temperature gradient on the Py-GC-MS reasonably mimics the ramped pyrolysis technique (prior to oxidation). At lower temperatures, more volatile, low molecular weight compounds are released. As the temperature increases, macromolecules within a sample are decomposed in the absence of oxygen, producing identifiable smaller molecules that are indicative of their precursor compounds. It has been used to characterize the molecular composition of woods; soils; lacustrine, fjord, wetland and marine sediments; petroleum hydrocarbons; and others (Pouwels et al. 1987; Saiz-Jimenez and De Leeuw 1986; Ralph and Hatfield 1991; Van Bergen et al. 1997; Pulchan et al. 2003; Fabbri et al. 2005; van Bergen and Poole 2002; Saiz-Jimenez 1995; Carr et al. 2010; Terán et al. 2009; Zhang et al. 2016; Seeley et al. 2018). Py-GC-MS can be used to answer questions about sedimentary organic matter composition, provenance, contamination, preservation, degradation, and diagenesis (Terán et al. 2009; Carr et al. 2010; Zhang et al. 2016; Seeley et al. 2018).

RPO-AMS has been supported by Py-GC-MS to understand the environmental impact of the Deep Water Horizon spill using thermal slicing techniques at pre-determined intervals to analyze common petroleum hydrocarbons (O'Connor et al. 2020; Pendergraft et al. 2013; Pendergraft and Rosenheim 2014; Seeley et al. 2018). Another study examined the range of turnover rates in soil carbon pools using stepped temperature (as opposed to ramped temperature) Py-GC-MS at the maximum split temperature for each RPO fraction (Sanderman and Grandy 2020). Py-GC-MS is a desirable technique for paleoenvironmental reconstruction due to its rapid and inexpensive semi-quantitative analysis, small sample mass, minimal sample pre-treatment requirements, no requirement for derivatization, and selective sample purification by thermolability (Pouwels et al. 1987; Terán et al. 2009; Carr et al. 2010).

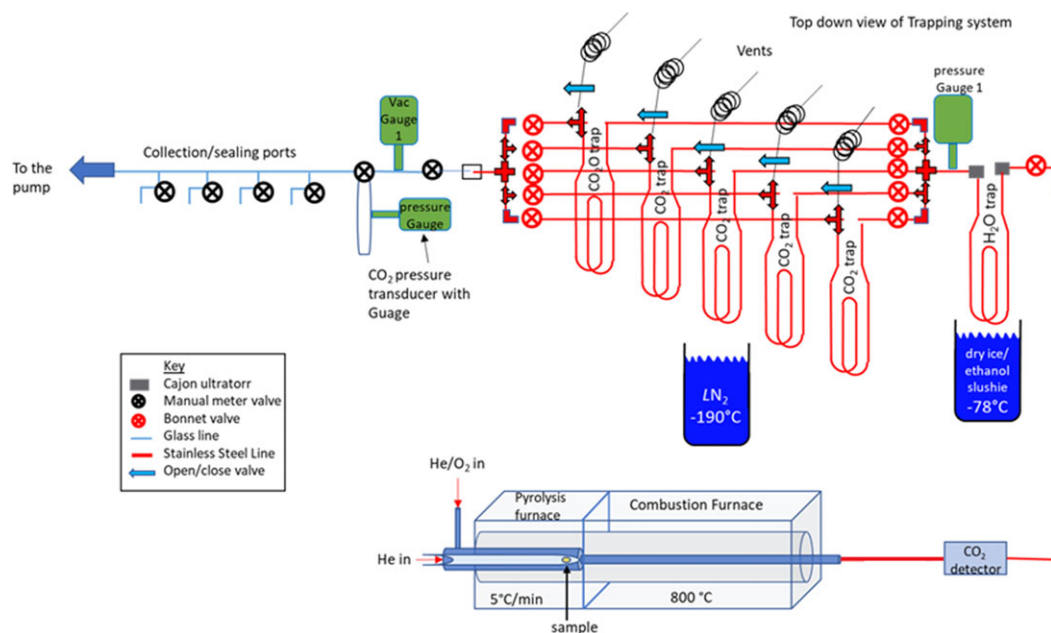


Figure 1 RRL RPO schematic. The new RPO line at RRL has been based on previous designs with a few minor modifications. The line is constructed from stainless steel where possible to address fragility, availability, and cost of specialised low-volume glass. The furnace geometry is horizontal to reduce bleed-through heat between the two furnaces. The number of CO₂ collection traps has been increased from two to five to increase sampling resolution capability.

Objectives of This Study

We describe the development of a new RPO-AMS system alongside ramped Py-GC-MS analysis at Rafter Radiocarbon Laboratory (RRL). We use three Antarctic sediment case studies to demonstrate how using these two techniques in tandem may allow RPO-AMS sample selection, reduce the number of fractions measured by AMS, and increase confidence in the reliability of the determined sediment age. We provide a tool to promote more comprehensive stratigraphic chronologies and further understand highly detrital depositional environments.

METHODS

Ramped Pyrolysis Oxidation

RPO processing line design and installation: The RPO system at RRL is based on previous designs (Rosenheim et al. 2008) with some minor modifications to improve operability (Figure 1). The pretreated sediment sample (acid washed in 1N HCl at room temperature for 16 hours, rinsed, and freeze-dried) is loaded in a pyrolysis reactor between 1 cm pre-combusted quartz wool plugs and placed inside the pyrolysis furnace chamber. Ultra-high purity (UHP) helium is continuously flowed at 35 mL/min as the temperature, monitored at sample position, of the thermocouple-controlled pyrolysis furnace is ramped from ~20°C to 1000°C at a rate of 5°C/min. The volatilized carbon compounds are then oxidized to CO₂ with O₂ (4 mL/min) in helium (7 mL/min) downstream from the sample in a combustion furnace at 800°C over 20 cm of intertwined platinum, copper, and nickel wires, and then passed over a

4 cm silver wire plug and a coiled nickel wire that holds the combustion furnace components in place. The product gas is passed through a CO₂ detector (LI-COR Li-820), producing a thermograph recording the evolution of CO₂ with time (as a proxy to be converted to increasing temperature at the rate of 5°C/min). Thermograph shape represents the presence of multiple components within the organic carbon mixture, and inflection points can be used as a first-order approximation of temperature intervals that should be sampled to separate those components (Rosenheim et al. 2008). Aliquots of CO₂ must be a measurable minimum of 0.1 mg C for the AMS measurement, with small samples ranging from 0.1–0.3 mg C and large samples from 0.3–1.2 mg C, which equates to 100–400 mg of dry sediment depending on carbon content.

Water is removed prior to cryogenically trapping the CO₂ into one of five parallel stainless-steel traps (Figure 1). The remaining gas mixture is discarded through a 3 mm diameter, 20 m long plastic vent tube to prevent backflow through the system. The sample stream is diverted into a different trap at each chosen split temperature, producing multiple CO₂ aliquots partitioned by temperature range interval. The trapped CO₂ is then transferred and quantified in a known volume cold finger and then sealed into Pyrex tube pre-loaded with 180–200 mg of pre-combusted CuO and 2 cm Ag wire for recombustion at 500°C for 4 hours to eliminate any compounds such as sulfur that may prevent graphitization. The CO₂ is then graphitized and measured for radiocarbon content (Turnbull et al. 2015; Zondervan et al. 2015). For this initial study, the AIOM was also radiocarbon dated following standard sealed tube combustion protocols (Norris et al. 2020; Turnbull et al. 2015).

Blank corrections: We diagnose both time-dependent and time-independent modern and dead carbon contributions following existing methods (Fernandez et al. 2014; Hemingway et al. 2017; Santos et al. 2007). Time-dependent contamination is attributed to leaks in the RPO system and flow-through combustion furnace chemistry and is diagnosed by measuring a constant sample size for a range of different flow times (i.e., temperature ranges). Time-independent blank contributions encompass processes such as chemical pre-treatment, recombustion of CO₂, graphitization, and AMS measurement. The time-independent component is diagnosed by measuring samples of the same material in different size ranges. We monitor modern carbon contamination (MCC) using a radiocarbon-dead kauri wood, called Kauri Renton Road (KRR). Dead carbon contamination (DCC) is monitored using Oxalic I (OxI) modern standard (Stuiver and Polach 1977), which is also used as the primary standard at RRL. The uncertainty assigned to these corrections is 100% of the determined MCC and DCC value, due to variability in the blanks, particularly for small sample size graphitization, and the limited data set attributable to establishing a new system. To confirm our corrections are appropriate, we repeatedly measure FIRI-D, a wood used in radiocarbon intercomparison exercises, with an AMS-measured consensus radiocarbon age of 4532 BP (Scott 2003). A detailed description of the blank correction determination is given in the Supplementary Material. As a final check, we compare bulk and RPO radiocarbon ages for authentic sediment samples (Table S1).

Our time-dependent modern carbon contribution is 2.57×10^{-7} mg C/s and the time-independent modern carbon contribution is 0.0011 mg C (Figure S1). When dry ice was used in sample preparation, the time-dependent dead blank component was calculated to be 1.1×10^{-6} mg C/s, and the time-independent component is 0.0017 mg C (Figure S2). This time-independent component was larger than the 0.0006 mg C observed with sealed tube combustion samples at RRL. For samples >0.3 mg C, only the time-dependent blank is

considered, as the time-independent dead blank contribution is implicitly included in the measurement of primary standards.

We identified that dry ice used in water removal could be a source of dead carbon contamination in the laboratory atmosphere, affecting both time-dependent (atmospheric leaks in the flow through system by proximate traps) and independent (pretreatment, sample loading, graphitization, measurement) blanks. All dry ice was removed from the lab in 2021 (after the completion of all measurements presented here). No change in the MCC was observed when dry ice was removed from the lab, as expected. However, the time-dependent dead-carbon contribution improved slightly to 9.25×10^{-7} mg C/s and the time-independent component decreases to zero, consistent as observed with non-RPO, traditional sealed tube combustion results in the lab since the removal of dry ice (Figure S3). All case studies herein were conducted prior to the dry ice removal. The remaining time-dependency suggests a potential dead-carbon contribution in the helium carrier gas.

Data quality assessments: FIRI-D is run at various sample sizes first for the full “bulk” RPO temperature range and, more similarly to the unknown sediment samples, are also partitioned into two thermal fractions. Fifteen measurements ranging from 0.2 to 0.7 mg C all agree with the consensus value within one standard deviation once the modern and dead blank corrections are applied. Neither the sample size nor partitioning of the CO₂ impacts the radiocarbon results (Figure S4).

We also compared the bulk radiocarbon measurement with the weighted average of the RPO thermal fraction radiocarbon measurements for five authentic sediment samples. The weighted average of the splits and the bulk RPO runs always agree within one sigma, but small differences from the sealed tube bulk sediment combustion are observed in some cases, explained by methodological differences (Table S1), which has been previously observed by others (e.g., Rosenheim et al. 2013a; Subt et al. 2016).

Pyrolysis-GC-MS Analyses

Method Development: Approximately 10–35 mg (depending on carbon content) of the same decarbonated sediment used in RPO-AMS was analyzed by Py-GC-MS. Prior to analysis, samples were neither extracted with solvents nor demineralized to prevent losses and/or alteration of the extractable organic matter pool. Samples were analyzed by one-step, full pyrolysis using thermal desorption mode with a ramp from 50 to 650°C and stepwise, ramped pyrolysis with up to five temperature splits adapting previously reported methods (Naeher et al. 2019; Zhang et al. 2016).

Samples were pyrolyzed in thermal desorption mode (i.e., ramped temperature oven program of the pyrolyzer) in deactivated stainless-steel cups (Eco-Cups SF; 50 µL) using a microfurnace-based Frontier Lab PY-2020iD Double-Shot Pyrolyzer fitted with a Frontier Lab MJT-1030E Microjet Cryo-Trap. The cryotemperature was -190°C (maintained with liquid nitrogen) and the pyrolysis interface temperature to the GC was set to 300°C. Evolved carbon compounds were cryogenically frozen until completion of the temperature ramp of each split, and then transferred to the GC with helium as carrier gas with a constant flow of 1 mL/min. The pyrolyzer was coupled to an Agilent 7890A GC System, equipped with an Agilent J&W DB-5MS capillary column (60 m × 0.25 inner diameter × 0.25 µm film thickness) and with a splitter to an Agilent 5975C inert MSD mass spectrometer (MS) and flame ionization detector (FID). The front inlet was set to a 5:1 split. The GC oven program started at 40°C (held 5 min

isothermal), ramped to 300°C at 5°C/min, and then held isothermal for 5 min. The MS was operated in full scan (m/z 50–700) and electron impact ionization mode at 70 eV using a source temperature of 230°C.

For one-step, full pyrolysis using Py-GC-MS, samples were run in thermal desorption mode with a ramp of 100°C/min from 50°C to 650°C. For stepwise, ramped pyrolysis using Py-GC-MS, temperature steps for thermal split analysis were determined using the RPO thermograph of the same sample. Utilizing the thermal desorption mode of the pyrolyzer, samples were heated at 10–25°C/min depending on the sample starting at 50°C for the first split and then ramped up to the desired maximum temperature for the first split and held for 10 seconds. The sample cup was then removed from the furnace and the GC-MS program for this split was run. Iterative higher temperature fractions were obtained by reinserting the same sample cup and heating to the next split maximum temperature. This method reasonably replicates the RPO conditions, allowing progressive release of organic compounds rather than rapid, instantaneous heating to the maximum temperature of each thermal fraction as in stepped temperature Py-GC-MS (Zhang et al. 2016; Sanderman and Grandy 2020). We also considered whether because of the complexity of pyrolysis, the amount of sediment could influence pyrolysis efficiency and therefore make the RPO and Py-GC-MS methods less comparable. We tested this by comparing two RPO runs of the same parent sediment with different masses and find no apparent difference in CO₂ yield and thermograph shape.

One-step bulk Py-GC-MS with prior derivatization using tetramethylammonium hydroxide (TMAH, thermochemolysis) was run on selected samples to determine *n*-fatty acid distributions, which are only preserved by methylation of the functional groups in the presence of TMAH and are otherwise converted to *n*-alkanes during pyrolysis (Mannino and Harvey 2000; Pulchan et al. 2003; Fabbri et al. 2005).

Py-GC-MS Data Interpretation: Among the large diversity of organic matter composition, several key compound classes that are diagnostic indicators of organic matter sources are identified from the Py-GC-MS data. For example, short chain *n*-alkanes (C₁₅–C₁₉) with an odd over even chain length preference are generally of aquatic (algal and bacterial) origin; mid-chain (C₂₁–C₂₅) are moss and aquatic macrophyte sources; and long chain *n*-alkanes (C₂₇–C₃₃) are derived from higher terrestrial plants (Carr et al. 2010; Fabbri et al. 2005; Naeher et al. 2022; Pulchan et al. 2003). *n*-Alkanes can also have a petrogenic, mature source where no chain length preference is evident due to weathering and degradation processes (Eglinton et al. 1996; Eglinton et al. 1997; Naeher et al. 2022). Simple monoaromatic hydrocarbons such as toluene and styrene are common in recent sedimentary organic matter (Terán et al. 2009). Large aromatic compounds are often indicative of kerogen cracking (Seeley et al. 2018). Lignin phenols can differentiate angiosperm, gymnosperm, and grass lignins (Carr et al. 2010; Pulchan et al. 2003; Saiz-Jimenez 1995; Saiz-Jimenez and De Leeuw 1986). There is precedent for categorizing pyrolysis products by compound groups such as carbohydrate markers, lignin markers, proteins, chlorophylls, etc. (Pouwels et al. 1987; Fabbri et al. 2005; Terán et al. 2009; Carr et al. 2010; Sanderman and Grandy 2020) to quantify and interpret the molecular composition of a sample and its control on the carbon cycle in the matrix.

Compounds are identified using the NIST mass spectral library database as well as diagnostic mass spectra and characteristic m/z fragments reported in the literature (e.g., Saiz-Jimenez 1995; Fabbri et al. 2005; Naeher et al. 2013; Moldoveanu 2021). To key in on specific compound groups, we utilize diagnostic fragmentograms such as m/z 57 for *n*-alkanes.

Odd/even carbon number predominance of *n*-alkanes typically indicate natural, well-preserved distributions, and a lack of this preference would suggest the carbon has been reworked. For higher temperature splits, pyrolytic alteration occurs in addition to thermal desorption, which would also yield low or no carbon predominance and higher amounts of alkenes in addition to alkanes (e.g., Zhang et al. 2016). Corresponding peaks areas are determined from the mass chromatograms and the percentage peak area relative to the whole of identified compounds are used to convey the relative contribution of each compound (Fabbri et al. 2005; Zhang et al. 2016). While ionization efficiencies (response factors) of different compound groups influence relative abundances in a fully quantitative assessment, our semi-quantitative approach compares changes in relative abundance of compound groups in different temperature splits.

We acknowledge there are some limitations that affect the comparison of RPO-AMS and Py-GC-MS results due to differences in the pyrolytic conditions including gas flow rates, system pressure, and temperature ramp rates. Additionally, differences in sample size, sample matrix effects (Hemingway et al. 2019), and any non-GC-amenable compounds evolved may influence comparison of data produced by the two methods. However, valuable information can be acquired to semi-quantitatively characterize the sample to inform chemical composition and support interpretation of the RPO-AMS splits.

RESULTS AND DISCUSSION: CASE STUDIES

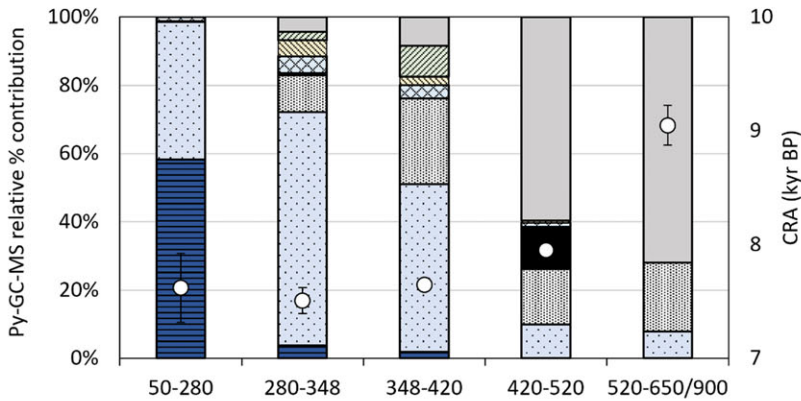
We present case studies in which we combine RPO-AMS and ramped-Py-GC-MS techniques to analyze depositional sediment from three different Antarctic environmental settings. Case study one demonstrates the archetypal refining of sediment chronology using thermal fractionation to measure the depositional age more accurately. Case study two shows that some depositional environments are too overwhelmed by detrital carbon to achieve this separation with a single RPO-AMS analysis, obscuring any modern depositional signatures. In case study three, we examine a setting in which significant biomarker compounds that were expected to record deposition may actually originate from translocated, older depositional sources, and reflect glacial and environmental change rather than direct syndepositional environmental information. As the focus of our study is on the utility of the techniques, we discuss the study sites only briefly. Complete thermograph (Figure S5), Py-GC-MS (Figure S6), and conventional radiocarbon age (CRA) (Table S1) data are provided for the three case studies in the supplementary information.

Case Study One: Py-GC-MS as a Screening Tool for RPO-AMS Dating

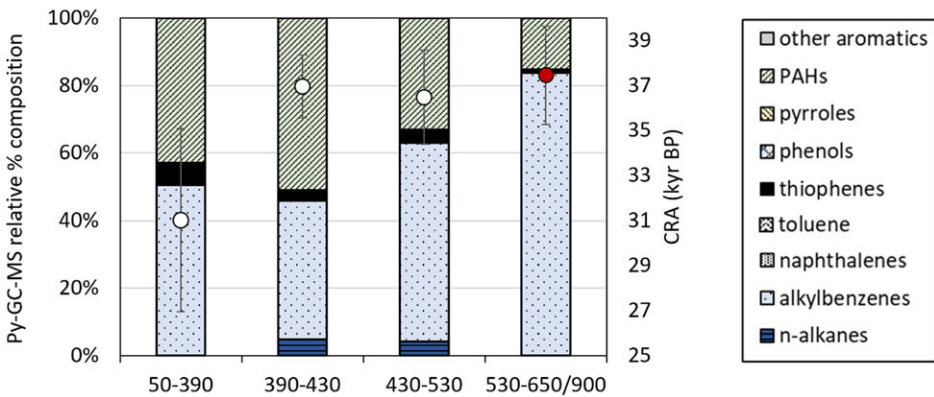
Samples for case study one were collected during the KOPRI 2017 Bellingshausen Sea cruise from the Crystal Sound basin, Antarctica from three sites (Station 16: Lat -66.62558 , Long -66.94394 , 1442 m; Station 17: Lat -66.63991 , Long -66.91006 , 1451 m; Station 18: Lat -66.73772 , Long -66.93494 , 1218 m). These samples were deposited during the transition from sub-ice shelf to an open marine environment (Lee 2017). The purpose of this study was to reconstruct paleoclimate and paleoenvironmental changes since the Last Glacial Maximum. These samples demonstrate model RPO-AMS behavior, where thermal fractionation separates the syndepositional carbon from detrital carbon to refine depositional age by several hundred years.

For the three sites analyzed in this case study, the CRA of the first and second measured splits are statistically indistinguishable, indicating a potential low temperature age plateau with regards to the splits that were collected (Figure 2A, Table S1). Age increases with the

(A) Case Study One. BS17-GC17_3.90-3.92 (Station 17)



(B) Case Study Two. KIS-1 GC2 0.5-2.5 cm



(C) Case Study Three. 318-U1357A-20H-3W-19-21

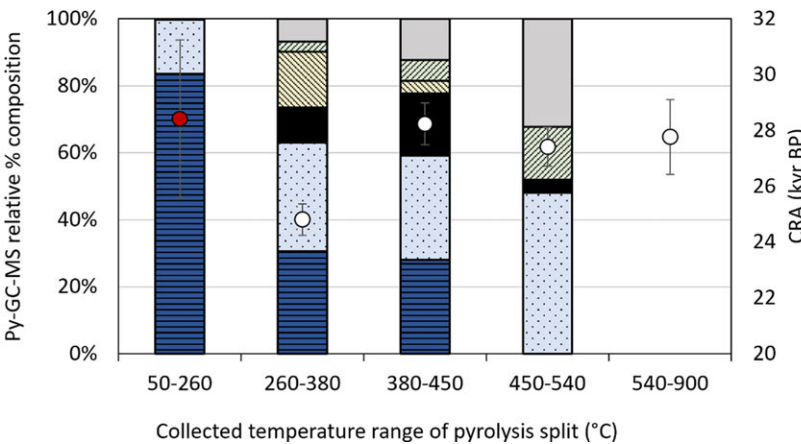


Figure 2 The CRA and Py-GC-MS results for a representative sample from each case study. CRAs displayed in red are indistinguishable from background measurements. The highest temperature split is not typically characterized by Py-GC-MS (e.g., Figure 2C) due to temperature limits of the instrument. The maximum temperature of the Py-GC-MS is 650°C, thus the 650°C molecular fingerprint is the closest match to the 900°C CRA. Full CRA (Table S1) and Py-GC-MS (Figure S6) results are in the Supplementary Information. A. Case Study One. B. Case Study Two. C. Case Study Three.

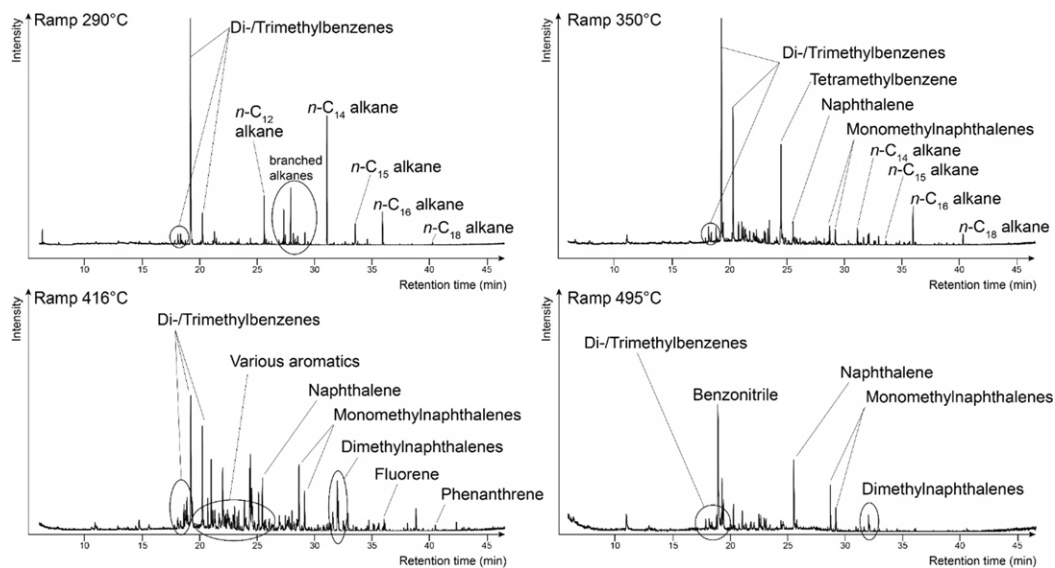


Figure 3 Case Study One. Py-GC-MS chromatograms correspond to RPO splits at the indicated maximum temperature of each split and show the qualitative molecular fingerprint of each split. Increasing aromaticity is observed with increasing pyrolysis temperature of CO₂ evolution. The presence of biomarker compounds indicative of deposition is comparably negligible to aromatic components after the second measured split.

subsequent splits as temperature increases. The radiocarbon age of the low temperature splits is several hundred years younger than the bulk radiocarbon age. The bulk age from RPO-AMS is equivalent to the weighted average of all the splits combined and is skewed older than the depositional carbon age by the detrital contributions of the highest temperature split.

Rather than just measuring the first few splits to discern the youngest possible limiting depositional age, we use matched Py-GC-MS analyses to validate sample selection. A full, one-step Py-GC-MS run determined the overall composition of the sample prior to matching thermal fractions, to verify if suitable compounds for dating were present in the mixture. Ramped Py-GC-MS runs then identified the compounds in each RPO thermal fraction (Figure 3). Identified peaks from the total ion chromatograms (TIC) of each thermal fraction were quantified and summarized into compound classes to facilitate the interpretation and intercomparison of carbon sources relative to thermochemical stability (Figure 2A).

Small aromatic compounds (benzene and alkylbenzenes) are present in the lowest temperature split measured in most of these samples. These compounds are common in marine sediments (Terán et al. 2009) but are not easily attributable to a distinct source. They could indicate syndepositional contributions from aromatic biomolecules present in the sediments or degradation of reworked material in the detrital sediment column through natural diagenetic processes. RPO-AMS typically assumes that the lowest measured temperature split coincides with the youngest material. However, in the Crystal Sound samples, the second collected and measured larger split (split 3) has trended younger, though statistically indistinguishable from the first collected and measured split (split 2), which is smaller resulting in larger error bars.

The Py-GC-MS results suggest that the older material may have resulted from diagenetic alteration to more volatile small aromatic compounds or higher contributions of volatile petrogenic matter that are released in the first measured split (split 2). Benzene and toluene for example are volatile, non-source specific, and known to be common in marine sediments (Terán et al. 2009). Compounds observed in the second collected split (split 3) that were released by thermal desorption are characterized by larger molecular weights and include more diagnostic compounds.

Short chain *n*-alkanes and branched alkanes suggest contributions of syndepositional marine carbon in the first two measured splits (split 2 and 3) (Fabbri et al. 2005). Pyrroles in the second measured split (split 3) also indicate this fraction contains syndepositional carbon as tetrapyrrole pigments such as chlorophylls and their derivatives are found in phytoplankton such as diatoms (Naehler et al. 2013, 2016). Higher temperature splits were comprised mainly of diagenetically stable aromatic carbon structures that are likely derived from older, reworked material, consistent with the older radiocarbon ages (Socolo et al. 2000; Figure 2A).

Combining analytical results from both RPO-AMS and Py-GC-MS for these samples reveals that characterizing the chemical composition of the more volatile organic matter enriched splits provides more robust estimates of the depositional timing. These results refine the chronostratigraphy for the dated stratigraphic horizons and indicate these sediments are several hundred years younger than bulk measurements suggest, as a maximum limiting age, assuming the youngest age yielded by RPO-AMS is closest to depositional age. Combining both techniques can shorten the necessary RPO run times to collect only the desired split temperatures that contain more volatile compounds that suggest in-situ deposition and reduce the overall number of requisite radiocarbon measurements per sample. Overall costs could be reduced, and comprehensive age models could be enhanced by increasing the number of distinct samples dated.

Case Study Two: Improved Interpretation of Sedimentological Processes

Case study two comprises samples from an 0.5 m thick diamict from beneath the sea floor near the grounding zone of the West Antarctic Ice Sheet offshore the Siple Coast. The sediments were collected with a gravity corer that was deployed through a 590 m thick hot water borehole in the Ross Ice Shelf and a 30 m thick water column in the cavity between the base of the ice shelf and sea floor. The borehole site was about four km seaward of the present Kamb Ice Stream ground zone (Lat -82.78411 , Long -155.26267 ; Lawrence et al. 2023) and is located approximately 500 km inland from the ice shelf edge and open marine environment. Despite the remote, dark, and relatively inhospitable nature of the site, recent work shows radiocarbon is present in sediments currently under grounded ice at other locations along the Siple Coast (Kingslake et al. 2018; Venturelli 2021; Venturelli et al. 2023) and at the grounding zone of Whillans Ice Stream (Venturelli et al. 2020).

Sub-ice shelf sediments are challenging for radiocarbon measurement due to the very low carbon content and an abundance of reworked, glacially eroded sediment, visible in the form of common Tertiary-aged diatoms (Subt et al. 2017; Calkin 2021; Venturelli et al. 2020, 2023). Reworking explains the RPO-AMS ages of >31 kyr BP that are recorded for all temperature fractions from samples throughout the diamict. The actual depositional age is more likely late Holocene based on modern depositional setting and chronologies produced from other methods (e.g., ^{210}Pb results indicate recent deposition; Calkin 2021; Figure 2B).

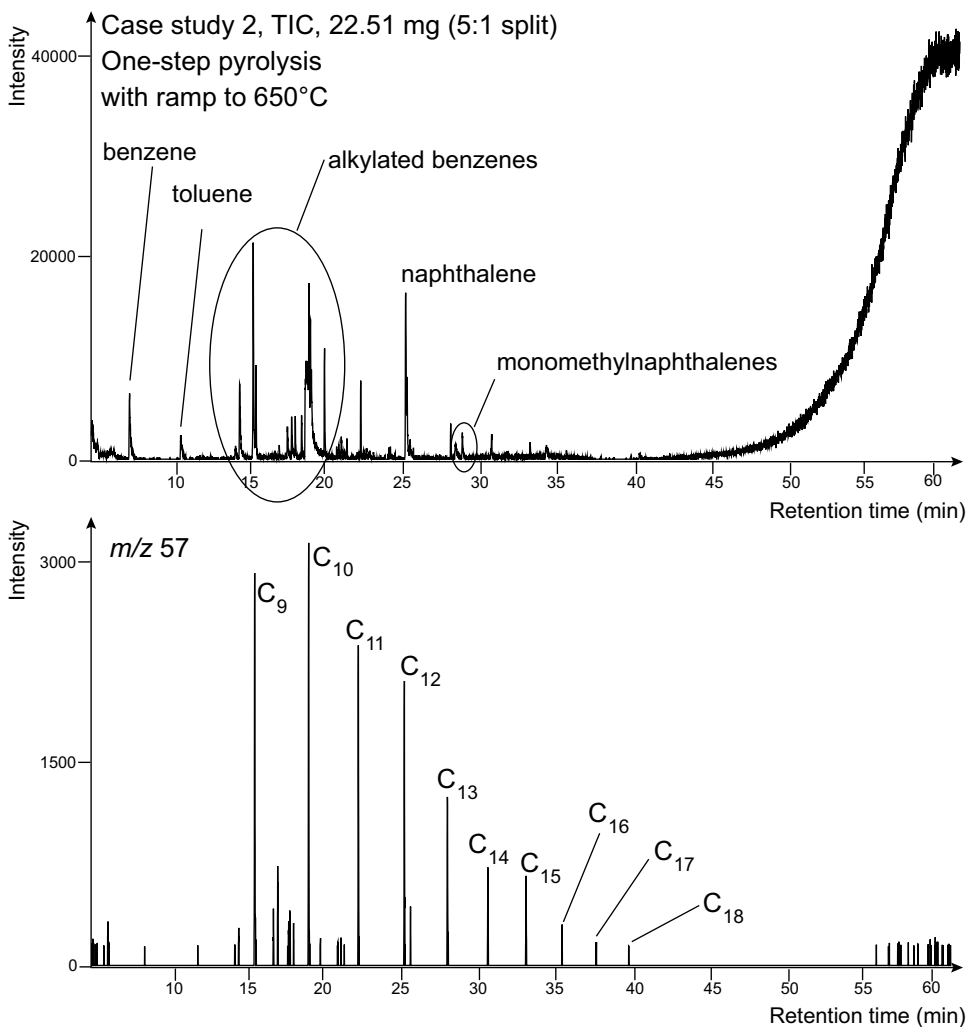


Figure 4 Case Study Two. The TIC and m/z 57 fragmentogram of the bulk sediment indicates no odd/even preference in comprising n -alkanes, suggesting weathered and/or translocated rather than depositional carbon.

From the Py-GC-MS analysis, a few n -alkane biomarker fragments were detectable (Figure 4). Yet all splits, including the lowest temperature splits typically associated with depositional age, are dominated by largely undiagnostic aromatic compounds, especially toluene, alkylbenzenes, and thiophenes which are indicative of reworked, diagenetically stable material (Figure 2B). Their presence in lower temperature splits could originate from various sources including natural degradation processes (Terán et al. 2009). Very low carbon content of these samples (<0.4% C) is also indicative of reworking.

The m/z 57 fragmentogram of the Py-GC-MS chromatograms specifically examined the n -alkane distributions (Figure 4). Due to the thermal desorption process, alkenes (m/z 55) which would be typical pyrolytic products in flash pyrolysis (e.g., Zhang et al. 2016) are less abundant (or absent) relative to alkanes particularly in the lower temperature splits.

The C₉ to C₁₂ alkanes are non-diagnostic short chain degradation products. The C₁₅-C₁₉ alkanes are very low in intensity with no odd/even chain length preference and decreasing abundance of *n*-alkanes with increasing molecular mass. However, distributions of *n*-alkanes are typically dominated by odd over even chain length homologues in thermally immature sediments. Thus, the lack of such preference suggests the reworked carbon has either a petrogenic or pre-aged, translocated origin, or a combination of multiple origins in a single matrix (Eglinton et al. 1996, 1997; Fabbri et al. 2005). Nonetheless the finite radiocarbon age suggests that some syndepositional carbon is present, however, it is dominated by reworked, pre-aged carbon in all splits at all core depths. Aggregated RPO-AMS (Subt et al. 2017) or CSRA might allow separation of such syndepositional carbon compounds, but the very low carbon content would make this especially challenging. Venturelli et al. (2023) demonstrated that these challenges could be overcome with a combination of compound specific and RPO work.

In this case study, Py-GC-MS was used to determine that either insufficient syndepositional carbon was present in these sediments or the carbon was highly degraded, such that it is unlikely that reliable age estimates for the timing of sediment deposition can be acquired. Our combination of RPO-AMS and Py-GC-MS suggests that (a) the small amount of carbon present in these sediments is almost entirely old, reworked material and (b) the molecular composition supports interpretations of localized environmental processes. Our results are consistent with previous applications of RPO in this setting (Venturelli et al. 2020), and suggest that the older than expected bulk radiocarbon ages determined from a nearby sediment core (Kingslake et al. 2018) may be explained by this mechanism.

Case Study Three: Source Identification and Environmental Interpretation Tool

In case study three, the samples were obtained from the Holocene section recovered at Site U1357 located on the >1000 m deep Adélie Basin, a glacially scoured trough on the continental shelf off the Antarctic Wilkes Land margin (Lat -66.41332, Long 140.42501, 1014.9 m water depth; Expedition 318 Scientists 2011; Escutia et al. 2011). High sedimentation rates at the site produced a 180 m thick Holocene section primarily composed of biogenic material (diatoms) (Crosta et al. 2005, 2007, 2008; Denis et al. 2006, 2009; Leventer et al. 2006; Escutia et al. 2011; Johnson et al. 2021). Samples analyzed in this study are from the base of this sequence above the glacial diamicton but in a layer with significant clastic detrital material. Easterly winds, sea ice extent, and ocean dynamics associated with the Antarctic Polar Frontal Zone all impact the depositional environment of this core. Until the end of the last glaciation, this site was covered by ice that inhibited the growth and deposition of diatoms. The expected age range for the samples at the bottom of this core is approximately 10–11 kyr BP (Leventer et al. 2006; Mackintosh et al. 2011).

Radiocarbon measurements obtained in this study were older than expected, ranging from about 20 to 28 kyr BP in the two samples, except for the first measured split (split 2) in sample 318-U1357A-20H-3W-19–21, which was indistinguishable from background, most likely due to small sample size causing large error bars (Figure 2C). Py-GC-MS revealed that branched and *n*-alkanes were dominant (>80%) in that first measured split. The second measured split (split 3) contains about 30% alkanes. As in case study one, pyrroles are most abundant in split 3. These are likely derivatives of tetrapyrrole pigments, which are labile compounds that can be rapidly transformed (e.g., Naeher et al. 2013), so their presence indicates intact pigments, which are typically produced by primary producers. Split 3 yields the youngest CRA and, in both discrete samples, is 2–2.5 kyr BP younger than the bulk radiocarbon age.

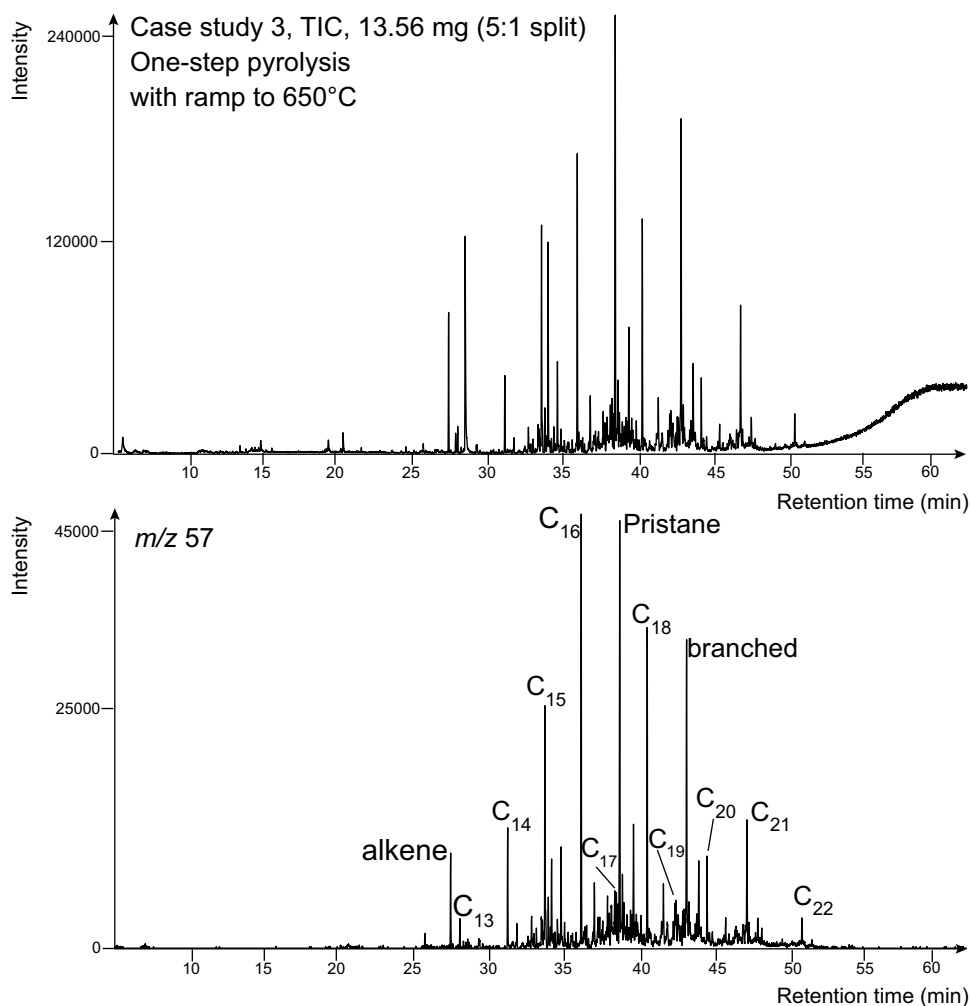


Figure 5 Case Study Three. The TIC and m/z 57 fragmentogram of the bulk sediment shows even/odd preference of n -alkanes. When coupled with TMAH derivatization, some of these n -alkanes are confirmed to be derived from the conversion of fatty acids during pyrolysis.

Higher temperature RPO splits increase in radiocarbon age and have corresponding relative increases in aromatic compounds.

There is an unusual even over odd preference in the n -alkane distributions, opposite to what is expected for thermally immature, unaltered sediments (Figure 5, Fabbri et al. 2005). To further investigate this counterintuitive pattern, TMAH thermochemolysis was used to identify that some of the n -alkane distributions were derived from conversion of fatty acids present in the sediment, which typically have even/odd carbon preference (e.g., Naeher et al. 2022). This result indicates high contributions of fatty acids and alkanes derived from algal and bacterial sources (Mannino and Harvey 2000).

C_{14} - C_{18} fatty acids with an even/odd preference have previously been found to reflect modern depositional carbon which is far more enriched in ^{14}C than the bulk sediment carbon

(Ohkouchi et al. 2003; Ohkouchi and Eglinton 2008; Berg et al. 2020), including previous work in the Adélie Basin (Yamane et al. 2014). Yet the RPO-AMS ages in our case study are much older than expected from the timing of deglaciation. These ages could indicate dilution by detrital fossil carbon, contamination from older biomarker compounds released during ice sheet retreat, or incorporation of older, reworked carbon sources into modern depositional organic matter. The oceanographic setting, prevailing winds, and sea ice extent all complicate the interpretation of the radiocarbon data. This case illustrates that, as in CSRA, specific biomarker compounds can be derived from multiple sources, representing a mixture of both syndepositional and pre-aged origin. Whereas desired compounds can be isolated either specifically or in thermochemical groupings, the radiocarbon age can inform and substantiate environmental interpretations even if the age is not as expected. In this case with higher carbon content, compounded RPO-AMS (Subt et al. 2017) or CSRA might be effective to separate syndepositional carbon. Importantly, the combination of RPO-AMS and Py-GC-MS analysis provides key insight into factors that influence the radiocarbon age that are critical when used to interpret glacial history. In this case, we were able to identify that sediments immediately above the diamict contain reworked carbon. While the RPO-AMS dates likely include older “contaminant” carbon, they still improved the maximum limiting age of deposition relative to the bulk measurement.

CONCLUSIONS

We have demonstrated how combining RPO-AMS and Py-GC-MS provides more robust information on the composition and source of the organic matter that is dated, and effectively reduces contributions of pre-aged organic matter for improved radiocarbon dating of detrital sediments from Antarctica.

Our first case study shows an archetypical example of the expectation that RPO-AMS separates younger depositional material from reworked detrital carbon, thereby improving the depositional date. Py-GC-MS characterizes the molecular fingerprints of each split and reveals relative contributions of each indicator derived from distinct organic matter sources to guide radiocarbon analysis. This potentially allows fewer radiocarbon measurements, reducing cost and promoting more comprehensive downcore age resolution. The second case study is an example where Py-GC-MS demonstrated that insufficient syndepositional carbon was present in this sub-ice shelf environment to provide a reliable estimate of depositional age. This outcome clarified why RPO-AMS measurements did not match other chronological information. Case study three illustrates that, as in CSRA, pre-aged or multiple carbon sources of specific biomarker compounds can complicate RPO-AMS analyses. Careful evaluation of the combined data from each sample is required to identify the likely sources of organic matter and inform the reliability of radiometric age estimates. Whereas Py-GC-MS can be used to identify compounds that typify deposition, the age of fractions containing these compounds may reflect multiple sources or translocation of those carbon compounds rather than depositional timing. Yet these coupled molecular fingerprint and radiocarbon measurements provide valuable information to support interpretations of paleoenvironmental processes and are particularly useful in environments like Antarctica, where reworking of material is prevalent.

We have established a new RPO-AMS system at RRL and validated its functionality. RPO-AMS achieves a step change in Antarctic sediment chronology with higher accuracy than bulk measurements, improving depositional dates by several hundred years or more. Coupling ramped Py-GC-MS with RPO-AMS provides a rapid assessment of molecular composition of

each thermal fraction to support depositional environment interpretations and identify radiocarbon measurements that most closely reflect depositional timing. Focused measurements based on the identity of organic carbon source composition can shorten run times and reduce measurement costs to achieve more accurate and substantiated comprehensive stratigraphic chronologies adding overall value to the RPO methodology with added benefits to climate change research. Furthermore, the Py-GC-MS analysis provides new insight when radiocarbon measurements do not concur with expectation, enabling the broader context of the system and its carbon sources to be considered for environmental interpretations.

While CSRA is extremely useful for determining the age of individual compounds, it requires large amounts of material and has complex processing requirements. Further, it is impractical to isolate and measure every compound of interest in a sediment. RPO-AMS coupled with parallel Py-GC-MS gives information about the full suite of volatilized compounds within a sediment, providing complementary information to CSRA, with the added benefit of less complex sample processing and smaller amounts of sediment required.

SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit <https://doi.org/10.1017/RDC.2023.116>.

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CONTRIBUTIONS

JCT envisioned and directed the project for RRL; CEG, JPT, SR built the RPO system; BER, RAV collaborated on the RPO system build and trained RRL staff on the methodology; SN, AMP, CEG developed the Py-GC-MS methodology and ran analyses; SN interpreted Py-GC-MS results; CEG ran RPO analyses; AZ ran AMS analyses; CEG, JCT, AZ applied blank correction analyses; RHL, KCY, GD, TC, CE, JGP collaborated with RRL in the case studies and provided samples; RAV provided figure S5 for the SI; CEG, JCT, SN primarily prepared the manuscript, with contributions from all coauthors.

CONFLICT OF INTEREST DECLARATION

The authors declare that they have no conflicts of interest.

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