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RESEARCH LETTER

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Key Points:

- Deep permafrost POC breakdown is indicated in the Alaskan Arctic
- Coastal peaty shoreline erosion is indicated in the Alaskan Beaufort Sea
- Ramped-temperature pyrolysis analysis indicates POC source in Arctic sediments

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Evidence for permafrost thaw and transport from an Alaskan North Slope watershed

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Abstract Burial of organic carbon (OC) in marine sediments is one of the most important linkages between the short-term biologic carbon cycle and the long-term geologic carbon cycle. Yet much is still unknown about the fate of terrigenous OC in marine coastal margins. Here the delivery of particulate OC (POC) to the Colville River deltaic region in the Alaskan Beaufort Sea by particulates of varying densities is studied through the use of ramped temperature pyrolysis and radiocarbon analyses. The Colville River is the largest river in North America whose watershed is underlain completely by high Arctic permafrost tundra. A variety of sources of POC are considered, including terrestrial soils, Pleistocene-aged yedoma-like sediments, coastal peat erosion, and marine POC. We provide the first evidence that riverine POC from the Colville River contains old (Pleistocene-sourced) OC, suggesting ongoing thaw and mobilization of yedoma-like permafrost OC from this northern Alaskan watershed. Additionally, much of this OC appears to be fairly labile and therefore could be readily oxidized and returned to the atmosphere.

1. Introduction

Riverine delivery of terrestrial organic carbon (OC) and subsequent burial is a significant sink for OC on Earth. This burial connects the short-term biologic carbon cycle and the long-term geologic carbon cycle through the delivery of recently fixed OC sourced from fresh vegetation and terrestrial soils. Yet the fate of terrigenous OC on marine shelves is still not well known [Hedges *et al.*, 1997; Burdige, 2005; Aller and Blair, 2006; Bianchi, 2011]. Despite progress in recent decades, the so-called “geochemical conundrum” [Hedges *et al.*, 1997] of greater terrestrial OC input by rivers to the marine environment than is found stored in sediments indicates that much of the terrestrial OC entering the marine system is recycled before deposition [Hedges *et al.*, 1997; Burdige, 2005]. Additionally, while marine OC is generally considered more chemically reactive, it still accounts for most of the OC buried in shelf sediments [Schlunz and Schneider, 2000; Burdige, 2005; Bianchi, 2011], and much still remains unknown about the exact fate of terrestrial OC on marine shelves worldwide. This is especially true on shelves that interface with large river delta-front estuaries, such as the Mississippi and Nile, among many others [Bianchi and Allison, 2009].

Critical to understanding burial of carbon on continental shelves is determining the physical mechanisms that contribute to particulate OC (POC) transport and storage. Hydrodynamic sorting of particles according to size and density is an important influence on the distribution and composition of sediments discharged by rivers [Prah *et al.*, 1994; Goni *et al.*, 1998; Bianchi *et al.*, 2002, 2007]. Additionally, physical action including waves and storms can resuspend and move sediments from their original deposition site [Hedges and Keil, 1995; Blair *et al.*, 2004]. While particles move across the land-sea interface, there is active exchange between terrestrial and marine OC associated with mineral grains [Hedges and Keil, 1995; Keil *et al.*, 1997; Goni *et al.*, 2005]. Once deposited, OC can still undergo chemical change for lengths of time determined by the sediment accumulation rate, the bioturbation rate, and amount of pore water exchange. Because the OC delivered to shelves can be from multiple different sources, especially at river outlets, all of these processes likely act at different rates on different OC constituents.

Estimates of terrestrial burial of OC from Arctic rivers are especially important, as half of the global soil carbon pool is stored in the top few meters of Arctic permafrost soils [Tarnocai *et al.*, 2009]. This carbon is particularly vulnerable to increasing Arctic temperatures, which may rise by as much as 3° to 10°C by 2100 [IPCC, 2013]. Much of this OC, more than twice the amount of carbon currently residing in the atmospheric CO₂ pool,

is thousands of years old and represents an important terrestrial sink for OC [Schuur *et al.*, 2009]. In fact, delivery of yedoma and permafrost OC has already been noted in the Russian Arctic, through both riverine transport and coastal erosion [Vonk *et al.*, 2012, 2013]. These changes are further exacerbated by an accelerated hydrologic cycle, including increasing river flows in some regions of the Arctic [McClelland *et al.*, 2006], increasing precipitation [Arctic Climate Impact Assessment (ACIA), 2005], and melting of ice stocks (sea ice and glaciers) [ACIA, 2005]. Riverine loads of dissolved and particulate OC [Gordeev and Kravchishina, 2009] and mineral particles [Gordeev, 2006] in the six largest Siberian Rivers are all predicted to increase over the next few decades. Increased sediment load will even further increase POC loads in rivers, due to the association of OC with mineral particles [Keil *et al.*, 1997]. Additionally, the Arctic Ocean has the greatest percentage of continental shelf area of any of the world's oceans and receives fresh water and sediments from numerous large river systems. The aforementioned changes in Arctic river discharge, sediment load, and OC cycling therefore have the potential to greatly alter OC storage and cycling on Arctic shelves [Macdonald *et al.*, 2004b].

This study builds upon previous work in the Colville River delta [Schreiner *et al.*, 2013], the largest river in North America in terms of both sediment and water delivery that drains only high Arctic, continuous permafrost tundra [Walker, 1998; Walker and Hudson, 2003; McClelland *et al.*, 2006]. This contrasts with previous studies of POC delivery that have focused upon large rivers whose watersheds integrate sediment from high Arctic continuous permafrost tundra to discontinuous/sporadic permafrost boreal forests, such as the Mackenzie [Goni *et al.*, 2000, 2005; Yunker *et al.*, 2005; Drenzek *et al.*, 2007] and the Yukon [Guo and Macdonald, 2006; Guo *et al.*, 2007]. Here we utilize ramped pyrolysis ^{14}C analysis on density-separated sediment samples from the Colville River delta. Combining the ^{14}C age spectra from ramped pyrolysis and biomarker analysis of terrestrially derived lignin-phenols allows determination of the fate of old and fresh OC transported by the Colville River into the delta and nearby coast. Additionally, fractionating the sediments by density prior to analyses gives information about sediment transport mechanisms as well as determining whether there is a difference between OC delivered as discrete particles and OC that is associated with mineral sediments.

2. Methods

2.1. Field Campaign and Sample Collection

Study site and sample collection methods are described in detail in Schreiner *et al.* [2013]. Briefly, samples were collected from the Colville delta and Simpson's Lagoon (see map, Figure 1) during a sea- and land-based campaign in August of 2010. Core top samples (0–2 cm) from cores of approximately 3 m in length were analyzed in this study. Two core tops were analyzed here: ND, located directly north of the Colville delta, and L3, located east of the Colville delta in the adjoining Simpson's Lagoon. These two sites were chosen to represent a direct deltaic deposit with strong riverine influence (ND) and a coastal shelf deposit with less riverine and more coastal erosional influence (L3) [Schreiner *et al.*, 2013].

2.2. Sample Preparation and Density Fractionation

Samples were prepared and fractionated by density as previously described [Schreiner *et al.*, 2013], modified slightly from Wakeham *et al.* [2009]. Briefly, core samples were frozen immediately upon collection and freeze dried upon return to land-based laboratories. Dry samples were homogenized and ground, a subsample was removed for bulk measurements, and the rest was fractionated by density. Density fractionations were performed by dispersal in sodium metatungstate solutions of varying densities, producing sediment fractions of density $<1.6\text{ g mL}^{-1}$, $1.6\text{ to }2.0\text{ g mL}^{-1}$, $2.0\text{ to }2.5\text{ g mL}^{-1}$, and $>2.5\text{ g mL}^{-1}$. Hereafter, fractions will be referred to as D1, D2, D3, and D4, respectively. After fractionation, all samples were well rinsed in C-free water (Millipore) and subsequently freeze dried. Over 90% recovery of sediment mass and carbon mass was obtained for all samples after the fractionation.

After freeze drying, carbonates were removed from all samples (except L3 bulk) by vaporization with concentrated HCl [Harris *et al.*, 2001]. L3 bulk was acidified by direct application of 10 M HCl and subjected to repeated centrifugation/rinse cycles until the pH of the supernatant approached neutrality. The use of two different acidification techniques is not ideal, but as these are both accepted, routine techniques for the removal of carbonates, the authors do not think it likely that a significant bias in the results was introduced.

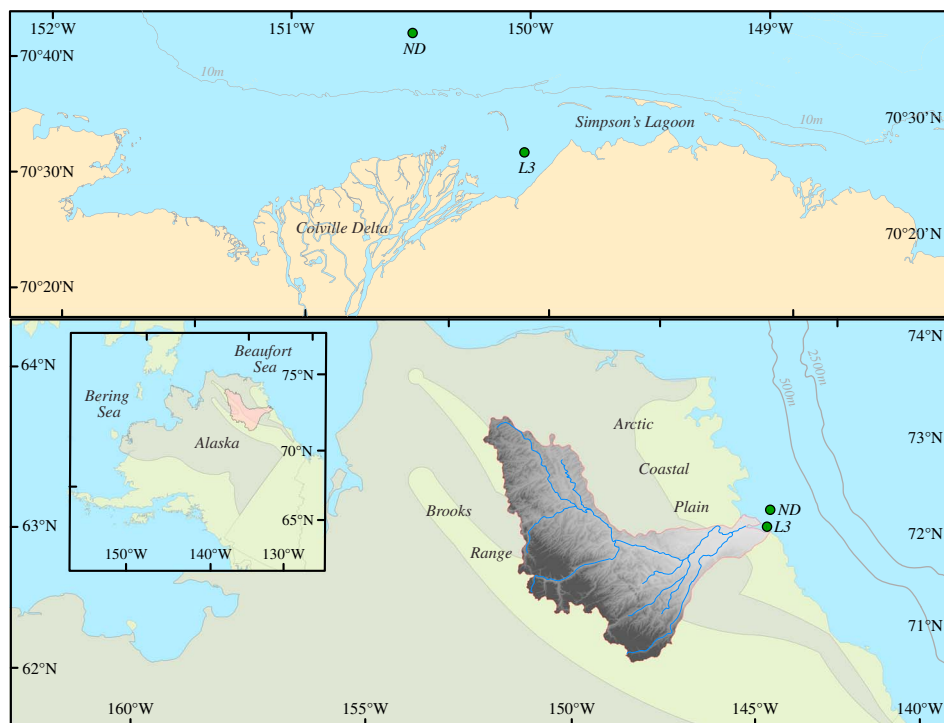


Figure 1. Map of Colville River and study area. The Colville has its headwaters in the Brooks Range of central Alaska, flowing northward over the Alaskan coastal plain and into the western Beaufort Sea. Inset shows a map of Alaska, including the Colville River watershed in pink overlying areas of significant yedoma deposit in grey from *Kanevskiy et al.* [2011]. (bottom) Yedoma areas, with the Colville River watershed shown as a digital elevation map, portraying its headwaters in the mountainous Brooks Range flowing over through the relatively flat Coastal Plain. (top) A close-up of the study site, with samples ND (north of delta) and L3 (lagoon sample) indicated.

2.3. Ramped Pyrolysis Measurements

Ramped temperature pyrolysis was performed on each of four density fractions (described above) from both ND and L3, as well as a bulk, unfractionated sample from each, for a total of 10 samples. As in previous work [*Rosenheim et al.*, 2008, 2013a, 2013b; *Rosenheim and Galy*, 2012; *Pendergraft et al.*, 2013], samples were heated at a constant rate of temperature increase ($5^{\circ}\text{C min}^{-1}$) until 1000°C or until quantitative removal of all carbon. Reaction vessels were plumbed with 100% He (ultrahigh purity, Airgas™) for pyrolysis, and oxygen (8%) was used to rejuvenate the Cu catalyst wires (intertwined with Ni and Pt) downstream of the reaction chamber (see *Rosenheim et al.* [2008] for a schematic diagram). Resultant CO_2 was quantified both photometrically (nondispersive infrared gas analyzer) and manometrically (capacitive diaphragm manometer). Individual aliquots of product CO_2 were subsampled and sealed into glass ampoules with copper oxide and silver wire to clean gases with in vacuo combustion prior to graphitization.

2.4. Radiocarbon Analysis

Samples were analyzed for radiocarbon content and stable carbon isotope composition at the National Ocean Science Accelerator Mass Spectrometer facility at the Woods Hole Oceanographic Institution. Aliquots of CO_2 were graphitized using standard methods after approximately 5–10% of the gas was taken for stable isotope determination via isotope ratio mass spectrometry. Stable isotope ratios were measured against the Vienna PDB standard and are reported in delta notation. Blank contamination from the ramped pyrolysis system was characterized by analysis of graphite (assumed radiocarbon-free, Alpha Aesar™) and International Atomic Energy Agency C3 cellulose (1.39 fraction modern) using the approach of *dos Santos et al.* [2007]. Both modern and dead blanks were calculated over the course of the entire pyrolysis run, and the blanks are divided by the number of splits taken for each individual run. Therefore, the modern blank for each of the five CO_2 splits from ramped pyrolysis analysis of each density fraction was determined

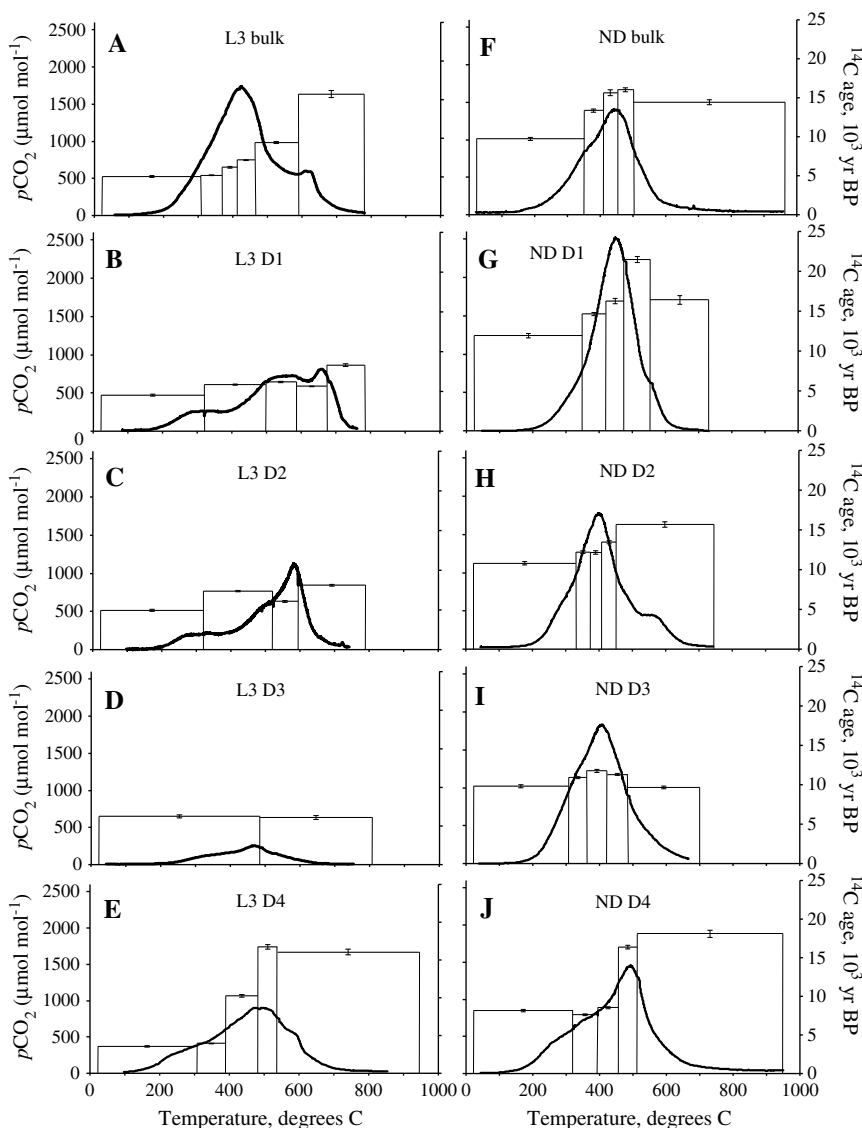


Figure 2. Pyrograms (thick black lines, left y axis) and ¹⁴C ages of CO₂ fractions (bars, right y axis). Lagoon (L3) samples: (a) bulk, (b) D1, (c) D2, (d) D3, (e) D4. Delta (ND) samples: (f) bulk, (g) D1, (h) D2, (i) D3, (j) D4. The low yield of sample L3 D3 is due to sample loss before analysis.

to be 1.9 μg C and the dead blank was determined to be 0.1 μg C during the time of these analyses. This blank determination was made over the course of 2 years of measuring about 35 blanks using both isotope dilution and a live-dead end-member model. Both calculations agree, and as stated above, the most significant contribution to the blank is modern. Reported results have been corrected for this blank contamination.

3. Results

Pyrolysis profiles and ¹⁴C ages for pyrolysis CO₂ fractions are shown for all 10 samples in Figure 2. (Note that much of sample L3 D3 was lost in transit prior to ramped pyrolysis analysis, allowing only two very small CO₂ fractions for analysis.) In general for sample L3, T_{max} (temperature of maximum CO₂ generation from each density fraction) decreased with increasing density, while for sample ND, T_{max} increased with increasing density (Tables 1 and 2). The highest T_{max} (658°C) for sample L3 was in D1, while the lowest T_{max} (469°C) for sample L3 (excluding bulk) was in D3. The highest T_{max} (492°C) for ND was in D4, while the lowest T_{max} (398°C) for ND was in D2.

Table 1. Isotopic and Radiocarbon Values of Individual Splits and Bulk Samples for Site ND^a

Sample	Split	CO ₂ (RP) (μmol)	T _{max} (°C)	Age (¹⁴ C yr)	Age Error	δ ¹³ C (‰)
ND Bulk	Whole	N/A	440	13,410	570	−26.5
	RP 1	22.3	352	9,730	200	−28.8
	RP 2	19.3	409	13,350	200	−26.4
	RP 3	20.5	453	15,630	360	−26.5
	RP 4	20.1	502	16,040	270	−25.8
	RP 5	21.3	964	14,430	320	−25.4
ND D1	Whole	N/A	450	16,080	820	−25.6
	RP 1	19.0	350	11,920	270	−28.3
	RP 2	35.5	420	14,630	190	−26.7
	RP 3	45.2	475	16,280	350	−25.8
	RP 4	37.4	555	21,480	420	−24.8
	RP 5	10.7	730	16,400	530	−25.2
ND D2	Whole	N/A	398	12,950	530	−26.8
	RP 1	21.8	330	10,790	230	−28.4
	RP 2	20.3	374	12,170	170	−27.9
	RP 3	21.3	408	12,160	230	−27.3
	RP 4	21.6	452	13,440	190	−26.6
	RP 5	33.5	745	15,690	350	−25.6
ND D3	Whole	N/A	407	10,780	390	−26.7
	RP 1	20.0	308	9,820	210	−29.8
	RP 2	24.0	361	10,910	130	−27.4
	RP 3	37.0	422	11,760	200	−27.2
	RP 4	30.8	484	11,280	120	−26.7
	RP 5	25.6	700	9,620	170	−26.3
ND D4	Whole	N/A	492	11,350	420	−26.4
	RP 1	18.3	320	8,160	170	−28.0
	RP 2	19.1	395	7,590	90	−28.1
	RP 3	21.2	456	8,520	140	−27.0
	RP 4	26.8	512	16,380	250	−26.5
	RP 5	29.4	950	18,110	480	−25.4

^aRP: ramped pyrolysis sample.

Stable isotopic values (δ¹³C, ‰, Tables 1 and 2) for each CO₂ fraction measured were within the range expected for C3 vegetation, by far the dominant vegetation in the Colville watershed [Naidu *et al.*, 2000; Dunton *et al.*, 2006]. ND had a range of −29.8‰ (D3, fraction #2) to −25.2‰ (D1, fraction #6), and L3 had a range of −29.9‰ (D1, fraction #2) to −24.3‰ (D4, fraction #6). In general, there was little variation in δ¹³C between samples.

In general, the oldest radiocarbon ages were found in ND samples, specifically ND D1. The widest age distributions (differences between the youngest and oldest fractions in a given sediment sample) in one sample were generally found in ND, though L3 D4 had the widest distribution (13,190 years). Generally, in each sample, the youngest radiocarbon ages in a single sample were found in the lowest-temperature fraction, and the oldest radiocarbon age was found in one of the two highest-temperature fractions which is similar to all previous ramped pyrolysis work [Rosenheim *et al.*, 2008, 2013a, 2013b; Rosenheim and Galy, 2012] except for sediments contaminated with oil pollution [Pendergraft *et al.*, 2013]. The average radiocarbon sample size was 270 ± 90 μg, while the modern blanks were on average 9.3 μg and fossil blanks were on average 0.5 μg, both of which were divided by CO₂ splits for most samples, so blanks (modern and dead) were generally less than 10% of the sample sizes.

4. Discussion

The three most important inputs of OC to Simpson's Lagoon are riverine terrestrial OC from the Colville River (and to a smaller degree the Mackenzie River), coastal erosional inputs from the Beaufort Sea coastline (primarily peaty deposits), and primary production OC from ice algae, freshwater riverine phytoplankton, and marine phytoplankton [Schreiner *et al.*, 2013]. Indeed, along much of the western Beaufort Sea coastline, coastal erosional inputs are more important as a source of OC to coastal sediments than riverine inputs [Macdonald *et al.*, 2004a]. Previous analysis of bulk OC and sedimentary biomarkers on bulk and density-fractionated sediments in this study area, and a mixing model calculated from the three inputs described above, shows

Table 2. Isotopic and Radiocarbon Values of Individual Splits and Bulk Samples for Site L3^a

Sample	Split	CO ₂ (RP) (μmol)	T _{max} (°C)	Age (¹⁴ C yr)	Age Error	δ ¹³ C (‰)
L3 Bulk	Whole	N/A	423	7,520	300	-26.5
	RP 1	16.5	308	5,040	110	-29.2
	RP 2	24.0	369	5,190	60	-28.2
	RP 3	24.0	412	6,240	100	-28.3
	RP 4	30.2	463	7,170	70	-28.3
	RP 5	36.7	589	9,440	160	-27.0
L3 D1	Whole	N/A	658	5,950	230	-27.0
	RP 1	10.2	320	4,530	110	-29.9
	RP 2	24.4	497	5,860	70	-26.7
	RP 3	24.2	586	6,200	100	-28.4
	RP 4	24.2	673	5,640	60	-28.5
	RP 5	9.8	783	8,290	180	-27.6
L3 D2	Whole	N/A	581	6,740	240	-26.5
	RP 1	7.9	321	4,940	140	-28.6
	RP 2	24.4	520	7,360	90	-26.2
	RP 3	22.9	594	6,060	110	-27.8
	RP 4	13.7	789	8,130	130	-26.1
L3 D3	Whole	N/A	469	6,190	320	-25.8
	RP 1	13.8	485	6,240	190	-26.0
	RP 2	7.7	807	6,110	260	-25.2
L3 D4	Whole	N/A	495	9,210	330	-25.7
	RP 1	14.2	307	3,540	100	-27.0
	RP 2	16.1	390	3,950	60	-27.3
	RP 3	28.1	482	10,230	170	-27.7
	RP 4	19.5	538	16,730	300	-26.2
	RP 5	24.8	946	16,030	380	-24.3

^aRP: ramped pyrolysis sample.

that the majority of OC inputs to ND are from the Colville River, with no coastal erosional and minimal primary production input (less than 1% of total OC input), while L3 has a mix of riverine, coastal erosional, and primary production inputs (approximately 47%, 29%, and 24% of total OC input, respectively) [Schreiner *et al.*, 2013]. However, this mixing model was performed on bulk sediments only.

An examination of density fractions allows a more nuanced view of delivery of OC to this Arctic coastal site. Particulate organic carbon from ND is, as a whole, both older and more reactive than the L3 site, as indicated by the generally lower pyrolysis temperatures seen for ND samples versus L3 samples. Ramped pyrolysis ¹⁴C analysis generates radiocarbon age distributions on the basis of the thermochemical stability of the components of the bulk OC in the sample. Pyrograms and radiocarbon data are distinct at the two stations,

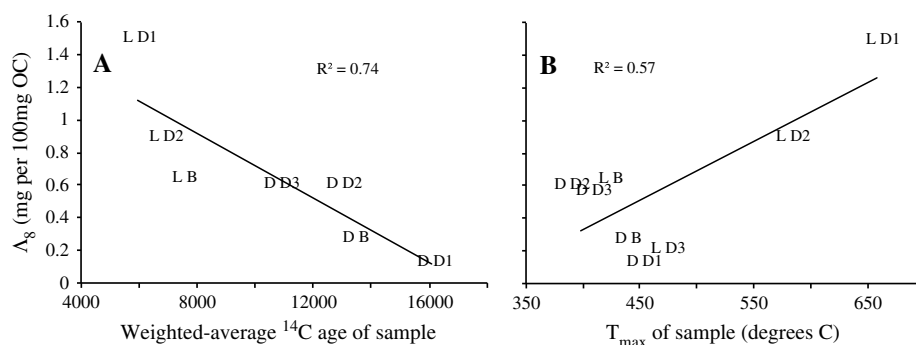


Figure 3. Pyrolysis and ¹⁴C data correlations with lignin-phenol concentrations. Lignin-phenol data from Schreiner *et al.* [2013]. (a) Correlation of Λ₈ (total lignin-phenols per 100 mg OC) to average ¹⁴C age of sample and, (b) correlation of Λ₈ to T_{max} of sample. Correlations in both plots are significant to at least *p* < 0.05 (Figure 3a significant to *p* < 0.01). On plot, “L” refers to density fractions or bulk sample (Figure 3b) from site L3, while “D” refers to the same from site ND.

with the deltaic ND station having generally older radiocarbon dates but lower T_{\max} values than the lagoonal station L3 (Figure 2). This at first seems counterintuitive, as it is generally accepted that older OC should be more diagenetically altered and therefore more chemically recalcitrant. However, the Colville River, as a large, high Arctic river, delivers OC from a watershed underlain with continuous permafrost. Soils under continuous permafrost can be high in OC content, and much of this OC is relatively reactive for its age due to slow rates of microbial degradation in permafrost soils [Weintraub and Schimel, 2003; Schuur et al., 2008]. Station ND is located in an area of the coast without a northerly barrier island and is exposed to wave action and storms from the Beaufort Sea. Thus, it is unlikely that old, chemically labile marine carbon is contributing to the low T_{\max} , since marine carbon, generally considered more labile than terrestrial carbon [Bianchi, 2011], would not likely be stored very long in these well-oxidized and frequently resuspended sediments. Moreover, previous work at this station has shown very low concentrations of algal pigments [Schreiner et al., 2013], including pheopigments, normally considered to be indicative of degraded marine OC [Bianchi and Findlay, 1991; Bianchi and Canuel, 2009]. These results suggest that there is likely a terrestrial source of OC at station ND that is both old and relatively labile.

The two important Colville River-derived terrestrial sources of older POC to these sites are surface permafrosted soils and the older Pleistocene-aged yedoma deposits that underlay these soils [Kanevskiy et al., 2011]. Figure 1 shows the estimated extent of these deposits in Alaska and specifically in the Colville watershed, which are second only to those in Siberia [Kanevskiy et al., 2011]. Yedoma deposits are located in areas of continuous permafrost that during glacial times were occupied by cold-steppe tundra environments [Zimov et al., 2006a, 2006b]. These sediments are organic rich (some areas contain up to 5% OC), and because of their long-term, frozen preservation much of this organic matter is relatively labile [Zimov et al., 2006a, 2006b; Schirrmeyer et al., 2011]. Because they consist of mainly fine-grained, mineral soils, they tend to be high in fatty acids and other aliphatic OC, in contrast to coarser-grained sediments, which tend to be high in lignin-phenol concentration [Wakeham et al., 2009; Xu et al., 2009]. These significantly different sources of OC (surface soils and subsurface yedoma) are illustrated by the comparison of the pyrogram and radiocarbon data to biomarker data of density fractions from Schreiner et al. [2013] (Figure 3). Lignin-phenol biomarkers, indicative of terrestrial OC because the lignin polymer is produced only by terrestrial plants, are classically used to trace terrestrial OC input to marine sediments [Hedges and Mann, 1979; Hedges and Ertel, 1982]. Lignin is often enriched in woody debris and coarser-grained particles in marine settings [Wakeham et al., 2009; Xu et al., 2009] and has been shown in the Siberian Arctic to trace inputs of relatively recent OC sourced from organic and surface soil horizons [Feng et al., 2013]. The radiocarbon age of both ND and L3 samples are significantly negatively correlated with lignin-phenol content of the samples, while T_{\max} is significantly positively correlated (Figure 3). This indicates that as the radiocarbon age of the sample increases (i.e., the sample gets "older") the sample contains less lignin and has a lower T_{\max} , supporting the findings of Feng et al. [2013] and indicating that lignin from this North American high Arctic watershed is also sourced from younger, surface soil layers. Deltaic sample ND appears to be receiving more OC from a source other than lignin-rich surface layers than lagoonal sample L3. This source is likely originating from Pleistocene yedoma-like deposits, as has been shown in other well-studied Siberian rivers [Vonk et al., 2012, 2013; Feng et al., 2013].

Yedoma deposits in the Siberian Arctic have been shown to be rich in fatty acids and low in lignin-phenols [Vonk et al., 2010; Feng et al., 2013], which corresponds well with the data summarized here. Samples low in lignin-phenols have the oldest ^{14}C ages and are likely sourced from fine-grained, deep, mineral soils from permafrost ecosystems that have been previously shown to be low in lignin-phenols in Arctic ecosystems [Xu et al., 2009]. L3, located in the lagoon and away from the majority of Colville riverine output, receives much of its OC from coastal peat deposits [Schreiner et al., 2013]. These deposits are rich in hydroxy phenols and lignin-phenols [Williams et al., 1998; Feng et al., 2013] and are younger than OC deposits at the delta station ND. Taken together, these results indicate that yedoma OC is an important source of the POC delivered to station ND, whereas peat and soil OC is an important source of the POC delivered to station L3. Combined with the fact that station ND receives the majority of its POC from the Colville River and L3 receives a substantial amount of its POC from coastal erosion, this indicates that much of the POC from the Colville outflow is sourced from old Pleistocene yedoma. To the best of the authors' knowledge, this is the first evidence for the thaw, erosion, and movement of yedoma deposits from the Alaskan North Slope to the Beaufort Sea, which has already been shown for other regions of continuous permafrost in the Siberian Arctic [Vonk et al., 2012;

Feng *et al.*, 2013]. Additionally, this yedoma OC is shown in the pyrolysis data to burn at relatively lower temperatures than aromatic-rich surface soils, indicating that this very old OC has the potential to be more reactive in the marine environment than younger, soil-sourced OC.

Age and pyrogram comparisons within each sample can also shed light on the nature of the Colville watershed. Similar ramped pyrolysis measurements have been performed to date on sediments from two other rivers: the Mississippi-Atchafalaya river system [Rosenheim *et al.*, 2013a], a large, passive-margin river, and the Narayani River (part of the Ganges-Brahmaputra river system) [Rosenheim and Galy, 2012], a smaller, mountainous, active-margin river. These two rivers produced significantly different pyrograms due to differences in their watersheds, the type of POC carried by each river, and the time required for sediments to travel through the watershed before deposition on the shelf. The Mississippi River contains well-integrated OC and has a large floodplain OC storage capacity, while the Narayani River carries OC that retains its distinct source characteristics, due to the short transit time of its sediments [Rosenheim and Galy, 2012; Rosenheim *et al.*, 2013a]. The Colville delta samples (ND) analyzed here have characteristics between these two end-member rivers; however, the analysis of density-fractionated samples allows for a much more nuanced interpretation. The bulk delta sample pyrogram closely resembles the Mississippi, indicating well-mixed and highly integrated riverine OC from a fairly large watershed. However, the ^{14}C ages seen for the Colville samples are much older on average than the ages seen for the Mississippi River (15,000 years before present (ybp) versus 2000 to 4000 ybp, respectively) [Rosenheim *et al.*, 2013a], which may further support the transport of old, permafrost-sourced POC to the Beaufort Sea. Station L3 had pyrograms that more closely resemble the Narayani River, with distinct sources that were not well mixed before deposition [Rosenheim and Galy, 2012].

5. Conclusions

The results summarized here provide the first evidence for the thawing and transport of Pleistocene yedoma-like deposits in northern Alaska and the delivery of old, yedoma-sourced POC to deltaic sediments in the Alaskan Beaufort Sea. Ramped pyrolysis and ^{14}C analysis indicate that old, lignin-phenol-poor POC is delivered to the Colville River delta and is likely sourced from yedoma. This POC is relatively more reactive than younger, soil-sourced POC and can be expected to be remineralized more readily than POC originating from surface soils and peats. Additionally, ramped pyrolysis indicates that younger, lignin-phenol-rich POC is delivered to a coastal lagoon site eastward of the delta mouth and is likely sourced directly from eroding coastal peats and soils. This supports previous findings from the Colville watershed and compound-specific biomarker work done in the Siberian Arctic. These results indicate for the first time that yedoma thaw and transport is occurring in the North American Arctic as has been previously shown in Siberia.

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References

- Arctic Climate Impact Assessment (ACIA) (2005), *Arctic Climate Impact Assessment*, Cambridge Univ. Press, New York.
- Aller, R. C., and N. E. Blair (2006), Carbon remineralization in the Amazon-Guianas tropical mud belt: A sedimentary incinerator, *Cont. Shelf Res.*, 26(17–18), 2241–2259.
- Bianchi, T. S. (2011), The role of terrestrial derived organic carbon in the coastal ocean: A changing paradigm and the priming effect, *Proc. Natl. Acad. Sci. U.S.A.*, 108(49), 19,473–19,481.
- Bianchi, T. S., and M. A. Allison (2009), Large-river delta-front estuaries as natural “recorders” of global environmental change, *Proc. Natl. Acad. Sci. U.S.A.*, 106(20), 8085–8092.
- Bianchi, T. S., and E. Canuel (2009), Photosynthetic pigments: Chlorophylls, carotenoids, and phycobilins, in *Chemical Biomarkers in Aquatic Ecosystems*, pp. 221–247, Princeton Univ. Press, Princeton, N. J.
- Bianchi, T. S., and S. Findlay (1991), Decomposition of Hudson estuary macrophytes: Photosynthetic pigment transformations and decay constants, *Estuaries*, 14(1), 65–73.
- Bianchi, T. S., S. Mitra, and B. A. McKee (2002), Sources of terrestrially-derived organic carbon in lower Mississippi River and Louisiana shelf sediments: Implications for differential sedimentation and transport at the coastal margin, *Mar. Chem.*, 77, 211–223.
- Bianchi, T. S., J. J. Galler, and M. A. Allison (2007), Hydrodynamic sorting and transport of terrestrially derived organic carbon in sediments of the Mississippi and Atchafalaya Rivers, *Estuarine Coastal Shelf Sci.*, 73, 211–222.
- Blair, N. E., E. L. Leithold, and R. C. Aller (2004), From bedrock to burial: The evolution of particulate organic carbon across coupled watershed-continent margin systems, *Mar. Chem.*, 92, 141–156.
- Burdige, D. J. (2005), Burial of terrestrial organic matter in marine sediments: A re-assessment, *Global Biogeochem. Cycles*, 19, GB4011, doi:10.1029/2004GB002368.
- dos Santos, G., J. R. Southon, S. Griffin, S. R. Beaupre, and E. R. M. Druffel (2007), Ultra small-mass AMS ^{14}C sample preparation and analysis at KCCAMS/UCI Facility, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 259, 293–302.
- Drenzek, N. J., D. B. Montlucon, M. B. Yunker, R. W. Macdonald, and T. I. Eglinton (2007), Constraints on the origin of sedimentary organic carbon in the Beaufort Sea from coupled molecular ^{13}C and ^{14}C measurements, *Mar. Chem.*, 103, 146–162.
- Dunton, K. H., T. Weingartner, and E. C. Carmack (2006), The nearshore western Beaufort Sea ecosystem: Circulation and importance of terrestrial carbon in Arctic coastal food webs, *Prog. Oceanogr.*, 71, 362–378.

- Feng, X., J. E. Vonk, B. E. van Dongen, O. Gustafsson, I. P. Semiletov, O. V. Dudarev, Z. Wang, D. B. Montlucon, L. Wacker, and T. I. Eglinton (2013), Differential mobilization of terrestrial carbon pools in Eurasian Arctic river basins, *Proc. Natl. Acad. Sci. U.S.A.*, *110*(35), 14,168–14,173.
- Goni, M. A., K. C. Ruttenberg, and T. I. Eglinton (1998), A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico, *Geochim. Cosmochim. Acta*, *62*, 3055–3075.
- Goni, M. A., M. B. Yunker, R. W. Macdonald, and T. I. Eglinton (2000), Distribution and sources of organic biomarkers in Arctic sediments from the Mackenzie River and Beaufort Shelf, *Mar. Chem.*, *71*, 23–51.
- Goni, M. A., M. B. Yunker, R. W. Macdonald, and T. I. Eglinton (2005), The supply and preservation of ancient and modern components of organic carbon in the Canadian Beaufort Shelf of the Arctic Ocean, *Mar. Chem.*, *93*, 53–73.
- Gordeev, V. V. (2006), Fluvial sediment flux to the Arctic Ocean, *Geomorphology*, *80*, 94–104.
- Gordeev, V. V., and M. D. Kravchishina (2009), River flux of dissolved organic carbon (DOC) and particulate organic carbon (POC) to the Arctic Ocean: What are the consequences of the global changes?, in *Influence of Climate Change on the Changing Arctic and Sub-Arctic Conditions*, edited by J. C. J. Nihoul and A. G. Kostianoy, pp. 145–160, Springer, Dordrecht, Netherlands.
- Guo, L., and R. W. Macdonald (2006), Source and transport of terrigenous organic matter in the upper Yukon River: Evidence from isotope ($\delta^{13}\text{C}$, D_{14}C , and d_{15}N) composition on dissolved, colloidal, and particulate phases, *Global Biogeochem. Cycles*, *20*, GB2011, doi:10.1029/2005GB002593.
- Guo, L., C.-L. Ping, and R. W. Macdonald (2007), Mobilization pathways of organic carbon from permafrost to arctic rivers in a changing climate, *Geophys. Res. Lett.*, *34*, L13603, doi:10.1029/2007GL030689.
- Harris, D., W. R. Horwath, and C. van Kessel (2001), Acid fumigation of soils to remove carbonates prior to total organic carbon or carbon-13 isotopic analysis, *Soil Sci. Soc. Am. J.*, *65*, 1853–1856.
- Hedges, J. I., and J. R. Ertel (1982), Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products, *Anal. Chem.*, *54*, 174–178.
- Hedges, J. I., and R. G. Keil (1995), Sedimentary organic matter preservation: An assessment and speculative synthesis, *Mar. Chem.*, *49*, 81–115.
- Hedges, J. I., and D. C. Mann (1979), The lignin geochemistry of marine sediments from the southern Washington coast, *Geochim. Cosmochim. Acta*, *43*, 1809–1818.
- Hedges, J. I., R. G. Keil, and R. Benner (1997), What happens to terrestrial organic matter in the ocean?, *Org. Geochem.*, *27*(5/6), 195–212.
- IPCC (2013), Summary for Policymakers, in *Climate Change 2013: The Physical Science Basis, Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by T. F. Stocker et al., Cambridge Univ. Press, Cambridge, U. K., and New York.
- Kanevskiy, M., Y. Shur, D. Fortier, M. T. Jorgenson, and E. Stephani (2011), Cryostratigraphy of late Pleistocene syngenetic permafrost (yedoma) in northern Alaska, Iktikillik River exposure, *Quat. Res.*, *75*, 584–596.
- Keil, R. G., L. M. Mayer, P. D. Quay, J. E. Richey, and J. I. Hedges (1997), Loss of organic matter from riverine particles in deltas, *Geochim. Cosmochim. Acta*, *61*(7), 1507–1511.
- Macdonald, R. W., A. S. Naidu, M. B. Yunker, and C. Gobeil (2004a), The Beaufort Sea: Distribution, sources, variability and burial of organic carbon, in *The Organic Carbon Cycle in the Arctic Ocean*, edited by R. Stein and R. W. Macdonald, pp. 177–193, Springer, Berlin, Germany.
- Macdonald, R. W., E. Sakshaug, and R. Stein (2004b), The Arctic Ocean: Modern status and recent climate change, in *The Organic Carbon Cycle in the Arctic Ocean*, edited by R. Stein and R. W. Macdonald, pp. 6–21, Springer-Verlag, Berlin, Germany.
- McClelland, J. W., S. J. Dery, B. J. Peterson, R. M. Holmes, and E. F. Wood (2006), A pan-arctic evaluation of changes in river discharge during the latter half of the 20th century, *Geophys. Res. Lett.*, *33*, L06715, doi:10.1029/2006GL025753.
- Naidu, A. S., L. W. Cooper, B. P. Finney, R. W. Macdonald, C. Alexander, and I. P. Semiletov (2000), Organic carbon isotope ratios ($\delta^{13}\text{C}$) of Arctic Amerasian Continental shelf sediments, *Int. J. Earth Sci.*, *89*, 522–532.
- Pendergraft, M. A., Z. Dincer, J. L. Sericano, T. L. Wade, J. Kolasinski, and B. E. Rosenheim (2013), Linking ramped pyrolysis isotope data to oil content through PAH analysis, *Environ. Res. Lett.*, *8*, Article 044038.
- Prahl, F. G., J. R. Ertel, M. A. Goni, M. A. Sparrow, and B. Eversmeyer (1994), Terrestrial organic carbon contributions to sediments on the Washington margin, *Geochim. Cosmochim. Acta*, *58*(14), 3035–3048.
- 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., K. M. Roe, B. J. Roberts, A. S. Kolker, M. A. Allison, and K. H. Johannesson (2013a), River discharge influences on particulate organic carbon age structure in the Mississippi/Atchafalaya river system, *Global Biogeochem. Cycles*, *27*, 154–166, doi:10.1002/gbc.20018.
- Rosenheim, B. E., J. A. Santoro, M. Gunter, and E. W. Domack (2013b), Improving Antarctic sediment C-14 dating using ramped pyrolysis: An example from the Hugo Island trough, *Radiocarbon*, *55*(1), 115–126.
- Schirmermeister, L., V. Kunitsky, G. Gross, S. Wetterich, H. Meyer, G. Schwamborn, O. Babiy, A. Derevyagin, and C. Siebert (2011), Sedimentary characteristics and origin of the Late Pleistocene Ice Complex on north east Siberian Arctic coastal lowlands and islands—A review, *Quat. Int.*, *241*, 3–25.
- Schlunz, B., and R. R. Schneider (2000), Transport of terrestrial organic carbon to the oceans by rivers: Re-estimating flux and burial rates, *Int. J. Earth Sci.*, *88*(4), 599–606.
- Schreiner, K. M., T. S. Bianchi, T. I. Eglinton, M. A. Allison, and A. J. M. Hanna (2013), Sources of terrigenous inputs to surface sediments of the Colville River Delta and Simpson's Lagoon, Beaufort Sea, Alaska, *J. Geophys. Res. Biogeosci.*, *118*, 808–824, doi:10.1002/jgrg.20065.
- Schuur, E. A. G., et al. (2008), Vulnerability of permafrost carbon to climate change: Implications for the global carbon cycle, *BioScience*, *58*(8), 701–714.
- Schuur, E. A. G., J. G. Vogel, K. G. Crummer, H. Lee, J. O. Sickman, and T. E. Osterkamp (2009), The effect of permafrost thaw on old carbon release and net carbon exchange from tundra, *Nature*, *459*, 556–559.
- Tarnocai, C., J. G. Canadell, E. A. G. Schuur, P. Kuhry, G. Mazhitova, and S. Zimov (2009), Soil organic carbon pools in the northern circumpolar permafrost region, *Global Biogeochem. Cycles*, *23*, GB2023, doi:10.1029/2008GB003327.
- Vonk, J. E., L. Sanchez-Garcia, I. Semiletov, O. Dudarev, T. Eglinton, A. Andersson, and O. Gustafsson (2010), Molecular and radiocarbon constraints on sources and degradation of terrestrial organic carbon along the Kolyma paleoriver transect, East Siberian Sea, *Biogeochemistry*, *7*, 3153–3166.
- Vonk, J. E., et al. (2012), Activation of old carbon by erosion of coastal and subsea permafrost in Arctic Siberia, *Nature*, *489*, 137–140.
- Vonk, J. E., P. J. Mann, K. L. Dowdy, A. Davydova, S. P. Davydov, N. Zimov, R. G. M. Spencer, E. B. Buljgina, T. I. Eglinton, and R. M. Holmes (2013), Dissolved organic carbon loss from Yedoma permafrost amplified by ice wedge thaw, *Environ. Res. Lett.*, *8*(035023), 1–9.

- Wakeham, S. G., E. A. Canuel, E. J. Lerberg, P. Mason, T. P. Sampere, and T. S. Bianchi (2009), Partitioning of organic matter in continental margin sediments among density fractions, *Mar. Chem.*, *115*, 211–225.
- Walker, H. J. (1998), Arctic deltas, *J. Coastal Res.*, *14*(3), 718–738.
- Walker, H. J., and P. F. Hudson (2003), Hydrologic and geomorphic processes in the Colville River delta, Alaska, *Geomorphology*, *56*, 291–303.
- Weintraub, M. N., and J. P. Schimel (2003), Interactions between carbon and nitrogen mineralization and soil organic matter chemistry in Arctic tundra soils, *Ecosystems*, *6*, 129–143.
- Williams, C. J., J. B. Yavitt, R. K. Wider, and N. L. Cleavitt (1998), Cupric oxide oxidation products of northern peat and peat-forming plants, *Can. J. Bot.*, *76*, 51–62.
- Xu, C., L. Guo, C.-L. Ping, and D. M. White (2009), Chemical and isotopic characterization of size-fractionated organic matter from cryoturbated tundra soils, northern Alaska, *J. Geophys. Res.*, *114*, G03002, doi:10.1029/2008JG000846.
- Yunker, M. B., L. L. Belicka, H. R. Harvey, and R. W. Macdonald (2005), Tracing the inputs and fate of marine and terrigenous organic matter in Arctic Ocean sediments: A multivariate analysis of lipid biomarkers, *Deep Sea Res., Part II*, *52*, 3478–3508.
- Zimov, S., S. Davydov, G. Zimova, A. Davydova, E. Schuur, K. Dutta, and F. Chapin III (2006a), Permafrost carbon: Stock and decomposability of a globally significant carbon pool, *Geophys. Res. Lett.*, *33*, L20502, doi:10.1029/2006GL027484.
- Zimov, S., E. Schuur, and F. Chapin III (2006b), Permafrost and the global carbon budget, *Science*, *312*, 1612–1613.