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ERRONEOUSLY OLD RADIOCARBON AGES FROM TERRESTRIAL POLLEN CONCENTRATES IN YELLOWSTONE LAKE, WYOMING, USA

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ABSTRACT. Accelerator mass spectrometry (AMS) dating of pollen concentrates is often used in lake sediment records where large, terrestrial plant remains are unavailable. Ages produced from chemically concentrated pollen as well as manually picked Pinaceae grains in Yellowstone Lake (Wyoming) sediments were consistently 1700–4300 cal years older than ages established by terrestrial plant remains, tephrochronology, and the age of the sediment-water interface. Previous studies have successfully utilized the same laboratory space and methods, suggesting the source of old-carbon contamination is specific to these samples. Manually picking pollen grains precludes admixture of non-pollen materials. Furthermore, no clear source of old pollen grains occurs on the deglaciated landscape, making reworking of old pollen grains unlikely. High volumes of CO₂ are degassed in the Yellowstone Caldera, potentially introducing old carbon to pollen. While uptake of old CO₂ through photosynthesis is minor (F¹⁴C approximately 0.99), old-carbon contamination may still take place in the water column or in surficial lake sediments. It remains unclear, however, what mechanism allows for the erroneous ages of highly refractory pollen grains while terrestrial plant remains were unaffected. In the absence of a satisfactory explanation for erroneously old radiocarbon ages from pollen concentrates, we propose steps for further study.

KEYWORDS: AMS dating, chronology, contamination, paleoecology, pine.

INTRODUCTION

Lake sediments are the primary archive for reconstructing late-Quaternary terrestrial climate, vegetation, fire, and limnobiological processes. Correlation between sites and comparison of independent proxies and paleoclimate model simulations requires sedimentary records with high-resolution age-depth control, most commonly accomplished through radiocarbon dating. The utility of radiocarbon dating pollen concentrates with accelerator mass spectrometry (AMS) has been well established in lacustrine settings where terrestrial plant remains are unavailable and where total organic carbon of (bulk) sediments are potentially contaminated by refractory carbon and reservoir effects. Pollen concentration through mechanical separation (Brown et al. 1989; Long et al. 1992; Mensing and Southon 1999), chemical maceration (Doher 1980), heavy liquid separation (Vandergoes and Prior 2003), and flow cytometry (Tennant et al. 2013) selectively removes anachronous sources of carbon (e.g. carbonates, algal remains, humic acids) from the sample. Although some studies suggest dating errors as a result of incomplete separation of non-pollen material (Regnéll 1992; Richardson and Hall 1994) or incorporation of reworked pollen grains (Mensing and Southon 1999; Zimmerman et al. 2019), pollen-concentrate ages typically produce more reliable chronologies than bulk-sediment ages where reservoir effects are a concern (e.g. Brown et al. 1989; Vandergoes and Prior 2003; Newnham et al. 2007; Fletcher et al. 2017).

Yellowstone Lake, Wyoming (44.5°N, 110.3°W, elev. 2360 m.a.s.l.), a large (352 km²), temperate, subalpine lake (Figure 1), is a good candidate for AMS dating of pollen

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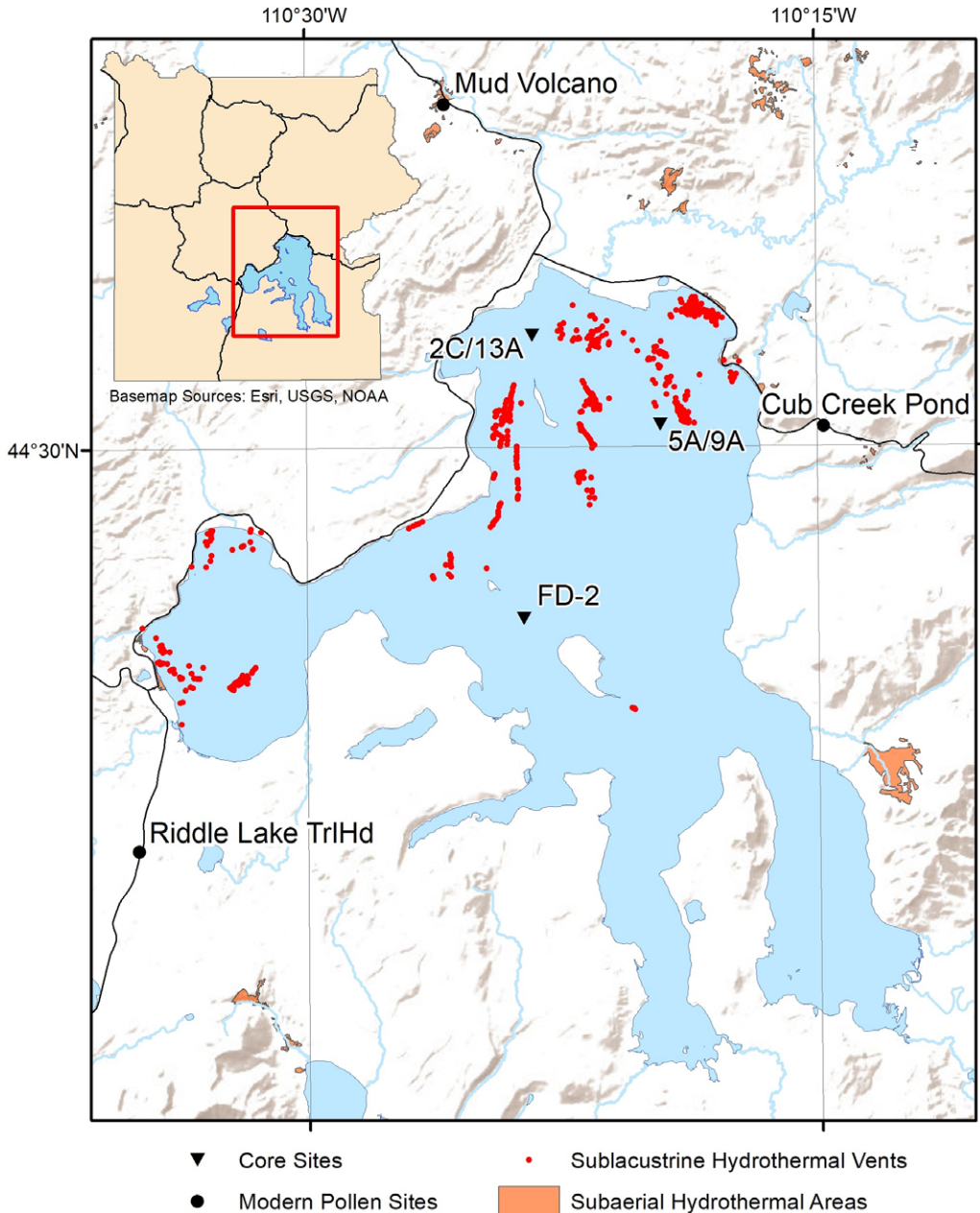


Figure 1 Map of the Yellowstone Lake basin, showing location of the collection of sediment cores and modern pollen samples. Subaerial hydrothermal areas based on Vaughan et al. (2014) and sublacustrine hydrothermal vents based on Morgan et al. (2007). All sites are located within or near the eastern half of the Yellowstone Caldera, where the majority of CO₂ degassing occurs from acid-sulfate hydrothermal vents (Werner and Brantley 2003).

concentrates, as few sufficiently large, terrestrial plant remains were recovered from recent coring efforts (2016, Table 1). The geology of the watershed is complex, resulting from an interplay of volcanic, glacial, and hydrothermal processes. The northern two-thirds of the lake basin lies within the Yellowstone Caldera that was formed ~630 ka (Christiansen 2001;

Table 1 Yellowstone Lake and vicinity age controls.

Accession no. ¹ (receipt no.)	Core depth (cm) ² / location	Material dated ³	C (µg)	δ ¹³ C ‰ VPDB	Age ¹⁴ C	F ¹⁴ C ⁴	2-σ cal BP age range (probability) ⁵	Source ⁶
FD-2								
C-5753	24.0	t. plant remains			430 ± 70	0.9479 ± 0.0082	307–552 (0.998) 614–616 (0.002)	Tiller 1995
C-5755	123.5	t. plant remains			1450 ± 100	0.8348 ± 0.0103	1179–1558 (1.000)	Tiller 1995
C-10034	225.5	humic acid			6060 ± 60	0.4703 ± 0.0035	6750–6767 (0.016) 6774–7030 (0.879) 7043–7070 (0.022) 7077–7086 (0.008) 7097–7156 (0.074)	This work
C-10035	225.5	humic acid			6030 ± 60	0.4721 ± 0.0035	6698–6700 (0.001) 6719–7022 (0.977) 7120–7152 (0.022)	This work
C-10048	295.5	t. plant remains			7950 ± 180	0.3717 ± 0.0082	8408–9289 (1.000)	Tiller 1995
C-10037	295.5	humic acid			7740 ± 60	0.3815 ± 0.0028	8410–8609 (0.991) 8618–8626 (0.009)	This work
C-10036	295.5	humic acid			7680 ± 60	0.3844 ± 0.0029	8389–8581 (1.000)	This work
C-5754	455.3	t. plant remains			9080 ± 100	0.3230 ± 0.0040	9915–10098 (0.149) 10110–10511 (0.851)	Tiller 1995
C-10039	475.5	humic acid			10460 ± 80	0.2720 ± 0.0027	12064–12596 (1.000)	This work
C-10040	475.5	humic acid			10280 ± 60	0.2781 ± 0.0021	11815–12244 (0.885) 12266–12383 (0.115)	This work
C-4977	476.6	t. plant remains			6290 ± 80	0.4570 ± 0.0045	7615–7879 (0.924) 7890–7931 (0.076)	Tiller 1995
C-10038	505.5	t. plant remains			7100 ± 210	0.4132 ± 0.0107	7580–8340 (1.000)	Tiller 1995
C-10047	505.5	t. plant remains			7060 ± 100	0.4152 ± 0.0051	7673–8051 (0.996) 8098–8102 (0.001) 8144–8149 (0.003)	Tiller 1995
C-9165	505.5	humic acid			11380 ± 80	0.2425 ± 0.0024	13079–13386 (1.000)	This work
C-9164	505.5	humic acid			10280 ± 90	0.2781 ± 0.0031	11651–11662 (0.003) 11705–12418 (0.997)	This work
	506.5	Mazama ash					7584–7682	Egan et al. 2015
C-4976	582.7	t. plant remains			8290 ± 120	0.3563 ± 0.0053	9010–9503 (0.997) 9511–9516 (0.003)	Tiller 1995
C-10042	582.5	humic acid			12350 ± 80	0.2149 ± 0.0021	14067–14830 (1.000)	This work

(Continued)

Table 1 (*Continued*)

Accession no. ¹ (receipt no.)	Core depth (cm) ² / location	Material dated ³	C (µg)	δ ¹³ C ‰ VPDB	Age ¹⁴ C	F ¹⁴ C ⁴	2-σ cal BP age range (probability) ⁵	Source ⁶
C-10041	582.5	humins			12050 ± 70	0.2231 ± 0.0019	13748–14088 (1.000)	This work
C-4974	657.0	t. plant remains			10200 ± 90	0.2809 ± 0.0031	11404–11568 (0.067) 11573–11576 (0.001) 11591–12189 (0.901) 12199–12237 (0.015) 12283–12301 (0.006) 12343–12376 (0.012)	Tiller 1995
C-4973	735.1	t. plant remains			10280 ± 80	0.2781 ± 0.0028	11757–12401 (1.000)	Tiller 1995
C-10044	766.5	humic acid			16850 ± 60	0.1228 ± 0.0009	20105–20523 (1.000)	This work
C-10043	766.5	humins			17090 ± 150	0.1191 ± 0.0022	20202–21013 (1.000)	This work
C-10046	778.3	humic acid			18240 ± 100	0.1032 ± 0.0013	21846–22366 (1.000)	This work
C-10045	778.3	humins			17950 ± 100	0.1070 ± 0.0013	21432–22027 (1.000)	This work
C-9162	854.0	humic acid			16420 ± 180	0.1295 ± 0.0029	19359–20279 (1.000)	This work
C-9163	854.0	humins			18900 ± 250	0.0951 ± 0.0029	22309–23445 (1.000)	This work
	855.0	Glacier Peak (B or G) ash					13410–13710 (1.000)	Kuehn et al. 2009
13A								
	0	core top					–67	
OS-142012 (153942)	1.0	bulk sediment	1559		5250 ± 25	0.5203 ± 0.0017	5928–6026 (0.729) 6047–6065 (0.029) 6077–6116 (0.160) 6152–6175 (0.082)	This work
OS-142223 (153938)	1.0	picked pollen	22		2310 ± 180	0.7505 ± 0.0164	1904–1907 (0.001) 1924–2755 (0.999)	This work
	12.0	1700 CE fire					240–260	Romme & Despain, 1989
2C								
OS-138757 (149875)	164.0	c.c. pollen	476		3860 ± 20	0.6185 ± 0.0016	4163–4166 (0.006) 4181–4198 (0.047) 4230–4407 (0.948)	This work
OS-135957 (147265)	328.0	t. plant remains	670	–26.3	2590 ± 20	0.7242 ± 0.0019	2723–2754 (1.000)	This work

(Continued)

Table 1 (Continued)

Accession no. ¹ (receipt no.)	Core depth (cm) ² / location	Material dated ³	C (µg)	δ ¹³ C ‰ VPDB	Age ¹⁴ C	F ¹⁴ C ⁴	2-σ cal BP age range (probability) ⁵	Source ⁶
OS-135958 (147266)	402.0	t. plant remains	1130	-28.0	3150 ± 25	0.6760 ± 0.0022	3272–3285 (0.038) 3339–3445 (0.962)	This work
OS-138692 (149876)	524.5	c.c. pollen	440		6280 ± 30	0.4574 ± 0.0017	7164–7263 (1.000)	This work
OS-136956 (147971)	624.0	t. plant remains	643		4510 ± 20	0.5707 ± 0.0016	5053–5190 (0.688) 5213–5296 (0.312)	This work
OS-142084 (153943)	755.0	t. plant remains	148	-10.9	9980 ± 45	0.2887 ± 0.0017	11259–11623 (0.985) 11675–11694 (0.015)	This work
OS-138693 (149877)	792.0	c.c. pollen	307		7220 ± 35	0.4068 ± 0.0018	7963–8072 (0.764) 8085–8158 (0.236)	This work
OS-142082 (153939)	934.5	bulk sediment	461		11150 ± 55	0.2497 ± 0.0016	12841–13112 (1.000)	This work
OS-142018 (153935)	934.5	picked pollen	58		10250 ± 170	0.2793 ± 0.0059	11348–11380 (0.011) 11386–12540 (0.989)	This work
	940.0	Mazama ash					7584–7682	Egan et al., 2015
OS-138622 (149869)	965.5	t. plant remains	190		5740 ± 30	0.4895 ± 0.0019	6453–6459 (0.012) 6462–6634 (0.988)	This work
OS-138700 (149878)	978.0	c.c. pollen	569		9870 ± 55	0.2928 ± 0.0019	11188–11405 (0.982) 11457–11465 (0.004) 11563–11593 (0.014)	This work
OS-138701 (149879)	986.0	c.c. pollen	248		9390 ± 50	0.3106 ± 0.0019	10500–10741 (1.000)	This work
OS-138866 (149880)	1160.5	c.c. pollen	545		12100 ± 110	0.2215 ± 0.0031	13639–13663 (0.004) 13707–14303 (0.996)	This work
9A	0	core top					–67	
OS-142011 (153941)	1.0	bulk sediment	2051		4080 ± 25	0.6017 ± 0.0019	4447–4470 (0.060) 4516–4644 (0.770) 4677–4692 (0.017) 4761–4800 (0.153)	This work

(Continued)

Table 1 (Continued)

Accession no. ¹ (receipt no.)	Core depth (cm) ² / location	Material dated ³	C (μg)	$\delta^{13}\text{C}$ ‰ VPDB	Age ¹⁴ C	F ¹⁴ C ⁴	2- σ cal BP age range (probability) ⁵	Source ⁶
OS-142222 (153937)	1.0	picked pollen	34		1910 \pm 110	0.7885 \pm 0.0109	1571–1583 (0.006) 1598–2120 (0.994)	This work
5A								
OS-135959 (147267)	364.5	t. plant remains	730	-27.1	3760 \pm 30	0.6261 \pm 0.0022	3993–4039 (0.127) 4074–4184 (0.727) 4188–4192 (0.007) 4195–4235 (0.139)	This work
OS-138998 (149881)	533.5	c.c. pollen	202	-0.4	6140 \pm 95	0.4654 \pm 0.0054	6792–7254 (1.000)	This work
OS-138868 (149882)	540.5	c.c. pollen	411		6600 \pm 45	0.4395 \pm 0.0024	7433–7566 (1.000)	This work
OS-142083 (153940)	782.0	bulk sediment	405		11050 \pm 50	0.2524 \pm 0.0016	12779–13057 (1.000)	This work
OS-142221 (153936)	782.0	picked pollen	43		5530 \pm 130	0.5021 \pm 0.0083	5999–6568 (0.977) 6586–6627 (0.023)	This work
	783.0	Mazama ash					7584–7682	Egan et al., 2015
OS-139001 (149883)	814.0	c.c. pollen	243	-25.5	9060 \pm 50	0.3236 \pm 0.0021	10157–10299 (0.975) 10320–10343 (0.012) 10352–10374 (0.013)	This work
OS-139002 (149884)	823.5	c.c. pollen	303	-25.2	9100 \pm 55	0.3222 \pm 0.0021	10184–10409 (1.000)	This work
OS-138869 (149885)	837.0	c.c. pollen	413		9340 \pm 70	0.3126 \pm 0.0027	10297–10357 (0.047) 10369–10723 (0.953)	This work
OS-139116 (149886)	941.5	c.c. pollen	390	-25.7	9020 \pm 50	0.3254 \pm 0.0021	9936–9992 (0.070) 10008–10030 (0.017) 10035–10062 (0.027) 10128–10255 (0.886)	This work

(Continued)

Table 1 (Continued)

Accession no. ¹ (receipt no.)	Core depth (cm) ² / location	Material dated ³	C (µg)	δ ¹³ C ‰ VPDB	Age ¹⁴ C	F ¹⁴ C ⁴	2-σ cal BP age range (probability) ⁵	Source ⁶
Modern								
Pollen								
OS-149977 (160235)	Riddle Lk. TrlHd.	modern pollen	247	-30.8	80 ± 15	0.9903 ± 0.0019	-5 (0.003) 33–74 (0.556) 79–81 (0.004) 98–107 (0.023) 113–136 (0.170) 224–254 (0.243)	This work
OS-149978 (160236)	Cub Creek Pond	modern pollen	343	-31.4	50 ± 20	0.9940 ± 0.0022	-5 (0.024) 35–70 (0.835) 117–131 (0.056) 231–244 (0.081) 248–250 (0.004)	This work
OS-149979 (160237)	Mud Volcano	modern pollen	268	-30.8	170 ± 20	0.9790 ± 0.0025	-5–31 (0.214) 138–158 (0.111) 164–222 (0.492) 258–285 (0.182)	This work

¹C-## (Chicago), OS-## (National Ocean Sciences Acceleratory Mass Spectrometry).

²Depths reported are tops of 1-cm intervals from which samples were collected.

³c.c. pollen (chemically concentrated pollen), t. plant remains (terrestrial plant remains).

⁴FD-2 F¹⁴C back-calculated from measured ¹⁴C age according to method of Reimer et al. (2004).

⁵Calibrated ranges calculated by CALIB and CALIBomb according to method described in text, parenthetical values relative area under probability distribution.

⁶Source listed for lithological context (FD-2) or calendar age of event.

Matthews et al. 2015; Wotzlaw et al. 2015), and the entire lake basin was covered by the Yellowstone glacial complex, 25,000–14,000 BP (Licciardi and Pierce 2018). The lake floor today has more than 660 active or recently active hydrothermal vents (Figure 1; Morgan et al. 2007).

Previous studies of sediment cores from Yellowstone Lake provide a postglacial limnogeologic (Tiller 1995) and paleoenvironmental (Theriot et al. 2006) record, making high-resolution age control desirable. In addition, Yellowstone Lake sediments preserve deposits from past hydrothermal explosions (Tiller 1995; Morgan et al. 2009) and volcanic ashes from eruptions in the Cascade Range to the west (Tiller 1995; Theriot et al. 2006). Sediment cores collected in 1992 (FD-2; Figure 1) were dated with radiocarbon ages from terrestrial plant remains (Tiller 1995; Table 1). However, previously unpublished radiocarbon ages collected from humic acid and humin during that study were up to thousands of years older than associated terrestrial plant remains (Table 1) and demonstrate the presence of an old-carbon pool (Figure 2). Radiocarbon ages of bulk sediments and pollen concentrates from Cub Creek Pond (44.505°N, 110.246°W, elev. 2510 m.a.s.l.) ~4 km east of Yellowstone Lake also yielded calibrated ages thousands of years older than established by terrestrial plant remains or tephrochronology (Whitlock 1993; Lu et al. 2017).

Our objective in this study was to answer the following questions: (1) How do radiocarbon ages from different terrestrial materials in Yellowstone Lake sediments compare? (2) What is the carbon source for pollen concentrates from Yellowstone Lake sediments that might lead to erroneously old ages? To answer these questions, we explore a suite of AMS radiocarbon ages from several sediment cores from the northern basin of Yellowstone Lake and compare them with independent age controls and the radiocarbon ages of living plant material.

METHODS

Sediment cores from the northwest area (core 2C, 44.53927°N, 110.38922°W, water depth 61 m) and southeast area (core 5A, 44.50782°N, 110.32685°W, water depth 102 m) of the northern basin of Yellowstone Lake were collected in September 2016 with a Kullenberg sampler (Figure 1; Kelts et al. 1986). Additional cores were retrieved near the 2C (13A) and 5A (9A) sites with a gravity sampler in July 2017 to recover the most recent sediments. Cores were transported to the National Lacustrine Core Facility (LacCore, University of Minnesota) where they were longitudinally split, photographed, and stored under refrigeration except when sampled or during core-scanning analyses. Kullenberg and gravity cores were correlated on the basis of core imagery and charcoal stratigraphy, producing two complete records for analysis, core 2C/13A and core 5A/9A.

Initial stratigraphic AMS age determinations for core 2C/13A were derived from terrestrial plant remains (needles, charcoal, or unidentified wood fragments) and pollen concentrates. Bulk-sediment ages were avoided based on erroneously old ages previously obtained from humin in the FD-2 core (Figure 2; Table 1). Plant remains were collected wherever present, identifiably terrestrial, and large enough for analysis. Five terrestrial plant remains were identified, extracted from core sediments, washed in distilled water, and placed under a dissection microscope where extraneous sediment was removed with a teasing needle. Initial pollen samples were collected from 1-cm intervals immediately above and below a thick hydrothermal explosion deposit and wherever substantial stratigraphic gaps occurred in the spacing of terrestrial plant remains. Pollen was concentrated by traditional pollen

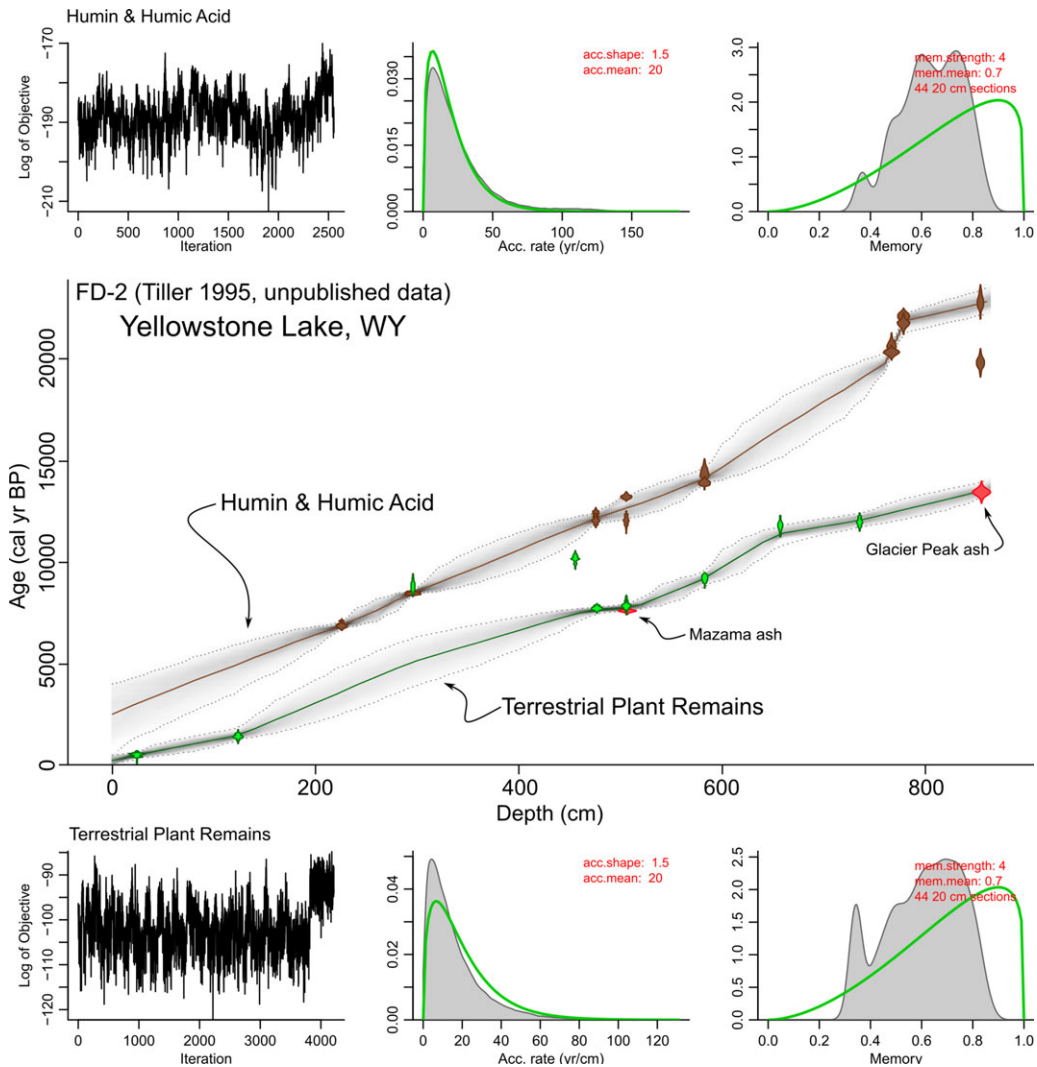


Figure 2 Bacon age-depth models for Yellowstone Lake (FD-2 from Tiller 1995) derived from bulk sediment components, humin and humic acid (brown), terrestrial plant remains (green; Tiller 1995), and ashes (red). Younger ash is Mazama (7682–7584 cal BP, 2- σ range, Egan et al. 2015) and the older is Glacier Peak B or G (13,410–13,710 cal BP, 2- σ range, Kuehn et al. 2009) as determined by petrographic analysis of Tiller (1995).

maceration procedures (Bennett and Willis 2001). Sediments were disaggregated and humic compounds removed with 0.9N KOH treatment (near-boiling hot bath, 2.5 min) and rinsed with distilled water, centrifuged, and decanted until the supernatant was clear. Large particles were wet-sieved with distilled water through a 180 μm mesh. Carbonates were removed with 2.7N HCl treatment (near-boiling hot bath, until no effervescence was observed) and silicates were removed with 28.9N HF (near-boiling hot bath, 60 min). Acetolysis was foregone in favor of oxidation in 15.9N HNO₃ (near-boiling hot bath, 3 min) to remove cellulose while avoiding carbon-bearing acetate solutions. Samples were rinsed with distilled water, centrifuged, and decanted until the slurry was neutral. These samples are hereafter referred to as chemically concentrated pollen.

Paired bulk-sediment and picked-pollen concentrate samples also were collected from stratigraphic locations (in 1-cm intervals) where ages were known independently. Bulk-sediment and picked-pollen samples were collected at the sediment-water interface (core top) in the gravity cores (13A, 9A) where the true age was approximately the year of coring (~67 cal BP). Further bulk-sediment and picked-pollen samples were collected from Kullenberg cores (2C, 5A) immediately above what is likely the Mazama ash (Tiller 1995; Theriot et al. 2006). These tephra (2C, 5A), along with a new analysis of the younger Tiller (1995) tephra from core FD-2, were sampled and analyzed at the New Mexico Bureau of Geology and Mineral Resources on a Cameca SX-100 electron microprobe to confirm the geochemical correlation between the cores, and to the Mazama ash. Picked-pollen samples were obtained utilizing the maceration procedures described above and a modified pipetting procedure from Mensing and Southon (1999). Sieving with 90 and 38 μm mesh screens targeted *Pinus* pollen and further concentration was managed by picking with a micropipette under a stereomicroscope (63 \times magnification). Pipette suction was gently produced by a syringe in place of the mouth. Identification under the stereomicroscope was generally only possible at the level of Pinaceae, so picked-pollen samples likely contained some mixture of *Pinus*, *Abies*, and *Picea*. It was not practical to count grains during the picking procedure, but resultant mass of C, 22–58 μg , was comparable to the yields of Mensing and Southon (1999).

Finally, to confirm that the carbon isotope composition of the pollen, like wood, reflects the atmospheric radiocarbon activity, modern pollen was collected from *Pinus contorta* trees in the Yellowstone Lake vicinity (Figure 1). Pollen (male) cones were collected from trees at three locations near Yellowstone Lake in June 2019: (1) upwind of Yellowstone Lake near the Riddle Lake Trailhead, (2) downwind of Yellowstone Lake near Cub Creek Pond, and (3) near Mud Volcano, where uptake of radiometrically old carbon has been previously documented in *Pinus contorta* tree rings (F^{14}C up to 0.35 lower than NHZ1 post-bomb curve; Evans et al. 2010). Due to a cold, wet spring, pollen production was late, and samples collected in June 2019 were probably from the 2018 crop. Pollen was rinsed off of cones and sieved through 90 and 38 μm mesh screens to remove extraneous material and treated with Schulze solution (1:10 wt (g)/vol (mL) mixture KClO_3 in 15.9N HNO_3 , near-boiling hot bath, 3 min) to remove extraneous organics (Doher 1980). Samples were rinsed in distilled water, centrifuged, and decanted until the slurry was neutral.

AMS age determinations were made by the National Ocean Sciences AMS (NOSAMS) facility at the Woods Hole Oceanographic Institute. Traditional pretreatment was conducted only for terrestrial plant remains using a modified acid-base-acid method to remove non-structural carbon (de Vries and Barendsen 1954) and bulk sediments were treated with 2.7N HCl (McNichol et al. 1994). Pollen-concentrate samples were combusted without any further treatment at NOSAMS since previous concentration procedures made further pretreatment redundant. Pollen-concentrate samples were generally very small, <0.1 mg total sample mass. To preserve as much of the sample as possible, concentrates were shipped in dilute HCl in distilled water with subsequent filtering onto pre-baked quartz fiber filters, rinsed to neutral, dried, and combusted at 850 $^\circ\text{C}$ in sealed quartz tubes. Carbon yields from pollen concentrates ranged from 22 to 569 μg C. Radiocarbon results were blank corrected for the possible addition of contaminants during sample processing and AMS measurement. For samples that yielded <100 μg carbon, a mass-balance correction was made according to Roberts et al. (2019). For larger sample masses, the mass-dependent correction is relatively small, and an average large mass blank value from acetanilide samples (used as a home

blank due to the unavailability of ^{14}C -free pollen material) measured concurrently with the unknown sample was used to correct the result. When samples were large enough, a split of CO_2 was sent to a stable mass spectrometer for $\delta^{13}\text{C}$ analysis to aid in the verification of results and identification of anachronous carbon sources including aquatic plants and carbonate rock.

Radiocarbon ages were calibrated with CALIB (version 7.1, Stuiver et al. 2019) utilizing the IntCal13 calibration curve (Reimer et al. 2013). Calibrated ages were further refined and interpreted in the context of stratigraphic depth through development of two age-depth models using Bacon software (rbacon version 2.3.9.1, Blaauw and Christen 2011) based on chemically concentrated pollen and terrestrial plant remains. *A priori* assignment of mean sediment accumulation rate was set to 10 yr cm^{-1} , as suggested by Bacon and closely matching our data, but is somewhat faster than Holocene sediment accumulation rates estimated for other, deeper parts of Yellowstone Lake ($\sim 15 \text{ yr cm}^{-1}$, Tiller 1995; $17\text{--}10 \text{ yr cm}^{-1}$, Johnson et al. 2003). Thickness for spline calculation was set to 20 cm, above which the model diverged greatly from provided age controls. *A priori* parameters were held constant for age-depth models based on chemically concentrated pollen and terrestrial plant remains, and independent age controls were included in both models. Instantaneous deposits resulting from volcanic ashfall or hydrothermal explosions were relatively thin in this core ($<5 \text{ cm}$) and not excised from the total core depth.

RESULTS

Radiocarbon Results

Calibrated radiocarbon ages for core 2C/13A are presented in Table 1, along with non-radiocarbon ages: the core top, a prominent charcoal peak from a large fire that occurred ca. 1700 CE (based on tree-ring analysis in the watershed; error assigned to ± 10 years on the basis of two prominent decades of stand establishment; Romme and Despain 1989; Higuera et al. 2010), and the geochemically fingerprinted Mazama ash (Table 2). All three lake-core tephra are geochemically identical to the Mazama ash (Jensen and Beaudoin 2016) allowing for time to be correlated across Yellowstone lake. The age of the climactic Mt. Mazama eruption is well established in ice-core records (7777–7477 cal BP, 2- σ range; Zdanowicz et al. 1999) and by thorough radiocarbon dating efforts (7682–7584 cal BP, 2- σ range; Egan et al. 2015). One radiocarbon result from unidentified plant remains (OS-142084) was excluded from the terrestrial plant age-depth model, given its erroneously old age and a $\delta^{13}\text{C}$ value of -10.9‰ , both of which are consistent with an aquatic plant fragment.

The age-depth models from chemically concentrated pollen and terrestrial plant remains diverge, except at the top of the core where closely spaced calendar ages enforce unity (Figure 3). Modelled median calibrated ages from pollen concentrates ranged from 1700 to 4300 years older than the modelled median calibrated ages from terrestrial plants. Ages from chemically concentrated pollen were internally consistent, with no ages falling outside the 2- σ range of the age-depth model, but they too did not agree with the age of the Mazama ash. The Mazama ash age was rejected by Bacon as an outlier in the chemically concentrated pollen model. Terrestrial plant remain ages were also internally consistent, with only one age outside the 2- σ range, and the age model aligned well with the age of the Mazama ash (Figure 3).

Table 2 Summary of normalized¹ geochemical data from Yellowstone Lake Mazama ash samples compared with UA2832 of Jensen and Beaudoin (2016).

Sample	n ²	P ₂ O ₅	SiO ₂	SO ₂	TiO ₂	Al ₂ O ₃	MgO	CaO	MnO	FeO ³	Na ₂ O	K ₂ O	F	Cl	Total	Analytical total
2C	9	0.07	72.77	0.01	0.45	14.22	0.43	1.64	0.05	2.00	5.25	2.84	0.10	0.17	100	99.09
<i>σ</i>		<i>0.03</i>	<i>0.08</i>	<i>0.01</i>	<i>0.03</i>	<i>0.06</i>	<i>0.03</i>	<i>0.04</i>	<i>0.02</i>	<i>0.04</i>	<i>0.08</i>	<i>0.04</i>	<i>0.01</i>	<i>0.01</i>		<i>1.35</i>
5A	12	0.06	72.78	0.02	0.42	14.20	0.43	1.64	0.06	2.03	5.28	2.79	0.11	0.19	100	97.33
<i>σ</i>		<i>0.03</i>	<i>0.15</i>	<i>0.01</i>	<i>0.04</i>	<i>0.10</i>	<i>0.03</i>	<i>0.06</i>	<i>0.02</i>	<i>0.06</i>	<i>0.18</i>	<i>0.07</i>	<i>0.01</i>	<i>0.04</i>		<i>1.32</i>
FD-2	9	0.08	72.87	0.01	0.41	14.25	0.42	1.62	0.05	1.99	5.24	2.77	0.11	0.19		97.56
<i>σ</i>		<i>0.03</i>	<i>0.21</i>	<i>0.01</i>	<i>0.04</i>	<i>0.08</i>	<i>0.03</i>	<i>0.05</i>	<i>0.01</i>	<i>0.06</i>	<i>0.12</i>	<i>0.05</i>	<i>0.03</i>	<i>0.07</i>		<i>2.63</i>
UA2832	21		72.84		0.44	14.73	0.47	1.64	0.05	2.01	4.88	2.77		0.18	100	96.97
<i>σ</i>			<i>0.93</i>		<i>0.07</i>	<i>0.34</i>	<i>0.11</i>	<i>0.25</i>	<i>0.02</i>	<i>0.28</i>	<i>0.16</i>	<i>0.16</i>		<i>0.03</i>		

¹ Data has been normalized to 100% and the analytical total are presented for each sample. Oxidized reported as wt. %. Glass shards were analyzed on a Cameca SX100 with four WDS spectrometers an accelerating voltage of 15 kV and a probe current of 10 nA and a beam diameter of 20 microns were used. Count times = 20s except S = 30s, Cl = 40 and F = 60. Analytical precision from microprobe analyses is calculated by the standard deviation of replicate analyses of secondary standard VG568, are as follows (in wt.%): P₂O₅ ± 0.01, SiO₂ ± 0.23, SO₂ ± 0.01, TiO₂ ± 0.02, Al₂O₃ ± 0.08, MgO ± 0.01, CaO ± 0.01, MnO ± 0.02, FeO ± 0.06, Na₂O ± 0.23, K₂O ± 0.06, F ± 0.08, Cl ± 0.01.

² Number of analyses.

³ FeO total.

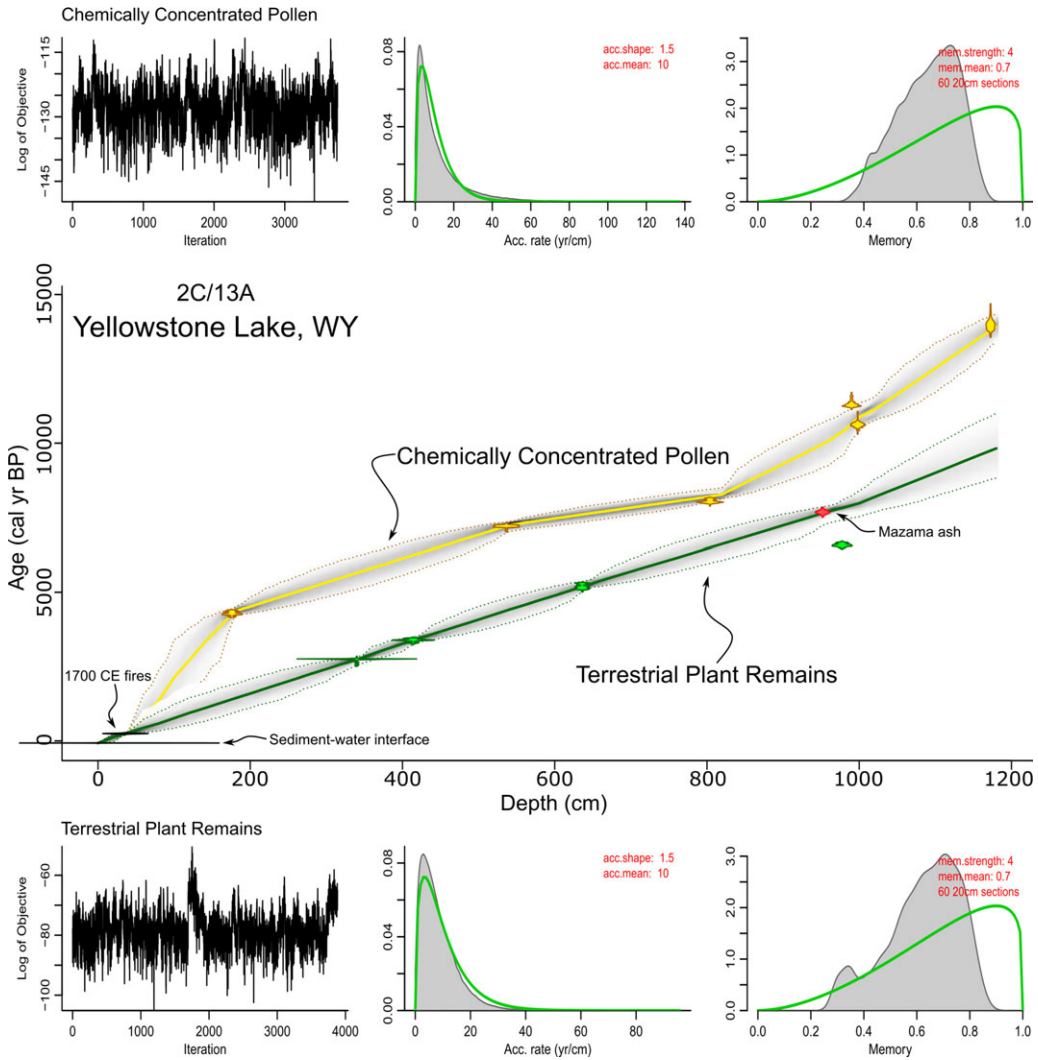


Figure 3 Bacon age-depth models for Yellowstone Lake (core 2C) derived from chemically concentrated pollen (yellow), terrestrial plant remains (green), the Mazama ash (red), and calendar ages of the coring date and a fire at 1700 CE.

Paired bulk-sediment and picked-pollen sample ages were calibrated utilizing Intcal13 (Reimer et al. 2013) and plotted with CALIB (version 7.1, Stuiver et al. 2019, Figure 4). Bulk-sediment ages were 4600 and 6000 cal years too old ($F^{14}C$ 0.6017 ± 0.0019 and 0.5203 ± 0.0017) at the sediment-water interface and 5300 and 5400 cal years too old directly above Mazama ash ($F^{14}C$ 0.2524 ± 0.0016 and 0.2497 ± 0.0016). Picked-pollen samples offered an improvement, with ages that were 1900 and 2400 cal years too old at the sediment-water interface ($F^{14}C$ 0.7885 ± 0.0109 and 0.7505 ± 0.0164). Directly above the Mazama ash, the picked pollen age from 2C/13A (OS-142018) was 4300 cal years too old directly above the Mazama ash ($F^{14}C$ 0.2793 ± 0.0059), while the age from 5A/9A (OS-142221) was 1300 cal years too young ($F^{14}C$ 0.5021 ± 0.0083). The lower precision and resultant posterior distributions of

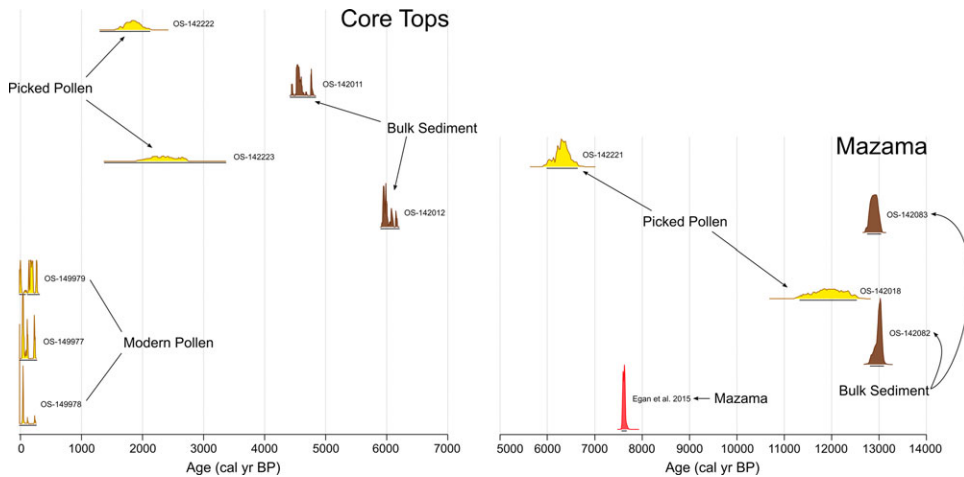


Figure 4 Probability density plots of dates from multiple materials at depths with known ages. Core top ages should be the approximate year of coring or pollen cone collection, -67 and -68 cal BP, respectively. The Mazama samples were collected immediately above the Mazama ash, which was deposited at 7682 – 7584 cal BP ($2\text{-}\sigma$ range, Egan et al. 2015). All ages from Yellowstone Lake cores, except OS-142221, are erroneously old by thousands of years. Picked-pollen ages have wide age distributions owing to small sample sizes.

picked-pollen ages were much wider than bulk-sediment ages, and understandably so, due to the larger uncertainties involved with small mass sample analysis.

Radiocarbon results from modern pollen from the Riddle Lake Trailhead, Cub Creek Pond, and Mud Volcano demonstrate virtually modern $F^{14}C$ values of 0.9903 ± 0.0019 , 0.9940 ± 0.0022 , and 0.9790 ± 0.0025 , respectively (Figure 4). These $F^{14}C$ values were calibrated utilizing CALIBomb (Reimer and Reimer 2004, Figure 4) with the NHZ1 post-bomb calibration (Hua et al. 2013) and IntCal13 pre-bomb calibration (Reimer et al. 2013).

$\delta^{13}C$ Results

Where samples were large enough, a split of CO_2 from combusted samples was analyzed for $\delta^{13}C$ as well as for radiocarbon, and the results were compared with existing $\delta^{13}C$ values obtained in earlier studies (Figure 5). Bulk sediments had less depleted $\delta^{13}C$ values than terrestrial plant remains, indicative of a non-terrestrial plant carbon source in the sediment. With the exception of one outlier, $\delta^{13}C$ values from terrestrial plant remains fell within the accepted range for terrestrial C_3 plants (Smith and Epstein 1971). Chemically concentrated pollen $\delta^{13}C$ values were widely variable, however, with one outlier nearly at 0 ‰ VPDB. All $\delta^{13}C$ values from sediment core samples were less depleted than those from modern pollen cones, which were -31.0 ‰ VPDB on average. $\delta^{13}C$ values did also vary somewhat from site to site, but with no apparent spatial pattern (Figure 5). Cub Creek Pond samples had the least depleted values (average -20.8 ‰ VPDB), with slightly more depleted values from 5A/9A (average -20.8 ‰ VPDB), Hedrick Pond (located 60 km south of Yellowstone Lake, $43.754^\circ N$, $110.590^\circ W$, elev. 2055 m.a.s.l.; average -25.8 ‰ VPDB), and 2C/13A (average -27.2 ‰ VPDB).

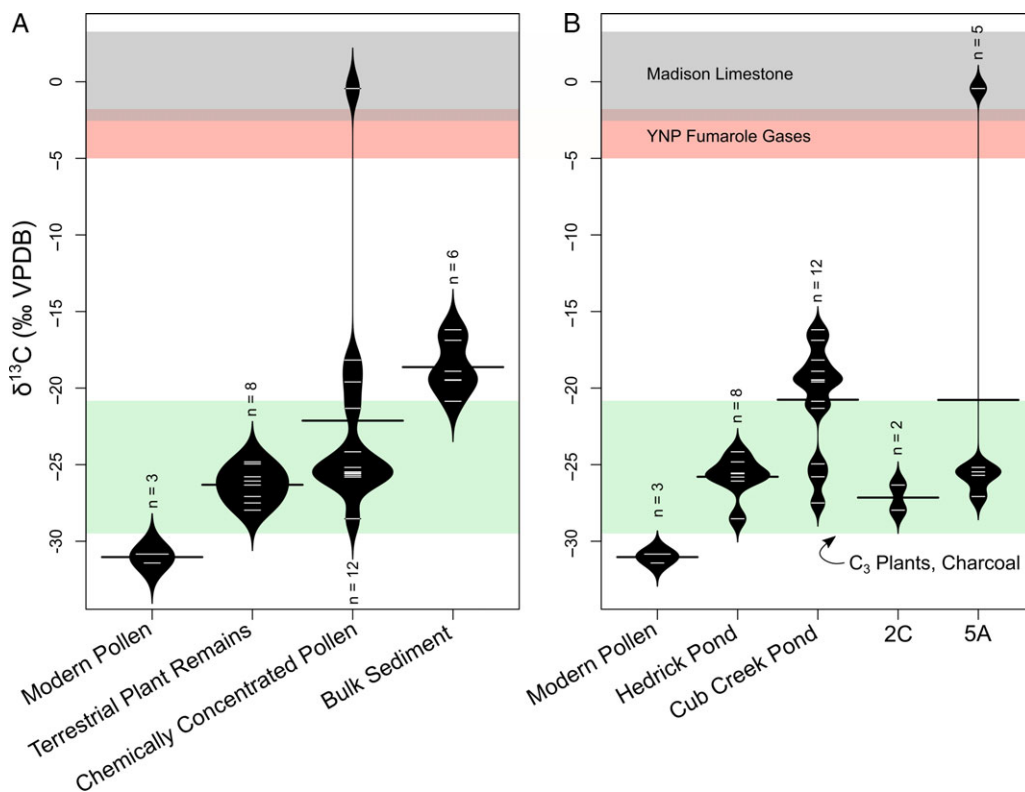


Figure 5 $\delta^{13}\text{C}$ values of radiocarbon materials are plotted using beanplot (Kampstra 2008) by material (A) and by site (B). C_3 plant and charcoal ranges are given by Smith and Epstein (1971). n is the number of samples included in each distribution. Yellowstone National Park (YNP) fumarole gas range taken from Craig (1963) and Werner and Brantley (2003) with Mississippian Madison Limestone range taken from Friedman (1970). Data from Hedrick Pond and Cub Creek Pond from Lu et al. (2017). Chemically concentrated pollen has a wide range of $\delta^{13}\text{C}$ values and the majority of least negative values come from areas near hydrothermal areas (Cub Creek Pond and Yellowstone Lake).

DISCUSSION

Comparison of Radiocarbon Ages from Yellowstone Lake

In Yellowstone Lake, ages from chemically concentrated pollen were systematically and erroneously old, compared with ages established from terrestrial plant remains, tephrochronology, or the date of the sediment-surface interface (Figure 4). Chemically concentrated pollen ages from core 2C/13A were systematically older than terrestrial plant remains ages by up to 4300 cal years and disagree with the established age of the Mazama ash (7682–7584 cal BP, 2- σ range; Egan et al. 2015) by 2300 cal years. Ages from strata of known age corroborate this finding, as picked Pinaceae pollen ages offered an improvement on bulk-sediment ages, but resultant ages remained too old by 1900 to 4300 cal years. These results are consistent with previous efforts at dating bulk sediments from Yellowstone Lake (Figure 2; Table 1) and bulk sediment and pollen concentrates from Cub Creek Pond (Whitlock 1993; Lu et al. 2017). Ages from living *Pinus contorta* pollen are virtually modern by comparison (in equilibrium with atmospheric CO_2).

Carbon Source of Yellowstone Terrestrial Pollen

Previous studies (referenced below) have reported erroneously old pollen ages in sediment cores and attributed the introduction of old carbon to (1) laboratory processes; (2) incomplete removal of non-pollen materials during concentration procedures; (3) reworked pollen; and/or (4) enrichment of old CO₂ in source material. The likelihood of these explanations is explored below.

First, accidental contamination is a major concern in laboratories that prepare samples for AMS radiocarbon dating. Most laboratories contain potential sources of old carbon including sodium bicarbonate (NaHCO₃) and petrochemicals. NaHCO₃ is found in most pollen preparation fume hoods to neutralize surfaces exposed to caustic acids; however, it was not actively used in the fume hood during these analyses and would have been removed through subsequent acidification. Petrochemicals were not used as reagents in the pollen preparation laboratory. Definitively, additional studies that used the same pollen preparation environment and procedure have not reported difficulty with old ages from chemically concentrated pollen (Krause and Whitlock 2013; Krause et al. 2015; Nanavati et al. 2019), making systematic laboratory contamination from old carbon or fractionation unlikely sources of error.

Second, old-carbon contamination from incomplete removal of non-pollen materials is commonly cited as an issue in procedures for concentrating pollen (Regnéll 1992; Richardson and Hall 1994), and sedimentological sources of old carbon exist in the vicinity. The Mississippian Madison Limestone, which is exposed in northern Yellowstone National Park outside the caldera, produces near-zero δ¹³C values (Figure 5; Friedman 1970), but does not crop out near or upstream of Yellowstone Lake nor does any other significant carbonate formation (U.S. Geological Survey 1972). Moreover, lake waters are relatively depleted in dissolved carbonate (<0.8 mM ΣCO₂, Balistrieri et al. 2007). Lake sediments themselves are not reported to contain carbonate mud (e.g. Tiller 1995), contain < 1 wt% CaO (Shanks et al. 2007), and do not effervesce when submerged in hot 2.7N HCl. Also, acidification treatments would remove most carbonates. Although our samples had no bituminous odor, we acknowledge that thermogenic hydrocarbons are found in several subaerial thermal areas of Yellowstone National Park (Love and Good 1970; Clifton et al. 1990) and probably occur in hydrothermally altered sediments of Yellowstone Lake (Shanks et al. 2007). Core 2C/13A is not located near known hydrothermal vents (Figure 1); however, hydrocarbon contamination remains possible in core 5A/9A. Importantly, pollen ages remained erroneously old (with the exception of OS-142221) regardless of increasingly thorough concentration procedures through Schulze treatment and manual picking. Although chemically concentrated pollen ages were unilaterally more accurate than bulk-sediment ages, suggesting concentration procedures removed some old carbon, the calibrated ages of chemically concentrated and picked pollen were similar. The manually picked pollen probably produces the purest pollen sample currently possible, so erroneous ages in these samples probably reflect the age of the pollen grains with minimal sediment contaminants. Examination of picked pollen concentrates under a transmitted light microscope at 400× magnification confirmed the general absence of sediment contaminants. Remaining contaminant particles would have been too small to be detected under the stereomicroscope and insoluble in our chemical treatments.

Third, reworked pollen is suggested as a major source of old-carbon contamination in lacustrine settings where extensive old lacustrine deposits occur at the surface (Mensing and Southon 1999; Zimmerman et al. 2019) or redeposition occurs from glacial melt (Neulieb et al. 2013; Zhang et al. 2017). There is no evidence of a Holocene glacial meltwater source in the Yellowstone Lake watershed. Given the size of the Yellowstone depositional basin and the preponderance of pollen types that are produced in great abundance and distributed widely (e.g. *Pinus*, *Artemisia*), a hypothetical ancient pollen source would need to be very large. Most unconsolidated surficial sediments were removed from the basin during repeated glacial episodes (Licciardi and Pierce 2018). Remaining exposures of ancient lake sediments occur upstream (Baker 1986) and downstream (Love et al. 2007) but are patchy and very small. Ancient shoreline facies also occur north of Yellowstone Lake (Pierce et al. 2007), but are situated upstream of the lake, probably too small to be the source area, and the coarse gravels and shallow-water depositional environments are not a good pollen preservation environment. Furthermore, pollen grains subjected to reworking should be observably broken and degraded under the light microscope (Tweddle and Edwards 2010; Howarth et al. 2013), but pollen preservation was generally excellent in Yellowstone Lake, as we observed that <1% of the pollen grains were unidentifiable and >50% of *Pinus* pollen had intact, distal membranes that allowed assignment to the subgeneric level under 400× magnification. Finally, dated terrestrial plant remains were clearly not out-of-sequence, and Holocene pollen spectra, dominated throughout core 2C by *Pinus* (>55%, <79%), are consistent with data from nearby sites within *Pinus contorta* forest (e.g., Baker 1976; Whitlock 1993; Whitlock et al. 1995; Theriot et al. 2006), further evidence against a significant component of reworked pollen.

Fourth, CO₂ vented from the Yellowstone Caldera is a somewhat unique source of old carbon in this region. Yellowstone Lake vents comprise a very active thermal area and account for an estimated 10% of the thermal water flux in Yellowstone National Park (Balistrieri et al. 2007); in addition, a small, subaerial thermal area exists upslope of Cub Creek Pond (Vaughan et al. 2014). These areas potentially constitute a large source of old-carbon flux, although no estimates exist for the hydrothermal carbon budget of Yellowstone Lake, and the Cub Creek Thermal Area is of unknown chemistry and considered potentially inactive (Vaughan et al. 2014). $\delta^{13}\text{C}$ values of pollen from Yellowstone Lake and nearby Cub Creek Pond (Lu et al. 2017) suggest an admixture of sources with less depleted $\delta^{13}\text{C}$ values than are typical for C₃ plants (Figure 5). Locally, fumarole gases produce the opposite end member of this admixture (Craig 1963; Werner and Brantley 2003). Large volumes of CO₂ are degassed from magmatic and pre-Tertiary basement sources at present, with daily, caldera-wide degassing estimated at 45 (\pm 16) kt primarily from acid-sulfate hydrothermal features (Werner and Brantley 2003). Uptake of volcanically derived old CO₂ has been inferred elsewhere. For example, lake-sediment cores from volcanic lakes in Anatolia with bulk-sediment ages document reservoir effects of up to 14,000 years (Roberts et al., 2001; Jones 2004). In other settings, uptake of old CO₂ through photosynthesis has been inferred in living plant tissue at sites near hydrothermal vents (Pasquier-Cardin et al. 1999; Cook et al. 2001; Evans et al. 2010; Lewicki and Hilley 2014) and industrial areas (Baydoun et al., 2015), but generally do not occur more than 1 km away from the old-carbon source (Pasquier-Cardin et al. 1999; Evans et al. 2010; Baydoun et al. 2015). This observation is consistent with dates from modern pollen near Yellowstone Lake (Figure 4), which suggest minimal uptake of volcanic CO₂ through photosynthesis.

Potential sources for old-carbon contamination are narrowed by the fact that cone pollen collected in 2018 has the same $F^{14}C$ as atmosphere and picked pollen from core tops is erroneously old. This limits the potential place of contamination to the water column or surficial lake sediments. However, it is unclear how hydrothermal carbon could be incorporated into pollen grains in either context, given that sporopollenins, which compose the chemically resistant coating of the pollen exine (outer wall), are "... probably the most resistant organic materials of direct biological origin found in nature..." (Brooks and Shaw 1978). This hypothesis is also unsatisfactory given that old-carbon contamination of organic compounds by hydrothermal carbon apparently did not impact other terrestrial plant remains in the sediments.

CONCLUSIONS

Pollen concentrate ages are systematically older than terrestrial plant remains ages in Yellowstone Lake by 1700 to 4300 cal years and we can offer no clear explanation for this puzzlement. The most likely sources of old carbon are (1) CO_2 degassing from magmatic and pre-Tertiary basement sources, which may be incorporated into pollen grains in the water column or in surficial sediments; or (2) reworked pollen from older sediments. Neither explanation is fully adequate. In our consideration, further study of the radiocarbon signature of modern pollen from its production to its release, transport, deposition, and final burial in lake sediments is required to locate the source of old-carbon contamination. Such an investigation should include radiocarbon dating of modern pollen from the cone, pollen intercepted from the local atmosphere, pollen in the water column and carbon isotope analysis of the DOC in lake water. Experiments may be also employed in the laboratory to explore the possibility of incorporation of old carbon from artificially sourced CO_2 into pollen grains in an aqueous mixture. Future experiments may also examine the impact of individual steps in pollen concentration procedures for carbon contamination, obtain ^{14}C -free pollen concentrates as a more representative blank material, and utilize SEM microscopy to detect remaining contaminants associated with pollen grains.

With the current problem of old radiocarbon ages from pollen concentrates and the lack of other suitable materials for radiocarbon dating, we continue to be limited in our ability to produce quality age control for paleoenvironmental and geological reconstructions from Yellowstone Lake, Cub Creek Pond, and potentially other sites in the Yellowstone Caldera (e.g. Lewis Lake, glacial Yellowstone Lake). Current results underscore the necessity of careful consideration of carbon source—even in terrestrial plant remains and pollen concentrates—where reworked sediments or old-carbon degassing are possible.

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