

A 12.8 ka microspherule and nanoparticle marker horizon in stratified Paleoamerican deposits at Smith Mountain Lake (44PY152), USA

Christopher R. Moore^{1,2,*}, Joseph A. M. Gingerich³, William A. Childress⁴, Malcolm A. LeCompte⁵, Allen West⁶, Mohammed Baalousha⁷, Michael Bizimis⁸, Terry A. Ferguson⁹, Siddhartha Mitra¹⁰, Chad S. Lane¹¹, Theodore R. Them II¹², M. Scott Harris¹², Victor Adediji¹³, Kurt A. Langworthy¹⁴, Mahbub Alam⁷, Paul A. Schroeder¹⁵, Aaron Thompson¹⁶, Jordan Jeffreys¹⁷ and Marc J. Defant¹⁸

¹South Carolina Institute of Archaeology and Anthropology, University of South Carolina, 1321 Pendleton Street, Columbia, SC 29208, USA 

²SCDNR Heritage Trust Program, Land, Water, and Conservation Division, South Carolina Department of Natural Resources, PO Box 167, Columbia, SC 29202, USA 

³Department of Sociology and Anthropology, Ohio University, 153 Bentley Annex, Athens, OH 45701, USA 

⁴Smith Mountain Gap Archeology (SMGA), 2657 Screechum Hollow Road, Bedford, VA 24523, USA

⁵Center of Excellence in Remote Sensing Education and Research, Elizabeth City State University, Elizabeth City, NC 27921, USA 

⁶Comet Research Group, Prescott, AZ, USA

⁷Center for Environmental Nanoscience and Risk (CENR), Department of Environmental Health Sciences, Arnold School of Public Health, University of South Carolina, Columbia, 29208, USA 

⁸Center for Elemental Mass Spectrometry Laboratory, School of Earth, Ocean and Environment, University of South Carolina, Columbia, SC 29208, USA 

⁹Department of Environmental Studies, Wofford College (ret.), Spartanburg, SC, USA 

¹⁰Virginia Institute of Marine Science, Gloucester Point, VA 23062, USA 

¹¹Department of Earth and Ocean Sciences, University of North Carolina Wilmington, Wilmington, NC 28411, USA 

¹²Department of Geology and Environmental Sciences, College of Charleston, Charleston, SC 29424, USA 

¹³Department of Natural Sciences, Elizabeth City State University, Elizabeth City, NC 27909, USA 

¹⁴CAMCOR, University of Oregon, 1443 E 13th Ave, Eugene, OR 97403, USA 

¹⁵University of Georgia, Department of Geology, Athens, GA 30602-2501, USA 

¹⁶University of Georgia, Department of Crop and Soil Science, Athens, GA 30602-2501, USA 

¹⁷School of Earth, Ocean, and Environment, University of South Carolina, 701 Sumter Street, EWS 617, Columbia, SC 29208, USA 

¹⁸School of Geosciences, University of South Florida, Tampa, FL 33620, USA 

*Corresponding author's e-mail address: MOORECR@mailbox.sc.edu

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ABSTRACT

Geoarchaeological investigations at site 44PY152 near Smith Mountain Lake, Virginia, document stratified Late Pleistocene–Early Holocene archaeological occupations preserved within ~1.7 m of floodplain alluvium. These deposits contain both in situ and eroding fluted Paleoamerican and Early Archaic projectile points. Here, we analyze a contiguous, high-resolution sedimentary sequence to evaluate the presence and stratigraphic integrity of microspherule and platinum-group element (PGE) anomalies associated with the onset of the Younger Dryas (YD). Analyses include Bayesian radiocarbon modeling, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDS), single-particle inductively coupled plasma time-of-flight mass spectrometry

(SP-ICP-TOF-MS), laser ablation ICP-MS (LA-ICP-MS), laser granulometry, bulk organic carbon and nitrogen, soot carbon, stable carbon isotopes ($\delta^{13}\text{C}_{\text{OC}}$ and $\delta^{13}\text{C}_{\text{soot}}$), magnetic susceptibility, and mercury (Hg). Results reveal a narrow microspherule-rich interval centered within the 14–15 cmbd sample that is accompanied by pronounced PGE mass anomalies consistent with proxy assemblages reported near the Younger Dryas Boundary at multiple sites worldwide. Bayesian age modeling places this interval within the broader temporal range of the Younger Dryas onset, although the modeled age uncertainty exceeds the narrower age range proposed by Kennett et al. [1]. Chondrite-normalized elemental systematics indicate selective Pt-centered enrichment decoupled from comparatively conservative rare earth element behavior, arguing against simple sedimentological concentration processes. The stratigraphic position and internal coherence of this proxy suite identify a discrete marker horizon consistent with the onset of the Younger Dryas at 44PY152. Subtle excursions in $\delta^{13}\text{C}_{\text{soot}}$ and Hg immediately above this interval may reflect associated environmental variability during the early Younger Dryas. Regardless of formation mechanism, the microspherule–PGE horizon provides a high-resolution stratigraphic marker confined to a 1-cm interval that may aid correlation and interpretation of pre- and post-12.8 ka archaeological sequences at stratified sites lacking abundant chronometric control.

INTRODUCTION AND BACKGROUND

Study site

Smith Mountain Lake is a large hydropower reservoir located in the southwestern Piedmont of Virginia southeast of Roanoke (Figure 1), where the Roanoke River creates a prominent landmark gap as it traverses one of the larger foothill landforms east of the Blue Ridge. The Smith Mountain Gap (SMG) Paleoamerican complex is represented by a cluster of deeply stratified sites associated with the Roanoke River's natural levee system below the dam constructed at the gap. Leesville Lake, a pump storage impoundment for the hydro project,

frequently inundates the sites as hydro releases impact the Holocene levee during power generation. Buried early sites, originally located on a relict Pleistocene strand line likely extending at least to the Pigg River outlet ~6 km downstream, are intermittently exposed by erosion on the foreshore and backshore of alluvial Pleistocene landform remnants beneath the modern levee. Some of these sediments have been dated as early as ~28,000 cal BP [2].

Since 1988, Archaeological Society of Virginia (ASV) survey and monitoring have recorded a total of 14 Early Archaic/Paleoamerican site locales on both sides of the lake and have

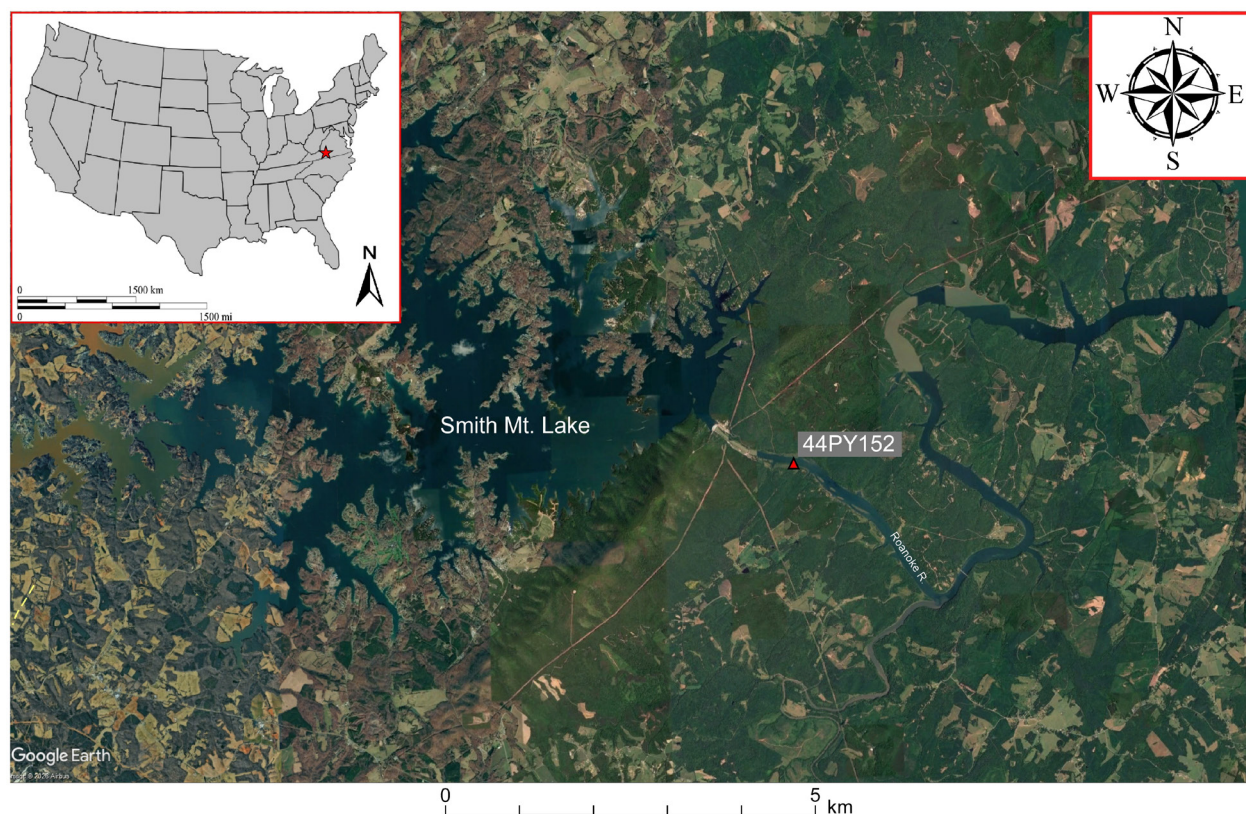


Figure 1. Location of the study site 44PY152 (37° 1'59.96" N; 79°30'59.11" W) in the Roanoke River alluvial terrace below the Smith Mountain Lake dam in the southwestern Piedmont of Virginia. Image: Google Earth, 2025 Airbus. Map inserts were created using ArcGIS (v. 10.4.1), and Canvas 11 (Build 1252) software. A red star symbol on the US map inset shows the approximate location of the site in Virginia.

documented more than 700 diagnostics from cultural horizons prior to circa 8,000 C¹⁴ yrs. BP. Over 15% of these diagnostics are contained within assemblages dating earlier than 10,000 C¹⁴ yrs. BP, which includes all known Paleoamerican projectile point types for the region including possible pre-Clovis unfluted early triangular lanceolate (ETL) forms [3]. Excavations at 44PY152 (N 37° 1'59.96"; W 79° 30'59.11"), the largest site in the complex, reveal the most complete picture of the late Pleistocene-Early Holocene occupation of the upper Roanoke drainage. Extensive erosion from dam releases has

scoured the upper ~1.7 meters of sediment along the shoreline, leaving a thin wedge of intact sediments containing Early Archaic and Paleoamerican components (Figure 2). In addition to artifacts recovered during controlled excavations, many artifacts are documented during systematic surveys of the eroding terrace while still embedded within the enclosing sediment matrix, allowing their stratigraphic positions to be recorded despite ongoing erosion.

The William & Mary Center for Archaeological Research (WMCAR) initiated Phase II investigations in 1994 following



Figure 2. View of site 44PY152 along the eroded Roanoke River floodplain terrace. Water releases from the Smith Mountain Lake dam have caused significant erosion of the floodplain deposits, removing as much as ~1.7 m of sediment in some areas and exposing buried Paleoamerican and Early Archaic archaeological materials.

ASV auger tests, which probed buried cultural horizons as deep as 2.5 meters below the levee surface. Exotic lithic materials recovered in the lower levels combined with diagnostics previously recovered on the beach suggested a Paleoamerican occupation [4].

Continued ASV monitoring at 44PY152 following WMAR's investigations confirmed the presence of at least two Clovis occupation clusters identified by two exotic Mississippian chert types probably brought into the region from Kentucky. One of these clusters yielded a Paoli chert Clovis assemblage, including three Clovis points and uniface tools of a blade-like technology that is seldom reported in Virginia. Most of the tools in this cluster were recovered within an area of about 4 meters in diameter, suggesting a single occupation event. By 2005, at least eight fluted points had been recovered at 44PY152 co-occurring with ETL, Dalton, Hardaway Side-Notched, Plano, Palmer, and Kirk Points [3,5].

Stratified early Paleoamerican through Early Archaic components at 44PY152 bracket the onset of the Younger Dryas (YD) climate event (ca. 12,875–12,775 cal BP; IntCal20) [1,6]. Chronologically, the lower YD boundary (YDB) represents the approximate end of the Clovis technocomplex in North America (13,050–12,750 cal BP) [7]. Proxy assemblages reported near the YDB in multiple sedimentary sequences [8–15] have been proposed as useful stratigraphic markers for inferring this boundary, even where chronometric dating or temporally diagnostic artifacts are sparse [16–18]. In this study, these proxies are evaluated primarily as stratigraphic markers within a buried archaeological sequence, not as stand-alone evidence of an impact origin. Establishing a robust chronostratigraphic framework for these deposits therefore requires evaluation of independent proxy evidence for the onset of the Younger Dryas.

Platinum and microspherule anomalies

In 2013, Petaev et al. [19] reported a ~21-year platinum (Pt) anomaly in Greenland Ice Sheet Project 2 (GISP2) ice core layers dated to ~12,800 years BP at the onset of the Younger Dryas, with average concentrations of ~30 ppt and a peak of ~80 ppt. This Pt anomaly has since been widely treated as a chronostratigraphic marker of the Younger Dryas Boundary (YDB), consistent with numerous terrestrial sedimentary sequences that exhibit anomalous Pt enrichment at the same approximate age [13,14,16–18,20]. Although Petaev et al. interpreted the Greenland signal as consistent with atmospheric deposition of Pt-rich dust, possibly including an extraterrestrial contribution, they noted that the precise source and mechanism remained uncertain.

The YD impact hypothesis has been debated extensively in the literature [21–24]. The present study does not attempt to resolve that broader debate, but instead evaluates whether microspherules and PGE-bearing nanoparticles form a stratigraphically coherent proxy assemblage that may provide a chronological marker for the YD onset within a deeply buried Paleoamerican archaeological sequence. Regardless of formation mechanism, documenting the stratigraphic distribution

and association of these proxies provides a basis for evaluating their utility as marker horizons within archaeological and sedimentary contexts.

Multiple studies [16–18,20] have documented a Younger-Dryas-onset-age Pt anomaly in sedimentary sequences across North America. Recent studies at the Wakulla Springs Lodge site (8WA329) near Tallahassee, Florida [20] and multiple sites along the Eastern Seaboard of the United States [17] have further demonstrated the utility of Pt anomalies, together with discrete peaks in the abundance of iron-rich and glassy microspherules, as chronostratigraphic markers for identifying the onset of Younger Dryas climate change and inferring the relative age of culturally stratified Paleoamerican lithic artifacts.

This study analyzes a contiguous sedimentary sequence sampled at 1-cm intervals from archaeological excavations at site 44PY152 on the Roanoke River floodplain below the Smith Mountain Lake dam. These sediments bracket excavated Early Archaic (ca. 11,450–8,900 cal BP) and early Paleoamerican (~13,050–12,750 cal BP) occupations buried within ~1.7 m of floodplain alluvium. Sampling was intentionally focused on a high-resolution interval bracketing the onset of the Younger Dryas to test for the presence, stratigraphic coherence, and vertical concentration and confinement of microspherules and PGE anomalies.

Sediment samples (n = 27) were ultrasonicated, wet-sieved, dried, and analyzed by optical microscopy for Fe-rich and glassy microspherules. Subsamples were used for bulk accelerator mass spectrometry (AMS) dating and in situ charcoal dating, as well as for additional analyses including single-particle inductively coupled plasma time-of-flight mass spectrometry (SP-ICP-TOF-MS), laser granulometry, soot carbon, carbon and nitrogen isotopes, magnetic susceptibility, and mercury (Hg). Microspherule candidates were examined using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

In addition to platinum (Pt), the nanoparticle analysis focused on the total masses of twelve key elements (e.g., Cr, Fe, Co, Ni, Cu, Ru, Rh, Pd, Hf, Os, and Ir) that are commonly enriched in extraterrestrial materials and have previously been reported as elevated in YD-age archaeological sites, ice cores, and marine or lacustrine sedimentary archives [8,9,12,15–19,25,26]. Organic carbon (OC), total nitrogen (TN) abundance, and isotopes were determined using bulk sediments. Similarly, soot was isolated from subsamples of bulk sediment using a chemothermal oxidation technique (CTO-375) [27]. In addition to OC and TN isotopes, mercury (Hg) concentrations were examined to evaluate whether independent environmental changes are detectable near the same stratigraphic interval as the microspherule and PGE anomalies.

RESULTS

Radiocarbon dating and Bayesian age-depth model

We performed a Bayesian analysis using OxCal v4.4.4, r:5 [28] and the IntCal20 calibration curve (Tables 1 and 2,

Table 1: Accelerator Mass Spectrometry (AMS) dates for 44PY152 used in this study.

Method	Material	Unit	Sediment column depth (cmd) ^a	Elevation	Lab#	RCYBP	error	Cal. BP (2-sigma) ^b
AMS	Charcoal	N98 W25	—	497.452	Beta-456850	8209	24	9,305–9,018 (99.3%)
AMS	Charcoal	N97 W24	~2–3	497.362	UGA-69329	8,930	30	10,225–9,895 (99.7%)
AMS	Charcoal	N99 W32	~5–6	497.338	Beta-624542	10,300	40	12,280–11,823 (80.1%)
AMS	GLC ^c	N98 W24	11–12	497.265–497.275	221026c-2	10,690	110	13,005–12,096 (99.6%)
AMS	Sediment	N98 W24	14–15	497.235–497.245	UGA-64265	10,650	30	12,735–12,611 (98.4%)
AMS	Charcoal	N98 W21	~16–17	497.22	Beta-661185	11,310	40	13,314–13,097 (99.7%)

^aCentimeters below datum (cmbd).^bCalibrations were done with IntCal20 [6].^cGlass-like carbon.

Figure 3, Supplementary Information “Bayesian Coding,” and Supplementary Table S1). AMS radiocarbon dates on charcoal, glass-like carbon (GLC; e.g., carbonized and indurated tree sap), and bulk sediment were incorporated into the Bayesian age–depth model, along with the accepted age range for Early Archaic “Palmer” diagnostic artifacts (ca. 9900–9000 RCYBP) [29] recovered in situ from the site. Because these dated materials differ in depositional and taphonomic behavior, they are not equally diagnostic of primary depositional age and should not be interpreted as chronologically equivalent. In particular, the bulk-sediment determination may reflect averaged or mobile organic carbon rather than a discrete depositional event. The proxy horizon is directly associated with a radiocarbon determination from the same 1-cm interval; however, because this date is derived from bulk sediment, it is treated as supporting rather than definitive depositional age control. In addition, post-depositional mobility of younger organic carbon within floodplain sediments can cause bulk-sediment AMS determinations to appear younger than the original depositional event represented by the enclosing sediment. Accordingly, the Bayesian model is used here to integrate all available chronological constraints and estimate the most probable age–depth relationships within the sampled interval; however, its output should be interpreted cautiously and evaluated against independent archaeological and stratigraphic evidence.

The platinum (Pt) anomaly first identified in Greenland ice by Petaev et al. [19] and subsequently reported from multiple well-dated terrestrial sedimentary YDB sequences [13,14,16–18,20] provides an externally established chronological benchmark for the Younger Dryas onset that is used here for comparison only. This inferred Pt anomaly age range is not used as an input constraint in the Bayesian calculations. Instead, the modeled age–depth relationship at 44PY152 is compared with this published Younger Dryas onset age range [1] to assess whether the observed stratigraphic position of the Pt, microspherule, and nanoparticle anomaly is chronologically consistent with it. Bayesian interpolated ages were calculated at 0.5 cm intervals between elevations of 497.452 and 497.220 meters below datum (mbd), with modeled ages ranging between ca. 9,000 and 13,400 cal BP. These values represent model-derived interpolations rather than independently dated stratigraphic horizons. The model incorporates archaeological

and stratigraphic priors to estimate age–depth relationships within the sampled interval; however, because the dated section is vertically compressed and constrained by a small number of dates, the resulting interpolation should be treated as an aid to stratigraphic interpretation rather than as a source of high-resolution, centimeter-scale chronological precision.

Soils and granulometry

Sediment samples from N98 W24 are composed of 75–80% silt and clay and 20–25% sand, with virtually nothing coarser than medium sand (see Supplementary Figures S33–S36 and Supplementary Table S2). Soils from the area sampled by our sediment column are characterized as a 4Btb horizon, which is a 7.5YR 4/6 Strong Brown clay loam. The 4Btb horizon is overlain by a 4ABtb horizon that begins near the top of our sediment column (~4.397 m below datum [bd]) and, based on the Bayesian model and other chronological constraints, is Early Holocene/Early Archaic in age. This heavy loam to clay loam 4ABtb horizon shows a decrease in sand and a slight increase in silt relative to sedimentation documented during the late YD and Holocene transition [2,4].

Overall, the laser granulometry data within the sediment column indicate texturally distinct coarsening- and fining-upward sequences. These sequences are consistent with a compressed stratified sequence composed predominantly of silt with smaller amounts of sand and clay, likely derived from overbank flood events of varying magnitude and energy within the master 4Btb horizon (see Supplementary Figures S33–S36 and Supplementary Table S2). Within the sampled column, these data are interpreted as ~7 microstratigraphic sedimentological zones (I–VII) (Figure 4; Supplementary Figure S36). These zones indicate internal textural variability within the section, but they do not by themselves exclude some degree of post-depositional mixing or vertical translocation.

Bayesian age–depth modeling indicates that sediment stratigraphic Zones I and II ($z = \geq 497.115$ – 497.185 mbd) have a modeled age range of $\geq 13,385$ – $13,050$ cal BP at 94.5% probability; Zone III ($z = 497.185$ – 497.225 mbd) has a modeled age range of $\geq 12,954$ cal BP at 94.5% probability; Zone IV ($z = 497.225$ – 497.270 mbd) has a modeled age range of ca. 13,320–12,610 cal BP at 94.5% probability; Zone V ($z = 497.270$ – 497.325 mbd) has a modeled age range of ca. 13,115–12,028 cal BP at 94.5%

Table 2: Bayesian age-depth model interpolations at 0.5 cm intervals.

Elevation	Mu	Sigma	Years	Sed rate (cm/yr)	68.3% probability		95.4% probability		99.7% probability	
497.452	9230	100	15	0.033	9305	9100	9455	9035	9455	9015
497.450	9245	115	40	0.013	9345	9100	9492	9035	9501	9015
497.445	9285	150	35	0.014	9444	9100	9583	9034	9617	9015
497.440	9320	180	40	0.013	9544	9100	9675	9034	9733	9015
497.435	9360	215	35	0.014	9643	9100	9766	9033	9849	9015
497.430	9395	245	40	0.013	9743	9100	9858	9033	9965	9015
497.425	9435	280	40	0.013	9842	9100	9949	9032	10081	9015
497.420	9475	315	35	0.014	9941	9100	10040	9031	10197	9015
497.415	9510	345	40	0.013	10041	9100	10132	9031	10313	9015
497.410	9550	380	50	0.010	10140	9100	10223	9030	10429	9015
497.405	9600	375	60	0.008	10182	9156	10268	9087	10484	9066
497.400	9660	345	60	0.008	10185	9250	10282	9182	10500	9150
497.395	9720	315	55	0.009	10188	9343	10295	9277	10516	9234
497.390	9775	290	60	0.008	10192	9437	10309	9372	10532	9318
497.385	9835	260	60	0.008	10195	9530	10323	9468	10548	9403
497.380	9895	230	60	0.008	10198	9623	10336	9563	10563	9487
497.375	9955	200	55	0.009	10202	9717	10350	9658	10579	9571
497.370	10010	175	60	0.008	10205	9810	10363	9753	10595	9655
497.365	10070	145	210	0.002	10208	9904	10377	9848	10611	9739
497.360	10280	135	435	0.001	10398	10126	10569	10070	10807	9960
497.355	10715	150	435	0.001	10866	10540	11030	10484	11273	10385
497.350	11150	165	435	0.001	11335	10955	11490	10898	11740	10810
497.345	11585	180	435	0.001	11804	11370	11950	11311	12207	11235
497.340	12020	195	200	0.003	12273	11784	12411	11725	12673	11660
497.335	12220	195	40	0.013	12475	11982	12618	11922	12876	11850
497.330	12260	190	40	0.013	12499	12035	12656	11975	12902	11882
497.325	12300	185	45	0.011	12524	12088	12694	12028	12928	11915
497.320	12345	175	40	0.013	12549	12141	12733	12081	12954	11948
497.315	12385	170	40	0.013	12573	12194	12771	12134	12980	11981
497.310	12425	165	40	0.013	12598	12246	12809	12186	13006	12013
497.305	12465	160	45	0.011	12623	12299	12847	12239	13032	12046
497.300	12510	150	40	0.013	12647	12352	12886	12292	13058	12079
497.295	12550	145	40	0.013	12672	12405	12924	12345	13084	12111
497.290	12590	140	45	0.011	12696	12458	12962	12398	13111	12144
497.285	12635	135	40	0.013	12721	12511	13000	12451	13137	12177
497.280	12675	125	40	0.013	12746	12564	13039	12504	13163	12210
497.275	12715	120	40	0.013	12770	12617	13077	12557	13189	12242
497.270	12755	115	10	0.050	12795	12670	13115	12610	13215	12275
497.265	12765	115	5	0.100	12799	12673	13117	12619	13215	12336
497.260	12770	115	5	0.100	12803	12675	13118	12628	13215	12397
497.255	12775	115	10	0.050	12808	12678	13120	12638	13215	12458
497.250	12785	115	5	0.100	12812	12680	13122	12647	13215	12518
497.245	12790	115	5	0.100	12816	12683	13123	12656	13215	12579
497.240	12795	115	110	0.005	12820	12685	13125	12665	13215	12640
497.235	12905	105	105	0.005	12940	12796	13190	12761	13276	12743
497.230	13010	95	110	0.005	13060	12908	13255	12858	13338	12845
497.225	13120	90	105	0.005	13180	13019	13320	12954	13399	12948
497.220	13225	80	0	0.000	13300	13130	13385	13050	13460	13050
Holocene/Early Archaic					YD/Middle Paleoamerican					
YD/Late Paleoindian					YD onset					
					Late Pleistocene/Early Paleoamerican					

Note. “mu” is mean modeled age. The top of the sediment column (N98 W24) begins at an elevation of 497.385 meters below datum (mbd). YD = Younger Dryas.

probability; Zone VI ($z = 497.325\text{--}497.355$ mbd) has a modeled age range of ca. 12,694–10,484 cal BP at 94.5% probability; and Zone VII ($z = 497.355$ mbd and higher) has a modeled age range of 11,030–10,484 cal BP and younger at 94.5% probability (see Figure 4; Table 2; and Supplementary Figure S36).

Microspherules (MSps), metallic dust particles (MDPs), and authigenic grains

The analysis of contiguous (1 cm interval) sediment column samples from 44PY152 (N98 W24) revealed a pronounced abundance peak of Fe-rich dendritic microspherules

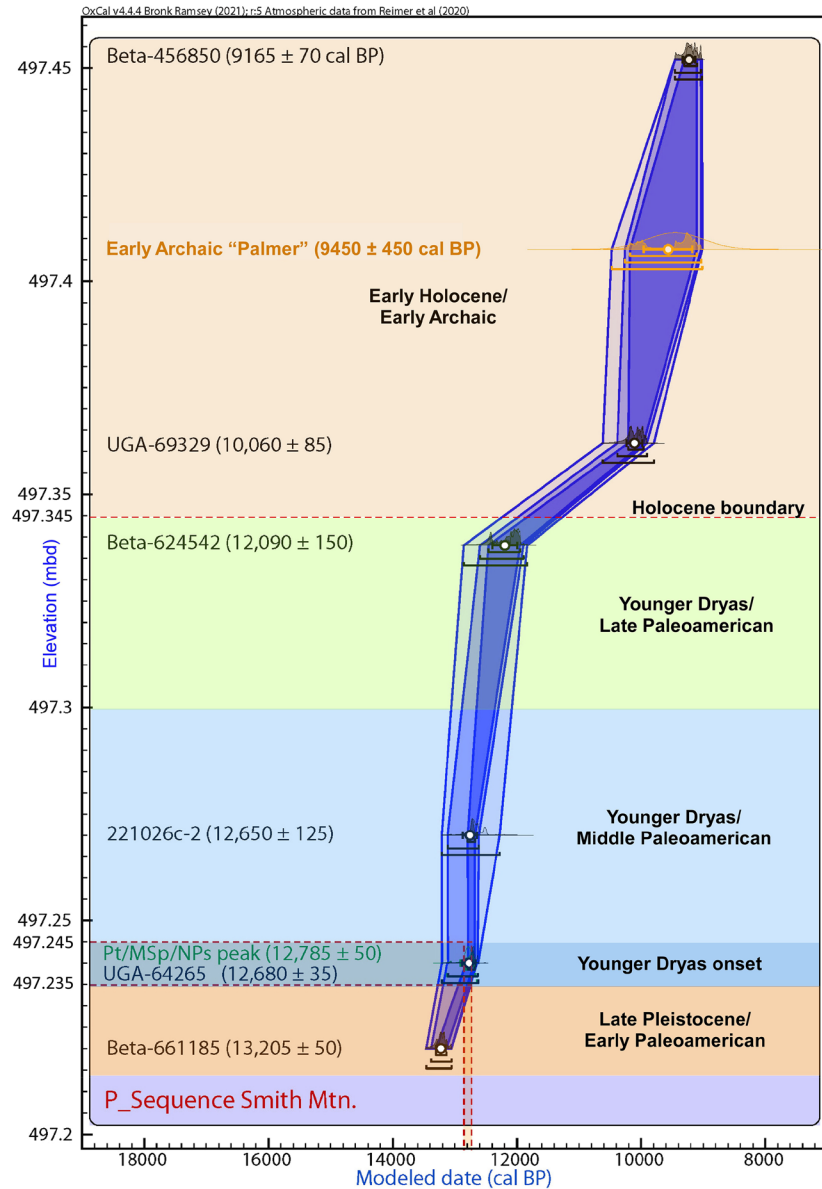


Figure 3. Bayesian age-depth model for 44PY152 (N98 W24). The model is based on six radiocarbon determinations (black text showing Bayesian modeled median ages; see Table 1 for unmodeled ages) and the estimated age range for the Early Archaic Palmer occupation (ca. 9900–9000 RCYBP) recovered in situ at the site (brown text) [29] (see Tables 1 and 2, Supplementary Information, “Bayesian Coding,” and Supplementary Table S1). Also shown for stratigraphic comparison is the inferred Younger Dryas Boundary (YDB) age range (green text) for the Pt, microspherule, and nanoparticle anomaly (Pt/Msp/NPs), based on the associated Pt proxy horizon reported in Greenland ice and multiple well-dated sedimentary sequences [1,16–20]. This comparison age range is $12,785 \pm 50$ cal BP (12,875–12,775 cal BP at 95.4% probability; updated to IntCal20) [1] and was not used in the Bayesian model calculations. Within this framework, the inferred position of the lower Younger Dryas Boundary (YDB) at 44PY152 falls between elevations of 497.235–497.245 meters below datum (mbd), and the modeled lower Holocene boundary begins at an elevation of 497.345 mbd. Bayesian age-depth modeling suggests an interval of comparatively increased alluvial sediment accumulation near the inferred onset of the YD. This interval spans elevations of 497.240–497.270 mbd and corresponds to a Bayesian modeled age range of ca. 13,125–12,610 cal BP at 94.5% probability.

(abundance extrapolated from sample as $\sim 440/\text{kg}$) centered in the 14–15 cmbd sample ($z = 497.235\text{--}497.245$ mbd), with a Bayesian modeled age of 13,190–12,656 cal BP at 94.5% probability (Tables 2 and 3). This microspherule peak begins abruptly and declines rapidly within a few centimeters above and below the central maximum. Examination of microspherule candidates with SEM (Figure 5) indicates that they are

Fe-rich and commonly exhibit dendritic surface textures indicative of melting and rapid cooling (see Supplementary Figures S1–S17 for EDS data). Most microspherules from 44PY152 range from $\sim 10\text{--}60\text{ }\mu\text{m}$ in diameter, with a few exceeding $300\text{ }\mu\text{m}$. In addition, Fe-rich metallic grains attached to some microspherules are highly oxygen-depleted (Figure 5C and M). Other microspherules are broken or perforated, indicating hollow

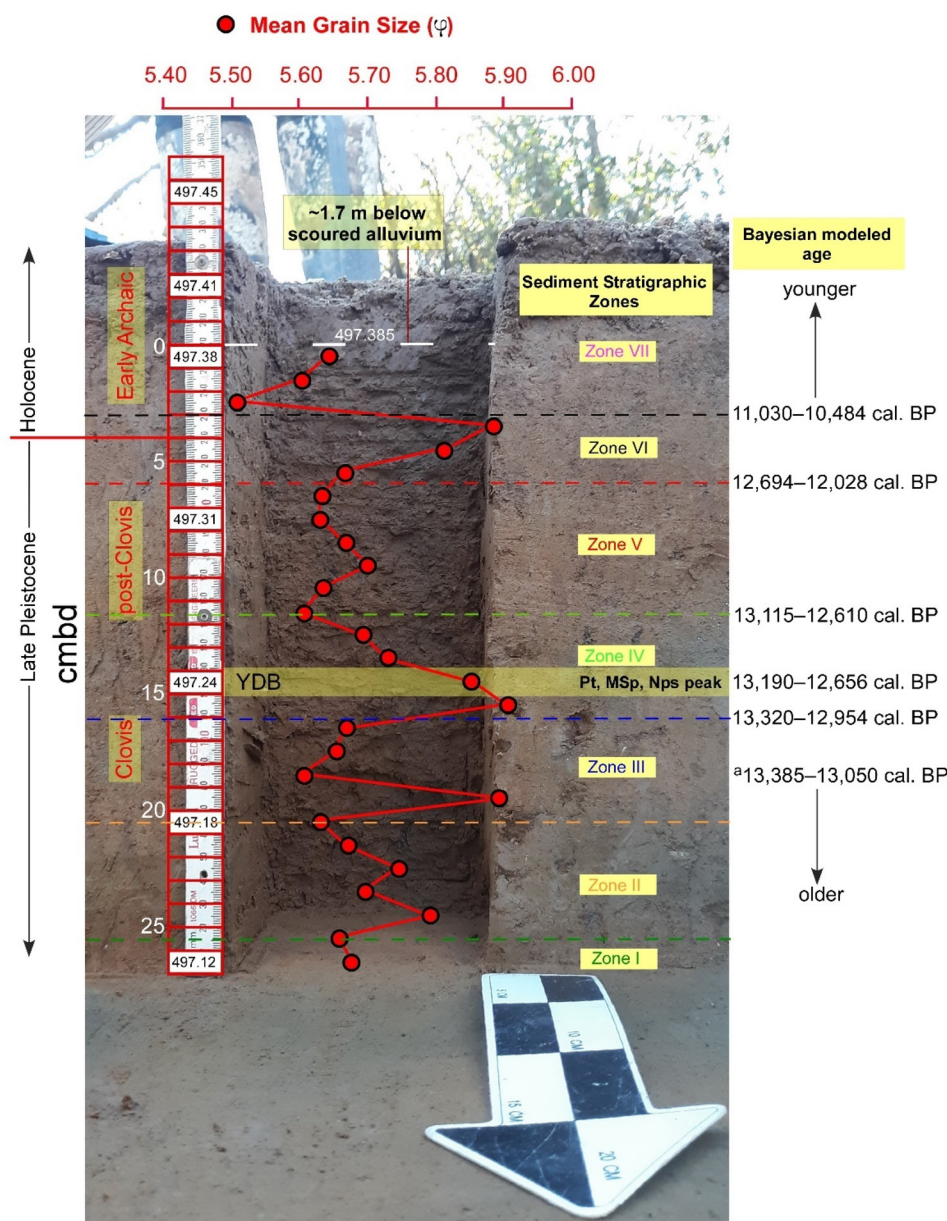


Figure 4. Interpreted sediment stratigraphic zones for 44PY152 (N98 W24). Shown are elevations (mbd) [white rectangles], mean grain size (red dots), interpreted sediment stratigraphic zones, and interpreted YDB zone (yellow band) with Pt, Msp, and nanoparticle peaks, and Bayesian modeled age ranges at 94.5% probability for sediment stratigraphic boundaries (see Table 2, Figure 3, and Supplementary Figure S36 and Supplementary Table S2). Bayesian modeled age ranges for sedimentological zones suggest that Zone I and Zone II likely correspond to early Clovis and/or pre-Clovis age sediments, Zone III to late Clovis, Zone IV to late Clovis and post-Clovis age (early YD), Zone V to ~Middle Paleoamerican age, Zone VI to both Late Paleoamerican and Early Archaic age sediments, and Zone VII to Early Archaic and later deposits (see Table 2, Figure 3, and Supplementary Figure S36). These cultural assignments are model-dependent and should be regarded as provisional to be evaluated with additional archaeological testing.

interiors (Figure 5E and F), or contain smaller microspherules embedded in larger microspherules, consistent with collision or coalescence while still molten (Figure 5O).

Metallic dust particles (MDPs) were identified with SEM and EDS in the same sediment samples containing microspherules (Figure 6J–L; Supplementary Figures S19–S23). These particles consist mainly of highly oxygen-depleted Fe or alloys composed

of chromium (Cr), iron (Fe), nickel (Ni), and tin (Sn). Similar MDPs have been reported from peat deposits [30–32] and interpreted as possible cosmic dust, although additional work is needed to evaluate that interpretation at 44PY152.

In addition to microspherules and MDPs, delicately structured authigenic Fe-rich grains are abundant within the microspherule peak sample (14–15 cmbd), with none observed above or

Table 3: Microspherules and microspherules/kg for 44PY152, N98 W24 profile.

Sample Depth (cmbd) ^a	Depth midpoint (cmbd)	Sample Weight (g)	# of microspherules	Spherules/kg ^b
0–1	0.5	nd	nd	nd
1–2	1.5	nd	nd	nd
2–3	2.5	100	0	0
3–4	3.5	120	0	0
4–5	4.5	100	0	0
5–6	5.5	100	0	0
6–7	6.5	100	0	0
7–8	7.5	100	0	0
8–9	8.5	108	0	0
9–10	9.5	100	0	0
10–11	10.5	100	0	0
11–12	11.5	100	0	0
12–13	12.5	90	1	11.1
13–14	13.5	98	0	0
14–15	14.5	90	40	444.4
15–16	15.5	83	10	120.5
16–17	16.5	90	3	33.3
17–18	17.5	120	1	8.3
18–19	18.5	125	0	0
19–20	19.5	nd	nd	nd
20–21	20.5	nd	nd	nd
21–22	21.5	90	0	0
22–23	22.5	nd	nd	nd
23–24	23.5	136	0	0
24–25	24.5	177	0	0
25–26	25.5	100	0	0
26–27	26.5	100	0	0

^aDepth is shown in centimeters below datum (cmbd). The actual depth below the top of the alluvial terrace is ~170–197 cm. The top of the sediment column is at a site elevation of $z = 497.385$. “nd” is no data.

^bSpherules are counted for a given sample weight (g), and their abundance is extrapolated to quantity per kg.

below this peak (see Figure 6A–I and Supplementary Figures S24–S32). XRD data were evaluated using Bruker evaluation software (EVA[®]), and best-fit patterns were matched using the PDF4+ database (Supplementary Figure S32). Minerals identified include hydrobiotite, goethite, rosetite, and lepidocrosite, which most likely formed post-depositionally through oxidation of Fe under saturated and fluctuating redox conditions. SEM and EDS analyses reveal that the bright (high-Z) areas are significantly oxygen-depleted, whereas the darker portions of the grains exhibit higher oxygen contents that correspond more closely to the stoichiometric ratios of the respective iron oxides (Supplementary Figure S31). Portions of these grains are also rich in chromium, iron, and nickel (NiCrFe alloys) (Figure 6C). Additional analysis is required to understand their formation mechanisms and their relationship to the Fe-rich microspherules at 44PY152.

Magnetic susceptibility

A Bartington MS2B magnetic susceptibility meter was used to collect K (Volume Susceptibility), X (Mass Specific Susceptibility), and $K_{fd}\%$ (Frequency Dependent Susceptibility) for 27 samples collected at 1 cm intervals from Smith Mountain Lake site 44PY152 (See Supplementary Table S3). Magnetic susceptibility (MS) is a property of sediments that measures the

susceptibility of mineral grains to an induced magnetic field. For a given sediment sample, MS indicates the combined strength of the magnetic minerals present in the sample. Overall, no magnetic susceptibility (MS) change across the YDB layer can be unequivocally attributed to either climate forcing or an impact-related process. In particular, MS does not exhibit a discrete anomaly coincident with the microspherule peak, nanoparticle enrichments, or platinum anomaly at the YDB, indicating that ferrimagnetic minerals were not preferentially concentrated within this horizon (Supplementary Table S3). Instead, MS varies gradually through the section, with a broader increase upward that may reflect longer-term environmental changes such as post-glacial warming [33] and/or increased soil formation, including natural or anthropogenic soil firing [34,35]. A pronounced shift in MS occurs between $z = 497.245$ and 497.285 mbd, corresponding to a Bayesian modeled age of 13,123–12,451 cal BP (94.5% probability), but this interval lies stratigraphically above the YDB and does not coincide with the YDB proxy suite. Magnetic susceptibility does not appear to be a strong proxy for bulk particle size [36], except in the case of frequency-dependent susceptibility ($K_{fd}\% \approx 10\%$), which indicates the presence of superparamagnetic grains and a grain-size dependence in the finest fraction ($<0.03 \Phi$) [37]. Further work is required to identify the specific magnetic mineral phases present.

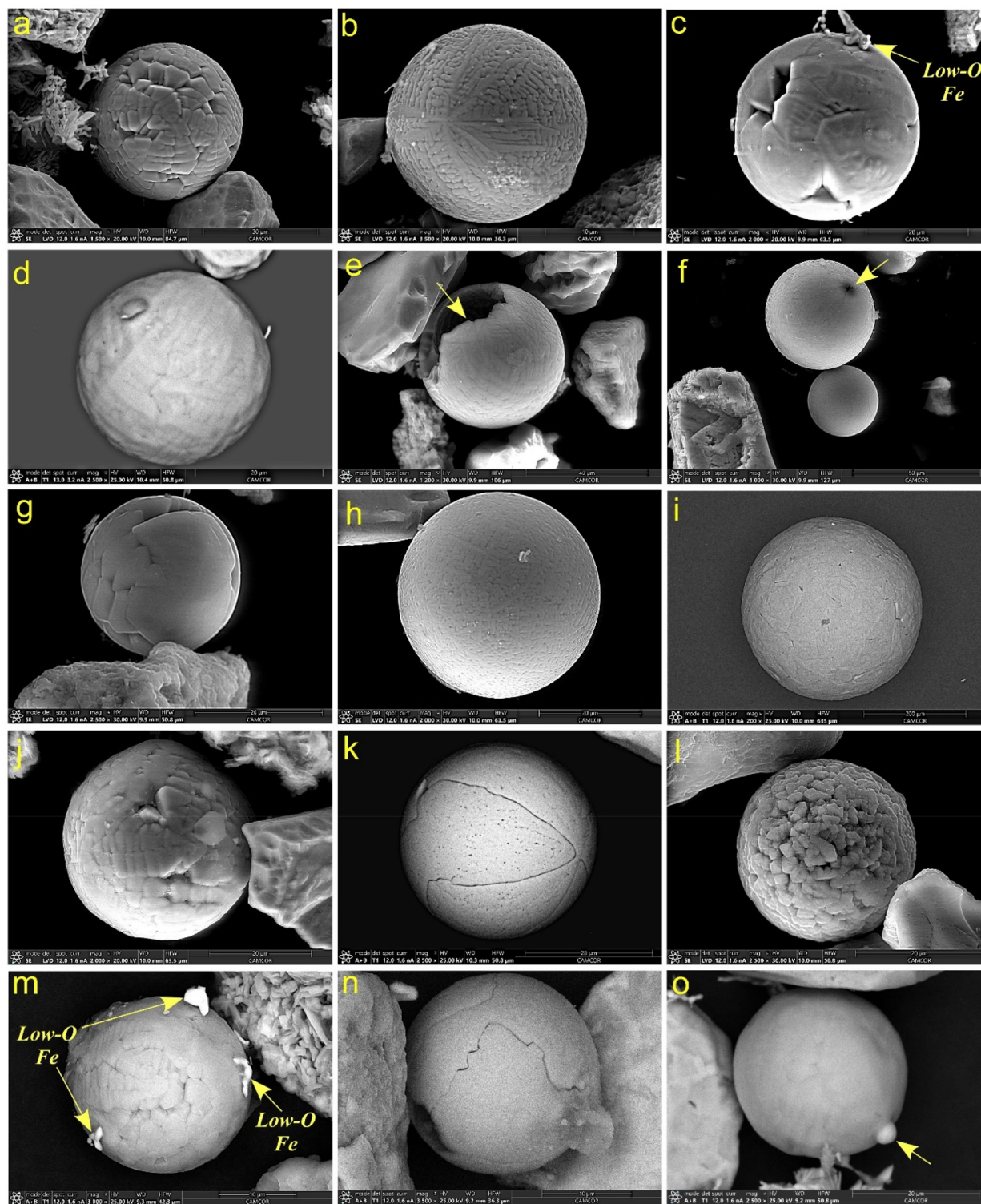


Figure 5. Examples of Fe-rich microspherules from 44PY152. Note that many microspherules have dendritic surface textures. Oxygen-depleted (low-O) Fe particles are stuck to microspherules in panels c and m. Panels e and f show broken microspherules with hollow interiors and panel o shows a smaller microspherule embedded on the outside of a larger microspherule (secondary impact). Microspherules from 44PY152 range from ~10–60 μm in diameter with a few over 300 μm . For elemental compositions of microspherules, see Supplementary Figures S1–S17.

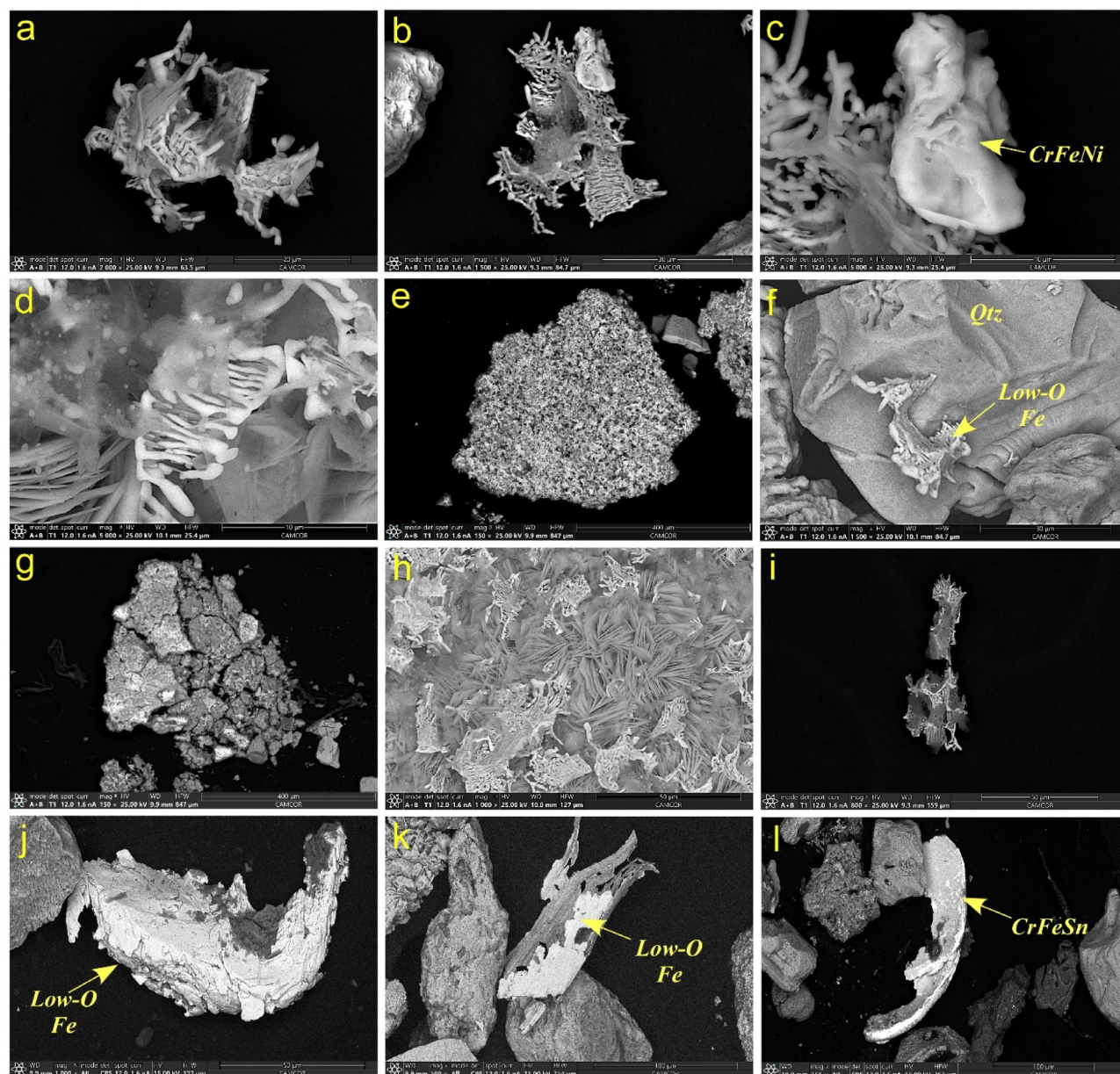


Figure 6. Examples of depleted-oxygen Fe authigenic grains (A–I) and metallic dust particles (MDPs) (J–L) from 44PY152 (14–15 cmbd) composed of depleted oxygen Fe (J), CrFe (K), and CrFeSn (I). See Supplementary Figures S18–S23.

Nanoparticle analysis

Nanoparticles from bulk sediments in suspension were analyzed using single particle inductively coupled plasma time-of-flight mass spectrometry (SP-ICP-TOF-MS). The nanoparticle analysis focused on the mass concentrations of 12 key elements (Cr, Fe, Co, Ni, Cu, Ru, Rh, Pd, Hf, Os, Ir, and Pt) that are commonly enriched in extraterrestrial material (see Figure 7 and Supplementary Table S4; <https://zenodo.org/records/13947879>). SP-ICP-TOF-MS is semi-quantitative and provides mean mass concentrations (ng/g) but not elemental abundances. These 12 elements, six of which are PGEs, are commonly enriched in extraterrestrial materials relative

to average crustal abundances: Ru = 2000×, Rh = 130×, Pd = 1100×, Os = 16,000×, Pt = 2000×, and Ir = 22,000× [38]. Six are transition elements that are also commonly enriched in extraterrestrial materials: Cr = 38×, Fe = 5×, Co = 34×, Ni = 331×, Cu = 6×, and Hf = 5× [38]. Sediment samples from 44PY152 display a consistent pattern of rapid increases in these elements within or immediately below the microspherule-rich interval. A comparison of elemental mass concentrations in the YDB sample (14–15 cmbd) indicates elevated values for multiple elements, including several PGEs, relative to the immediately underlying sample (15–16 cmbd) (Table 4).

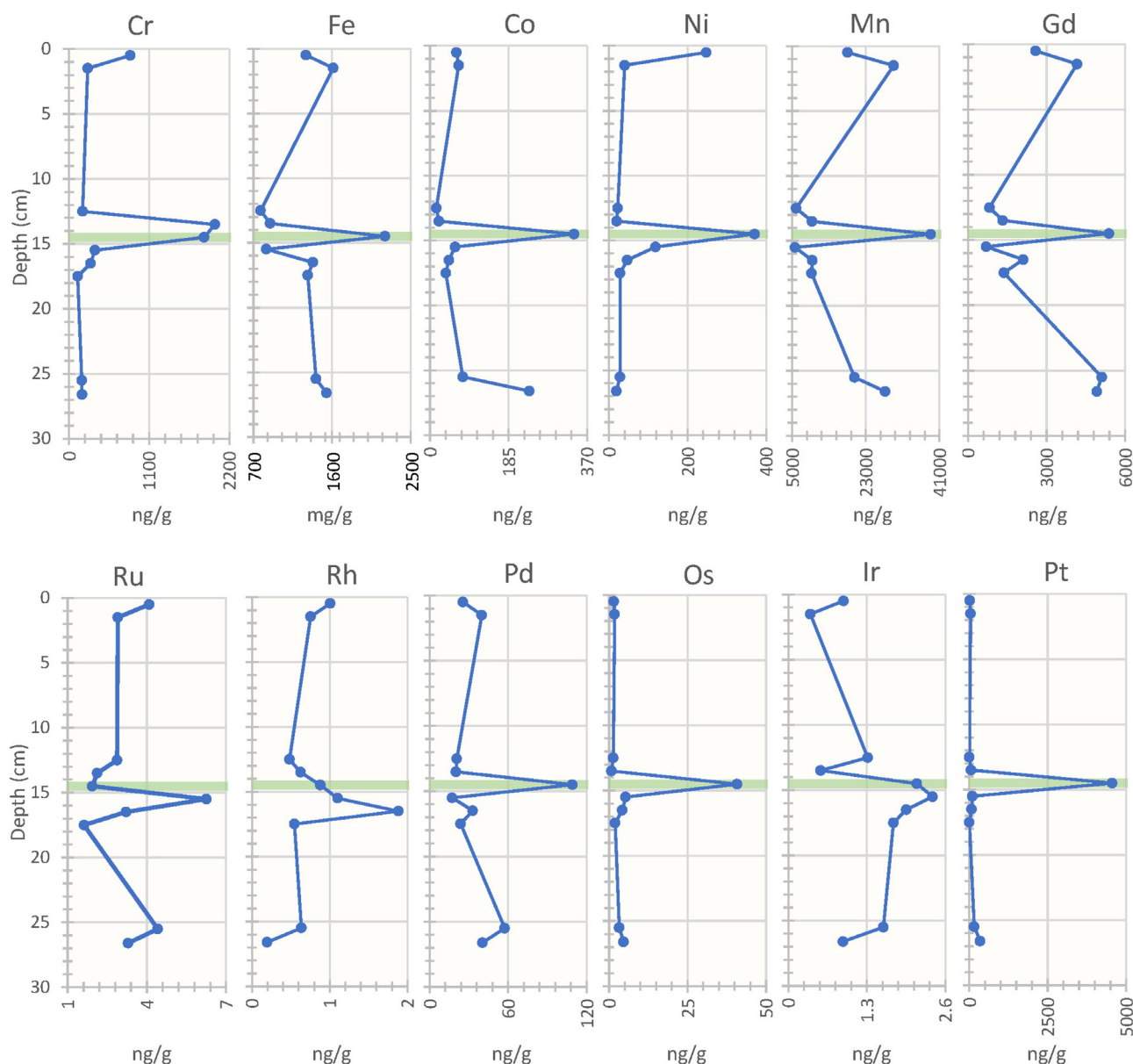


Figure 7. Mean mass concentrations of nanoparticles (NPs) determined by SP-ICP-TOF-MS. Mean mass concentration refers to the average elemental mass detected in nanoparticles per unit mass of bulk sediment, calculated from summed single-particle signals and normalized to sample mass, rather than to particle counts or bulk elemental composition. The x-axis is shown as mass (ng/g or mg/g), and the y-axis is shown as depth in centimeters below datum (cmbd) for the excavation unit. The sampled sediment column was originally buried beneath ~1.7 m of floodplain sediment. The green band marks the inferred Younger Dryas Boundary (YDB)-associated interval (14–15 cm; $z = 497.235\text{--}497.245$ mbd). These 12 elements, six of which are platinum-group elements (PGEs), are commonly enriched in extraterrestrial (ET) material relative to crustal averages: Ru = $\sim 2000\times$, Rh = $130\times$, Pd = $1100\times$, Os = $16,000\times$, Pt = $2000\times$, and Ir = $22,000\times$ [38]. Five additional transition elements are also commonly enriched in ET material: Cr = $38\times$, Fe = $5\times$, Co = $34\times$, Ni = $331\times$, and Cu = $6\times$ [38]. SP-ICP-TOF-MS is semi-quantitative and provides mean mass concentrations (ng/g) rather than elemental abundances. The 12 elements display the same pattern of substantial and rapid increase in total ng/g beginning within or immediately below the YDB-associated interval. These patterns are consistent with a rapid influx of elementally anomalous nanoparticles coincident with the microspherule-rich layer. Uncertainties for the YDB interval are as follows: Cr: $\pm 6.7\%$, Mn: $\pm 6.0\%$, Fe: $\pm 5.3\%$, Co: $\pm 1.2\%$, Ni: $\pm 2.2\%$, Ru: $\pm 1.5\%$, Rh: $\pm 1.5\%$, Pd: $\pm 1.3\%$, Gd: $\pm 7.3\%$, Os: $\pm 1.3\%$, Ir: $\pm 1.3\%$, and Pt: $\pm 1.3\%$. For nanoparticle data, see Supplementary Table S4 (<https://zenodo.org/records/13947879>).

In the YDB horizon, the chondrite-normalized PGE pattern differs sharply from the sediment immediately below it, most notably by a strong, Pt-centered enrichment, whereas the other PGEs remain comparatively low (Figure 8). Enrichment factors

(Table 4) show that Pt exhibits the largest relative increase ($\sim 43\times$), while other PGEs display more modest enrichments, indicating a selective enhancement of Pt rather than uniform PGE enrichment. The element-specific nature of this anomaly

Table 4: Elemental enrichment factors (YDB sample [14–15 cmbd] divided by the immediately underlying sample [15–16 cmbd]).

Elements	Enrichment factor (YDB/underlying sample)
Cr	5.21
Fe	2.60
Co	5.76
Ni	n.d.
Cu	5.13
Ru	n.d.
Rh	n.d.
Pd	6.34
Hf	5.06
Os	7.76
Ir	n.d.
Pt	43.12

and its confinement to the YDB horizon produce a stratigraphically discrete, event-like signature rather than a continuation of background geochemical variability. In contrast, the REE patterns for the YDB and underlying sample are broadly similar in shape, with the YDB sample uniformly higher in abundance (approximately parallel curves), consistent with an overall increase in REE concentrations rather than a major change in REE fractionation or sediment provenance (Figure 9). This decoupling between relatively conservative, lithogenically controlled REE behavior and sharply anomalous PGE enrichment suggests that the Pt anomaly reflects the addition of a chemically distinct particulate component rather than simple changes in detrital input or grain-size sorting.

Although platinum-group element-bearing nanoparticles show pronounced enrichment at the YDB (Figure 7), multiple independent datasets indicate that this signal is not readily explained by sedimentological concentration alone. The absence of sediment coarsening, improved sediment sorting (Supplementary Figure S36), or magnetic susceptibility enrichment (Supplementary Table S3) across the YDB interval, together with conservative REE fractionation patterns (Figure 9), argues against simple hydraulic concentration of heavy minerals as the sole cause of the nanoparticle enrichments. Instead, the decoupling of lithogenic indicators from PGE behavior suggests the addition of a chemically distinct particulate component superimposed on otherwise similar detrital sedimentation.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

A sample of Fe-rich dendritic microspherules from 44PY152 was analyzed with LA-ICP-MS to determine the abundance of major and minor elements, including elements often enriched in extraterrestrial (ET) material. The elemental concentrations of 44PY152 microspherules are normalized to crustal values in Figure 10 (see LA-ICP-MS data in Supplementary Table S5). Nine elements were detected at parts per million (ppm) concentrations, well above detection limits and above their

average crustal abundances. These elements are also commonly enriched over average values in ET sources: Pt = 1500 $\times$; Ni = 331 $\times$; Cr = 38 $\times$; Co = 33 $\times$; Cu = 11 $\times$; Fe = 5 $\times$; Zn = 4 $\times$; Mn = 3 $\times$; and Mo = 1 $\times$ [39].

The bulk composition of microspherules reflects dominantly terrestrial source material that experienced melting, while platinum-group elements are primarily hosted in compositionally distinct nanoparticle populations dispersed within the sediment. Consequently, low or undetectable iridium concentrations in individual microspherules do not preclude a coeval PGE anomaly at the sediment scale.

Total organic carbon and nitrogen isotopes

Sediments from 44PY152 were isolated for bulk sedimentary carbon (OC), total nitrogen (TN), and soot carbon concentrations (soot), as well as their stable isotopic signatures ($\delta^{13}\text{C}_{\text{OC}}$ and $\delta^{13}\text{C}_{\text{soot}}$; $\delta^{15}\text{N}$ not displayed) (see Supplementary Table S6 and Supplementary Figures S37 and S38). Trends in OC abundance suggest a consistent amount of bulk organic matter deposition at the site throughout the study period (mean = 0.20 ± 0.01 % of gram dry weight of sediment). Soot comprised ~20 to 36% of the bulk OC throughout the core.

There is no significant pattern in the profiles of OC and soot that suggests a possible cosmic impact event, as previously reported by Wolbach et al. [40,41]. Values vary throughout the sampled section, with periods of soot enrichment relative to OC, suggesting bulk OC and soot vary in their respective sources. This variation is reasonable as soot comprises relatively small-sized aerosols for which fate and transport are driven by aeolian forces prior to deposition on land. The downcore soot profile of soot is possibly related to climate-forced drought.

Mercury (Hg)

To investigate potential disruptions in the mercury (Hg) cycle across the YDB layer, we analyzed the Hg concentrations in sediments from 44PY152. Mercury is a sensitive tracer of large-scale environmental disturbance because it is efficiently mobilized during volcanism, biomass burning, and enhanced atmospheric dust loading, and can be rapidly redistributed and archived in sediments through atmospheric deposition and organic matter scavenging [42,43]. This complexity makes it difficult to interpret any potential climate signal, various natural, biotic, and abiotic processes can generate sedimentary Hg anomalies, including increased deposition of organic matter, volcanism, biomass burning, weathering and erosion of soil and rock (detrital input), and local redox changes [44,45].

At 44PY152, Hg concentrations gradually decrease from the lowermost samples, with a significant increase (positive excursion) preceding the YDB-associated interval (16–17 cmbd; $z = 497.205\text{--}497.225$ mbd; Bayesian modeled age $\geq 13,385\text{--}13,050$ cal BP at 94.5% probability) (Table 2; Supplementary Table S7; Supplementary Figure S39 [Hg and Hg/TOC]). The absence of a mercury enrichment at the YDB at 44PY152 is consistent with observations from White Pond [16] and contrasts with some lacustrine and ice-core archives, underscoring the

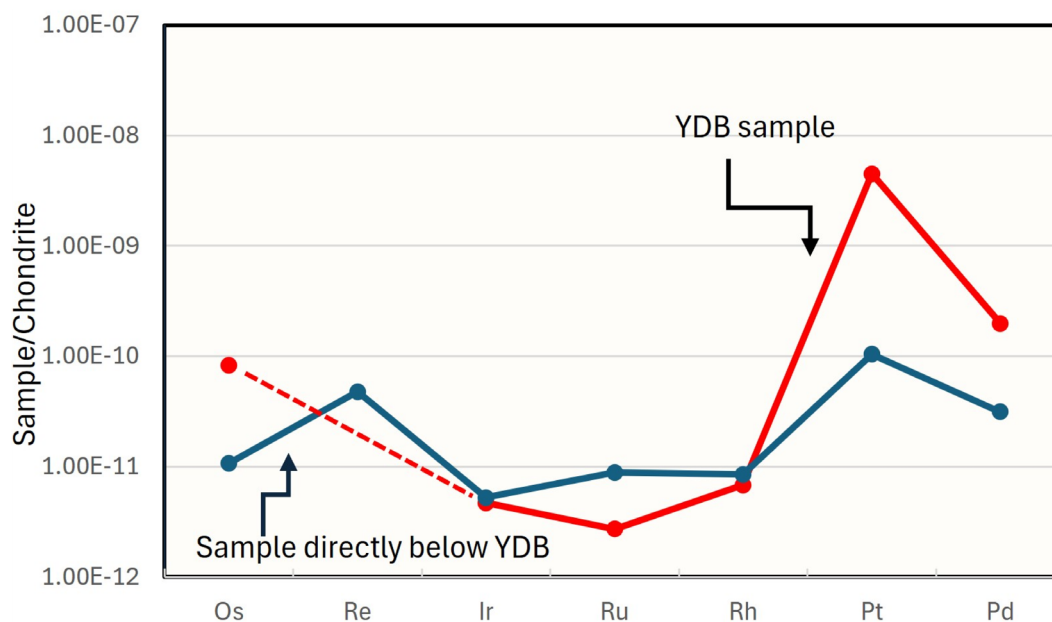


Figure 8. Chondrite-normalized platinum-group element (PGE) patterns for the Younger Dryas Boundary (YDB) sample and the sediment sample immediately below the YDB horizon. Concentrations are plotted as sample/chondrite on a logarithmic scale. The YDB sample (red) displays a pronounced Pt enrichment relative to the underlying sample (blue), whereas most other PGEs remain comparatively low and closer to the below-YDB values. Rhenium (Re) was not detected in the YDB sample (dashed segment indicates non-detect/absent value), and thus no continuous Re-based trend is implied. Chondrite normalization: McDonough and Sun [38].

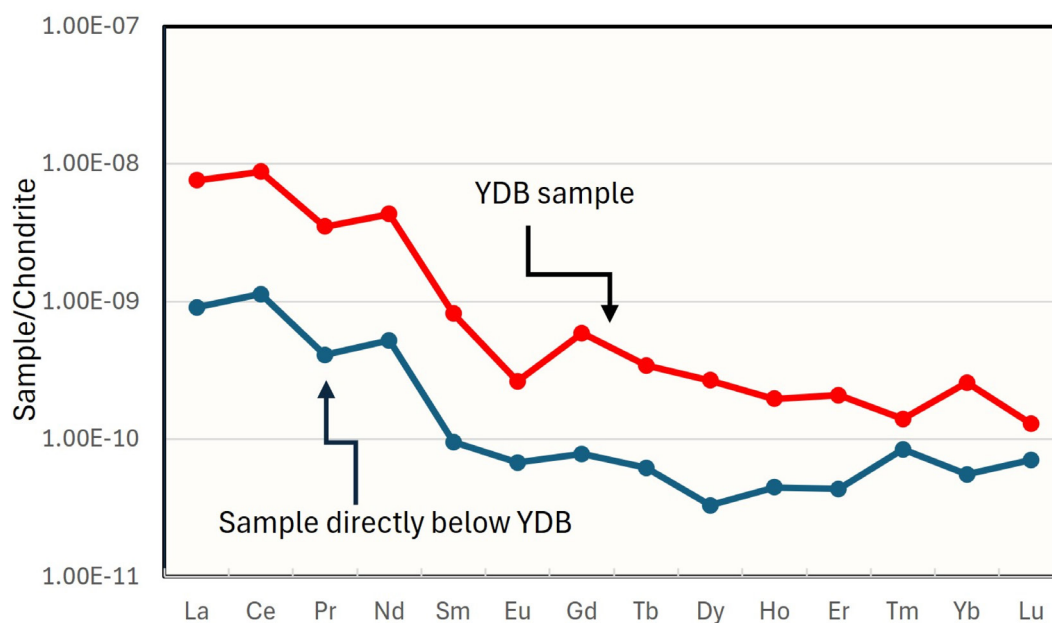


Figure 9. Chondrite-normalized rare earth element (REE) patterns for the Younger Dryas Boundary (YDB) sample and the sediment sample immediately below the YDB horizon. Values are plotted as sample/chondrite on a logarithmic scale. The YDB sample (red) is consistently enriched in REEs relative to the underlying sample (blue) while preserving a broadly similar pattern shape (approximately parallel curves), consistent with an amplitude (concentration) increase rather than a fundamentally different REE distribution. Chondrite normalization: McDonough and Sun [38].

archive-specific sensitivity of mercury deposition to environmental conditions. This pattern is more pronounced when Hg is normalized to total organic carbon (Hg/TOC) (Supplementary

Figure S39). Both total Hg and Hg/TOC values show a gradual decline beginning in the YDB interval and continuing through the Younger Dryas section at 44PY152. A shift toward Hg/TOC

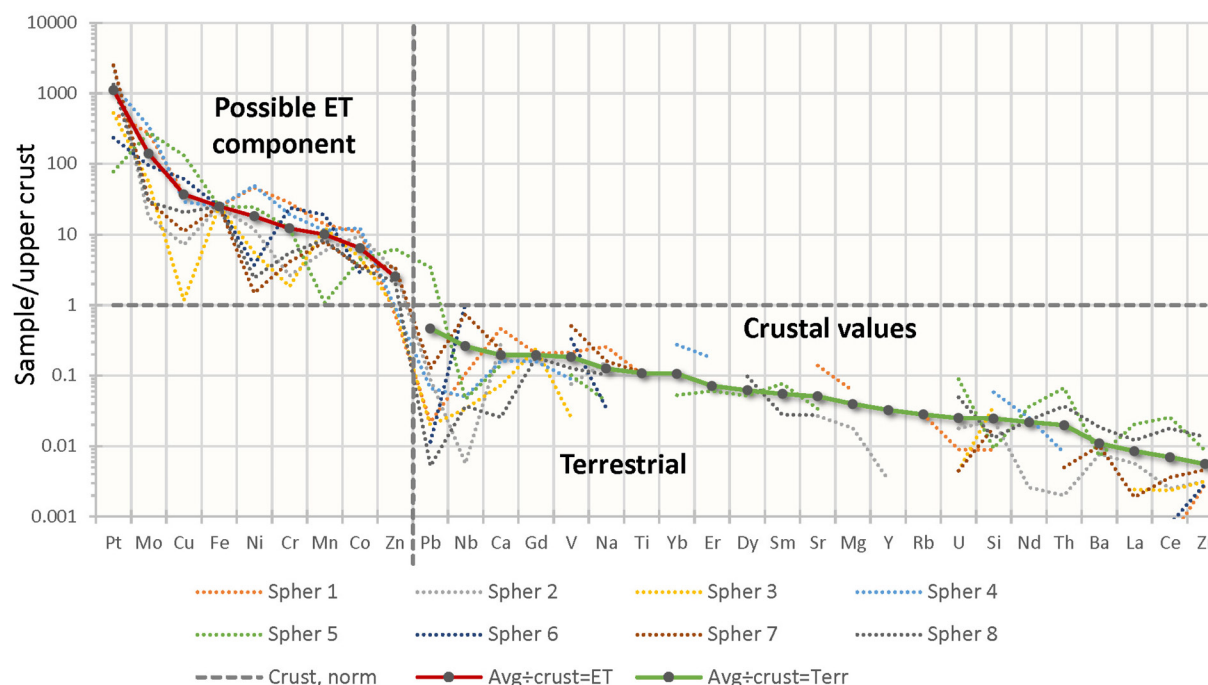


Figure 10. Comparison of 32 elements measured by LA-ICP-MS in microspherules from 44PY152, normalized to crustal abundances. Here, we compare crust-normalized Smith Mountain Lake elemental data to crustal abundances. Dotted lines represent values for individual spherules; gaps represent values below detection limits. The dashed black line represents crustal values, normalized to 1 (from Rudnick and Gao) [39]. “Avg÷crust=ET,” the solid red line, represents Smith Mountain Lake average elemental values divided by crustal values from Rudnick and Gao [39], interpreted as having a mostly ET origin. “Avg÷crust=Terr,” the solid green line, is interpreted as having a primarily terrestrial origin. The two groups are arranged in descending order of abundance, divided by a vertical gray dashed line. Normalized individual wt% for 8 microspherules and the crustal wt% (horizontal gray dashed line) reveals enrichment of several elements relative to crustal abundances, consistent with a mixed high-temperature melt product containing a minor high-enrichment component. Note the break between the two groups: potentially ET-enriched Zn is ~5× more abundant than terrestrial Pb, which is rare in ET material. See Supplementary Table S5 for LA-ICP-MS data. Iridium (Ir) was below detection limits (~0.01 ppm) in microspherules; however, a large peak in the mass of Ir-rich nanoparticles was detected in bulk sediment in the microspherule peak layer using SP-ICP-TOF-MS (Figure 7).

enrichment occurs near the top of the sediment column, corresponding to the Bayesian modeled lower Holocene boundary ($z = 497.345$ mbd; ca. 11,950–11,311 cal BP at 94.5% probability). The following sections evaluate the sedimentological, geochemical, and archaeological implications of these proxy distributions.

DISCUSSION

Granulometry and sedimentation rate

Granulometry data for samples collected at 44PY152 are consistent with up to 7 relatively distinct sediment stratigraphic zones (Supplementary Figure S36). These zones represent cycles of floodplain sedimentation (i.e., stacked sequence of coarsening and fining-upward sequences) from overbank flooding/higher energy water flow and fine suspension sediment deposition during the slackwater phase along the alluvial terrace. Periods of eolian loess deposition have been reported during the early Younger Dryas, when carbon isotopes and Hg deposition may suggest sustained periods of drought [46–50].

Sedimentation patterns estimated from the Bayesian age-depth model suggest that the sampled section records a shift

in depositional regime near the inferred onset of the Younger Dryas (YD), including an interval of finer-grained sedimentation followed by somewhat sandier input (Table 2, Figure 3, and Supplementary Table S2). The finer-grained interval is consistent with increased aeolian entrainment and deposition under drier conditions with reduced vegetative cover, whereas the subsequent increase in fine- to medium-grained sands may reflect renewed fluvial reworking and somewhat higher-energy sediment transport within the alluvial system. Given the compressed nature of the section and the limited chronological control, these changes are best interpreted as broadly consistent with climatic instability and hydrologic adjustment near the YD onset rather than as a precisely resolved sequence of short-term depositional events. Within this framework, the interval corresponding to microstratigraphic Zone V falls within a Bayesian modeled age range of ca. 13,125–12,610 cal BP (94.5% probability) (Table 2, Figure 3, and Supplementary Table S2). More broadly, cultural assignments discussed for the sedimentological zones are inferred from modeled age-depth relationships and generalized stratigraphic context at the site and should therefore be regarded as provisional rather than as independently dated associations.

Platinum Group Elements (PGEs)

Multiple studies have demonstrated that anomalous abundance peaks in Pt provide a useful chronostratigraphic marker for the onset of the Younger Dryas (12,875–12,775 cal BP; IntCal20) [16–18,20]. The YDB platinum anomaly was previously established from Greenland ice core data by Petaev et al. [19] and later confirmed in North American sedimentary sequences by Moore et al. [16–18,20] and numerous other studies globally [13,14,20,51]. In this study, we applied SP-ICP-TOF-MS in a novel approach to detect changes in mean mass concentrations (ng/g) of nanoparticles for a suite of key elements, including platinum and other PGEs in sediment samples that bracket the YD onset interval. Significantly elevated particle mass concentrations (ng/g) for Os, Ir, Co, Ni, Pt, and others, most within a single 1-cm sample interval, indicate potential exogenic enhancements in the 12,800-year-old sediment layer at 44PY152 (Figures 7–11). These enriched elements occur within or immediately adjacent to the microspherule peak, consistent with minor vertical dispersion due to particle settling behavior, bioturbation, or post-depositional processes. The key elemental abundances are highly heterogeneous within a given stratum and across several strata near the YDB. Minor vertical offsets among individual elements likely reflect a combination of particle size-dependent settling, heterogeneous source materials, and post-depositional redistribution rather than multiple depositional events.

Microspherules

Fe-rich and glassy microspherules containing high-temperature melt features and reduced metallic inclusions have been reported within stratigraphic units globally that date to the Younger Dryas onset [e.g., 9,11,15]. Oxygen-depleted metallic inclusions within these microspherules are consistent with formation under reducing conditions at temperatures exceeding those typically sustained in natural surface wildfires [8,15]. EDS analyses of selected microspherules document high-temperature phases and reduced metallic components, including oxygen-depleted Fe, chromferrite (CrFe) alloys, and FeTiZn metallic inclusions (Supplementary Figures S3, S8, S11, S12, and S17). Although microspherules are not unique to impact events, the co-occurrence at 44PY152 of high-temperature mineral inclusions, elevated platinum-group element concentrations, and a stratigraphically concentrated, deeply buried spherule-bearing interval is not readily explained by wildfire or anthropogenic processes alone.

A volcanic origin is not supported. Distal tephra deposits are dominated by silicate glass shards produced by magma fragmentation and do not typically contain metallic or reduced Fe melt products. The Fe-rich compositions, dendritic textures, hollow interiors, and reduced Fe phases observed in the Smith Mountain Lake microspherules are not characteristic of distal volcanic ash deposits and are not commonly reported from tephra sequences [8].

An origin as primary meteoritic ablation spherules is likewise unlikely, as such particles typically exhibit elevated MgO

relative to terrestrial melts, whereas YDB microspherules, including those at Smith Mountain Lake, are characterized by very low MgO contents, consistent with formation predominantly from melted terrestrial sediments, as has been proposed for microspherules at other YDB sites [9,11,52].

Together, the stratigraphically concentrated co-occurrence of high-temperature microspherules, oxygen-depleted metallic inclusions, and elevated platinum-group element abundances within a narrow horizon is consistent with an unusual short-duration depositional event involving high-temperature particulate input.

The microspherules at 44PY152 provide a probable chronostratigraphic marker for the YD onset (12,875–12,775 cal BP; IntCal20) [1] and help identify the temporal and stratigraphic transition between the Clovis technocomplex and later post-Clovis and Early Archaic occupations. This finding is similar to that reported recently for site 38DA75 at the Wakulla Springs Lodge site (8WA329) in Florida [20], where microspherule peaks were reported to correspond broadly to platinum peaks but included considerable vertical distributions above and below the peaks due to the loose, unconsolidated nature of the sand. At 44PY152, stiff silty sediments preserve a microspherule peak that is more vertically confined than at some unconsolidated sandy sites, providing a comparatively well-defined YDB-associated interval within the section (Figure 11).

Stable isotopes and mercury (Hg) as climate indicators

Analysis of carbon isotopes of soot carbon extracted from sediment samples at 44PY152 was done to determine if a regional climate signature could be detected (Figure 11). See Supplementary Figure S37 and Supplementary Tables S5 and S6. Notably, $\delta^{13}\text{C}_{\text{soot}}$ exhibits a small positive excursion in samples beginning in the microspherule and Pt anomaly sample that continues several cm upward in the profile representing the early Younger Dryas (Bayesian modeled age = 13,190–12,610 cal BP at 94.5% probability). Although subtle, these excursions may indicate a climate response with multidecadal drought conditions during the earliest and coldest part of the Younger Dryas [53,54]. Future multi-proxy studies are needed to verify this interpretation.

Mercury (Hg) concentration data normalized to total organic carbon (TOC) are also suggestive of climate change before and during the Younger Dryas, with a significant enrichment before the YD (Bayesian modeled age = $\geq 12,954$ cal BP at 94.5% probability) followed by a gradual decrease during the YD, and a rebound at the Pleistocene-Holocene boundary ($z = 497.345$ mbd; Bayesian modeled age = ca. 11,950–11,311 cal BP at 94.5% probability) (Figure 9, Table 2, Supplementary Figure S39 and Supplementary Table S7). These data are consistent with reduced wet deposition of mercury during much of the Younger Dryas, although post-depositional remobilization cannot be fully excluded. While we acknowledge that Hg can be remobilized in aqueous environments through redox conditions, pH changes, or microbial activity [56], decreased

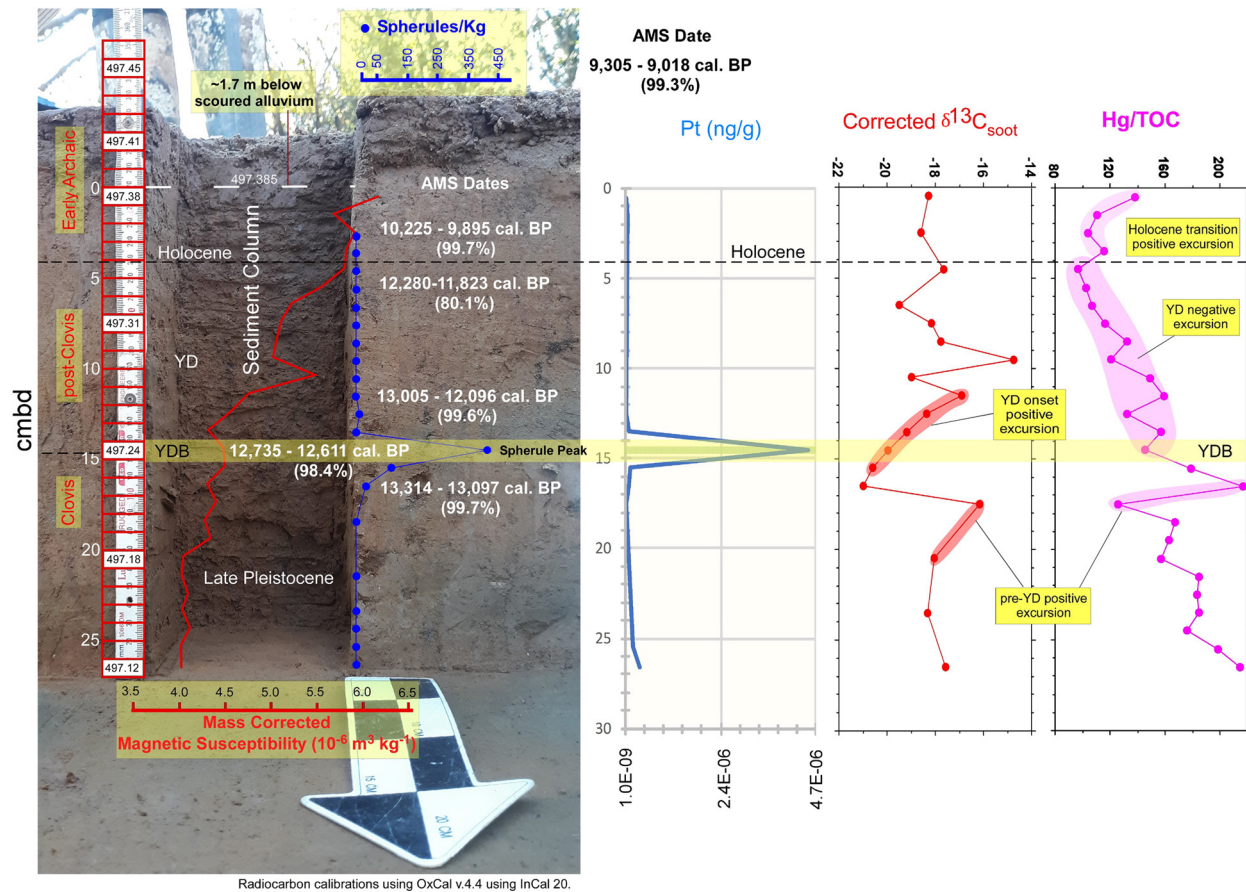


Figure 11. Sediment column sampled at 1-cm resolution from 44PY152 (N98 W24; south profile) showing mass-corrected magnetic susceptibility (red line), microspherule abundance per kg (blue dots plotted to the right of the sediment column), calibrated and unmodeled radiocarbon dates (Table 1), platinum (mean mass concentration [ng/g]), corrected $\delta^{13}\text{C}_{\text{soot}}$, and mercury (Hg) concentration normalized to total organic carbon (TOC). See Supplementary Figure S39 for raw Hg concentrations (ng/g) and Supplementary Tables S3, S4, and S6. The yellow band marks the inferred Younger Dryas Boundary (YDB)-associated interval (14–15 cmbd; $z = 497.235\text{--}497.245$ mbd), representing a stratigraphically discrete proxy horizon between lower Paleoamerican and overlying later archaeological deposits. The Bayesian modeled lower Holocene boundary is shown as a black dashed line at an elevation of 497.345 mbd (see Tables 1 and 2). Possible environmental variability is indicated by excursions in the $\delta^{13}\text{C}_{\text{soot}}$ record and variation in Hg/TOC values. Depth is shown in centimeters below datum (cmbd), and the top of the sediment column begins ~ 1.7 m below the floodplain terrace surface ($z = 497.385$ mbd) exposed by Roanoke River scour. Radiocarbon calibrations were performed using OxCal v4.4 and IntCal20 [6]. $\delta^{13}\text{C}_{\text{soot}}$ values were corrected for linearity (peak size) using a two-point correction to VPDB or AIR scales [55].

Hg deposition during the early YD is consistent with cooler and drier climatic conditions, which resulted in less wet deposition of mercury. Climate controls on Hg deposition are supported by a lack of correspondence between redox-sensitive elements such as Fe and Mn with Hg (Supplementary Tables S4 and S7). Other post-depositional pedogenic alterations to Hg from pH and microbial activity cannot be conclusively ruled out without additional research. Our inference of less wet deposition of Hg during the YD is similar to that reported for lake sediments in the Venezuelan Andes, suggesting that atmospheric cycling of Hg is affected by abrupt climate change that alters precipitation patterns, such as the YD [57]. Both Hg and the positive excursion in $\delta^{13}\text{C}_{\text{soot}}$ for the first few centuries of the YD are consistent with overall drier conditions during the YD at 44PY152.

It has been suggested that the Laacher See eruption or other large sulfur-rich volcanic events may have contributed to the onset of Younger Dryas (YD) climate change [58,59]. Large explosive volcanic eruptions are well known to release substantial quantities of mercury to the atmosphere, where Hg can be widely dispersed and deposited in downwind sedimentary archives, commonly producing distinct Hg enrichment horizons [45]. However, we observe no evidence for enhanced atmospheric mercury (Hg) deposition at Smith Mountain Lake (44PY152) at the YDB, which might be expected from a major volcanic source. Similarly, the Hg record reported for White Pond, South Carolina [16], shows no Hg enrichment or cryptotephra at the YDB. In contrast, the prominent Hg excursion below the YDB at 44PY152 may be related to the Laacher See eruption, as its Bayesian-modeled age ($\geq 13,385\text{--}13,050$ cal BP

at 94.5% probability) overlaps recent high-precision dating of the eruption at $13,006 \pm 9$ cal BP [60]. This timing places the eruption approximately two centuries before the onset of the Younger Dryas, making it unlikely to represent the primary trigger of YD climate change.

Total organic carbon and nitrogen isotopes

Smith Mountain Lake (44PY152) $\delta^{13}\text{C}_{\text{OC}}$ values are derived from predominantly C3 photosynthetic organic matter. In contrast, $\delta^{13}\text{C}_{\text{soot}}$ downcore is enriched compared to the bulk OC by $\sim 5.5\text{‰}$, suggesting multiple combustion sources were deposited at the site [61] (Supplementary Tables S6 and S7). The small, positive $\delta^{13}\text{C}_{\text{soot}}$ excursion immediately preceding the microspherule and nanoparticle PGE peak between 18–21 cmbd ($z = 497.18\text{--}497.210$ mbd; Bayesian modeled age of $>13,385$ cal BP at 94.5% probability) may be indicative of a small proportional increase in C4-derived soot or a change in carbon isotope fractionation during soot formation compared to preceding or succeeding periods (Table 2; Supplementary Tables S5 and S6, and Supplementary Figure S38). Hamilton and Hartnett [61] observed similar variations in $\delta^{13}\text{C}_{\text{soot}}$ values in modern ecosystems compared to bulk organic matter that they attribute to either pre- or post-depositional changes in fractionation dynamics during soot formation. Specifically, Hamilton and Hartnett highlight increased isotopic fractionation during soot formation from distal C4-derived plant matter that is not apparent in their localized C3-derived soot. Hamilton and Hartnett do not discuss the potential mechanisms of post-depositional isotopic fractionation of soot, an area that needs greater research.

The interpretation of positive $\delta^{13}\text{C}_{\text{soot}}$ excursions related to greater proportional C4 plant cover locally or regionally would seem feasible with documented evidence of concurrent multidecadal drought [54,62]. Immediately within and above the microspherule and PGE peak (14–15 cmbd), the increase in $\delta^{13}\text{C}_{\text{soot}}$, albeit small, may be indicative of ecosystem drought conditions that led to greater land cover and subsequent pyrolysis of proportionally more C4 vegetation during fire events and resulting increases in $\delta^{13}\text{C}_{\text{soot}}$ during the first few centuries of the YD [54,62]. This interpretation is further supported by regional isotopic evidence for increased regional C4 plant cover during the cold and arid periods of the Last Glacial Maximum [63,64], which may have also occurred to a lesser degree during the comparatively short YD.

Potential increases in relative C4 plant abundances related to cold/dry conditions have been noted from several sites during the Pleistocene/Holocene transition [63,65]. The competitive advantage of C4 photosynthesis under dry conditions, particularly with relatively low pCO₂ concentrations, has been invoked as the forcing mechanism responsible for this shift in relative abundance [66–68]. Note also that the $\delta^{13}\text{C}$ value of C3 plants typically increases under drought stress, thus the shift in $\delta^{13}\text{C}$ may simply be indicative of increased drought stress on C3 plants rather than an increase in relative C4 plant abundances [66–68].

Nanoparticles

Sediment samples from 44PY152 display a consistent pattern of substantial rapid increases within or just below the microspherule layer of 12 key elements (Cr, Fe, Co, Ni, Cu, Ru, Rh, Pd, Hf, Os, Ir, and Pt) that are typically enriched in extraterrestrial material. These enrichments document a pronounced increase in elementally anomalous nanoparticles coincident with the microspherule layer, interpreted in conjunction with independent microspherule evidence rather than as a standalone provenance indicator. This finding is consistent with dozens of other studies for YDB sites globally showing abundance anomalies for platinum and other PGEs in YD onset sedimentary sequences [9,10,12,13,16–18,20,40,41,69–73]. The apparent asynchronous enrichment of some elements slightly above or below the YDB layer (Figure 7) is possibly attributable to limited bioturbation of sediments at the site and to differences in thermal fractionation for some elements (e.g., Ir, Rh, and Ru) [74,75], as well as post-depositional pedogenic or biological alterations in elemental abundances by depth (e.g., plant uptake) [76]. SP-ICP-TOF-MS measurements quantify changes in elemental mass concentrations and do not, by themselves, determine particle origin; interpretation therefore relies on stratigraphic coherence and association with independent high-temperature proxies.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

LA-ICP-MS data for microspherules are consistent with a potentially small but significant ET component mixed with terrestrial material during their creation. This observation is identical to those reported for microspherules from YDB sites on multiple continents [9,11,12,15,20,77] and suggests that YDB microspherules at 44PY152 are not ablation spherules [77,78]. These results are also consistent with those of Petaev et al. [19], who found an ET Pt peak in the YDB layer in the Greenland Ice Sheet (GISP2) associated with anomalously low Ir values.

Site archaeostratigraphy

Archaeological investigations at 44PY152, including shoreline survey and systematic excavations, have revealed a shallowly stratified Paleoamerican complex through Early Archaic sites preserved in floodplain alluvium [5,46] and eroding out of scoured floodplain terrace deposits. More than 25 fluted points, 35 ETLs, 50 mid-late Paleo points, and 600 Early Archaic points have been documented from sites within this complex [3,5].

At 44PY152, archaeological excavations were conducted by 3-cm levels, using at total station to point province at all artifacts and charcoal. Multiple Early Archaic Palmer points and Kirk Points were mapped in situ at the site, with each respective type being mapped within 1 cm of elevation of each other across 1 to 16 meters of horizontal space. Charcoal samples excavated and mapped from these surfaces that provided acceptable radiocarbon ages associated with these diagnostics are presented in (Table 1). The YDB age range was previously determined through Bayesian modeling to ca. 12,875–12,775 cal BP (IntCal20) based on analyses of 354 dates from 23 sedimentary

sequences over four continents [1]. Using the modeled age estimates for 44PY152 (N98 W24) and the established date ranges for Paleoamerican sub-periods (Early, Middle, and Late Paleoamerican) and Early Archaic, we developed a generalized Paleoamerican and Early Archaic projectile point sequence for the region around Smith Mountain Lake using points recovered from 44PY152 or nearby sites along the river (Figure 12).

Assuming that the Clovis technocomplex ends by ca. 12,750 cal BP [7], in situ Clovis artifacts are expected to occur at or below the YDB microspherule, Pt, and PGE datum, subject to localized stratigraphic variability. At the sample location in the main block at 44PY152, this equates to a site elevation of 497.235–497.245 mbd; however, because sediment thickness and microtopography vary across the site, the absolute elevation of the YDB datum is expected to shift laterally, requiring localized verification in additional excavation units.

The Bayesian age-depth model utilizing AMS radiocarbon dates indicates that artifacts earlier than Clovis (13,050–12,735 cal BP) [7] will likely be found at elevations <497.22 mbd (Bayesian modeled age = 13,385–13,050 cal BP at 94.5%; see Table 2 and Figure 3) within the main excavation block where the sediment column was collected. The thickness of sediments and microtopography across the site will undoubtedly change slightly with distance from the sample location. In the future, these changes can be determined/monitored by examining multiple unit profiles for the microspherule peak and/or geochemical analysis of sediments for Pt or other PGEs.

Unfluted lanceolates in the region, referred to as Miller Lanceolates, Early Triangular Lanceolates (ETLs), and Haw River points, have been proposed as morphological types that may be pre-Clovis in age. Miller Lanceolates have been dated at Meadowcroft Rockshelter, and ETLs have been dated at Cactus Hill, supporting a possible pre-Clovis affiliation, although additional well-dated contexts are needed to confirm their age and broader chronological placement; Haw River points in the Carolinas currently lack chronometric dating [3,5,79–83]. Points similar to these types have been found at 44PY152 [2] and are provisionally included in this sequence as possibly pre-Clovis in age, but this model will require chronometric dating in a stratified context to establish their temporal placement. In South Carolina, morphologically similar points have been found made of Coastal Plain Chert (CPC) that are excessively weathered even when compared to Clovis points made of the same material, suggesting a possible pre-Clovis age [84]. Thus far, these points have yet to be excavated in situ at 44PY152 and have only been recovered in a secondary (i.e., displaced) context. Where found eroding in situ at other site locations, these un-typed lanceolates are at lower elevations and are thought to be Late Pleistocene in age, but Paleoamerican diagnostics have yet to be found in these contexts to determine their relative age.

CONCLUSIONS

Geoarchaeological investigations at site 44PY152 on the Roanoke River floodplain near Smith Mountain Lake document a rare, deeply buried, and stratified Late Pleistocene–Early

Holocene archaeological sequence preserved within ~1.7 m of fine-grained alluvium. The terrace deposits contain in situ and eroding Paleoamerican and Early Archaic diagnostics, providing a valuable context for evaluating the onset of the Younger Dryas (YD) within a culturally stratified framework. A principal outcome of this study is the identification of a probable, stratigraphically discrete marker horizon at the site. High-resolution (1-cm) sampling identifies a microspherule-rich interval accompanied by pronounced enrichments in platinum-group elements (PGEs) and elementally anomalous nanoparticle populations. The proxy suite is concentrated within a thin interval centered on a single 1-cm sample, with few to no microspherules and only background PGE signals in adjacent samples. This tight vertical clustering, together with microstratigraphic sedimentological zonation and the Bayesian age–depth model, supports interpretation of the microspherule–PGE horizon as a coherent depositional marker rather than the product of pervasive post-depositional mixing. Elemental systematics further support this interpretation, as chondrite-normalized spider plots show a selective, Pt-centered PGE enrichment decoupled from largely conservative REE fractionation patterns, inconsistent with simple sedimentological concentration or provenance change.

The Smith Mountain Lake horizon is consistent in character and stratigraphic behavior with Younger Dryas Boundary (YDB) proxy assemblages reported from other well-resolved sequences. Regardless of formation mechanism, the co-occurrence of high-temperature microspherules (including oxygen-depleted metallic inclusions), elevated PGE abundances, and anomalous nanoparticle mass concentrations defines a useful stratigraphic marker horizon consistent with the onset of the Younger Dryas. At 44PY152, the Pt, microspherule, and nanoparticle peaks are all tightly confined stratigraphically, with the principal anomaly restricted to a single 1-cm sampled interval. This unusually restricted vertical distribution provides a practical reference for correlating sediments and for placing archaeological materials relative to the YD onset, particularly in settings where radiocarbon control is limited by poor preservation, carbon mobility, or bioturbation. Although its numerical age remains dependent on model-based interpolation and comparison with externally established Younger Dryas age constraints, the microspherule–PGE–nanoparticle horizon nonetheless functions as a useful stratigraphic tie point that strengthens chronological interpretation of both pre- and post-12.8 ka occupations.

A further important contribution of this study is the application of single-particle inductively coupled plasma time-of-flight mass spectrometry (SP-ICP-TOF-MS) to a stratified Paleoamerican archaeological sequence. Unlike conventional bulk geochemical methods, SP-ICP-TOF-MS provides particle-scale geochemical resolution and enables detection of anomalous nanoparticle populations and element-specific enrichments within narrow stratigraphic intervals. At 44PY152, this approach was essential for identifying a chemically distinct YD-associated nanoparticle assemblage and for demonstrating that Pt- and PGE-bearing enrichments are decoupled from more conservative lithogenic

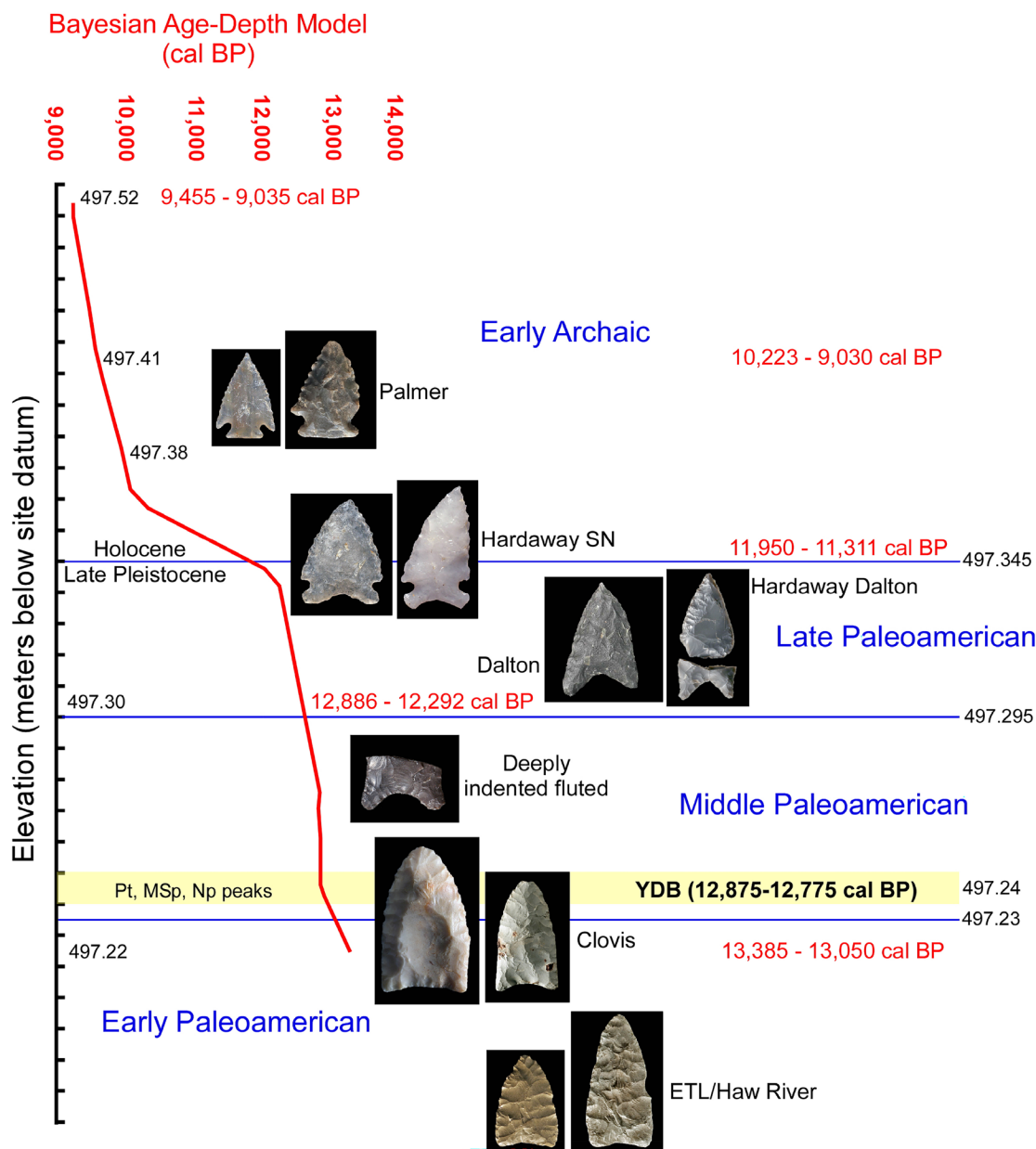


Figure 12. Generalized projectile point sequence for Smith Mountain Lake (44PY152) showing Early, Middle, and Late Paleoamerican and Early Archaic temporally diagnostic projectile points recovered at or near 44PY152 plotted based on the Bayesian age-depth model developed for 44PY152; N98 W24 (red line and red text for calibrated date ranges at 94.5% probability) (see Table 2, Figure 3, and Supplementary Figure S40). Note: Elevations vary across the site for all point types based on differences in sediment thickness and natural topographic variation. Site datum elevations (e.g., 497.24 mbd) are shown as black text, and the platinum (Pt), microspherule (MSp), and nanoparticle (Np) YD onset peak (ca. 12,875–12,775 cal BP; updated to IntCal20) [1] is shown as a yellow band between elevations of 497.235–497.245 mbd). Unfluted lanceolates, known as Haw River points, have been proposed as a morphological type that may be pre-Clovis in age but currently lack chronometric dating [3,5,79–81]. Early Triangular Lanceolates (ETL)/Haw River points are provisionally included in this sequence as possibly pre-Clovis in age, but this hypothesis will require chronometric dating in a secure stratified context.

geochemical patterns. These results highlight the value of SP-ICP-TOF-MS as a powerful analytical tool for detecting and characterizing subtle boundary-associated particulate signals in geoarchaeological and sedimentary archives.

Subtle excursions in $\delta^{13}\text{C}_{\text{soot}}$ and Hg immediately above the microspherule–PGE horizon may reflect localized environmental variability during the early Younger Dryas, although

the expression and significance of these proxies are likely archive-dependent.

Future work should prioritize replication of the horizon in additional intact profiles within the Smith Mountain Lake complex and expansion of proxy comparisons that help discriminate among sedimentological concentration effects, redox-related scavenging, and exogenic inputs (e.g., normalization to

conservative detrital proxies; targeted mineralogical and isotopic analyses of spherules and associated metallic particles; and integration with pollen or other paleoecological indicators). Even without resolving ultimate causation, the results demonstrate that the microspherule–PGE horizon at 44PY152 provides a robust stratigraphic marker within a compressed floodplain sequence that can materially improve correlation and interpretation of stratified Paleoamerican archaeological records.

METHODS

Microspherules and MDPs

To analyze sediment samples for microspherules and MDPs, we first weighed samples and then subjected them to 30 minutes of ultrasonication using a dispersant, sodium metaphosphate, to disaggregate the sediments. After ultrasonication, the samples were wet-sieved over a 20-micron sieve and dried under a heat lamp. The processed samples were then size sorted, and sediment fractions between ≥ 63 and < 125 microns and between ≥ 20 and < 63 microns were spread thinly on a large sheet of paper. A neodymium magnet, placed inside a plastic bag, was slowly moved over the size-sorted sediment fractions to extract the magnetic grains. This process is repeated three times to ensure the extraction of most magnetic grains. The extracted grains were then examined under a stereo binocular microscope to identify potential microspherules or metallic dust particle (MDP) candidates. When such candidates were present, they were placed on carbon SEM tape for further analysis by SEM and EDS (JEOL 6010 Plus LV). Only SEM and EDS analysis could confirm the identification of glassy or Fe-rich microspherules [11]. The microspherule counts and total sediment sample weight were used to estimate the number of microspherules per kilogram for each sample.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)

Standard practices were used for SEM analyses. At the University of Oregon, SEM images were acquired using a JEOL-6000 SEM system in low-vacuum mode and a ThermoFisher Apreo 2 SEM microscope to obtain high-resolution images of particles and their surfaces and to perform elemental analyses. At Elizabeth City State University, North Carolina, SEM images were acquired in low-vacuum mode using a JEOL-6000 SEM system. Using SEM-EDS, we manually selected for detection of the major elements with uncertainties of approximately $\pm 10\%$.

Bayesian radiocarbon chronology

For the Smith Mountain site, we used the OxCal Bayesian computer program with the IntCal20 calibration curve [6,28]. Within OxCal, we employed the “P_Sequence” code that produces models from groups of dates for which depth relationships are known. The program first calibrates all dates into calendar years, and then at every available depth, it selects the most probable age from each probability distribution. Next, it combines the ages for all depths into a depth profile for the age-depth model. Each date and the overall model are ranked on an

Agreement Index, where a value of $> 60\%$ approximately corresponds to a chi-squared distribution of $> 95\%$ probability. In OxCal, if the Agreement Index drops below 60% ($< 95\%$ CI), then that date is a potential outlier, i.e., either too old or too young for the model, and thus, a candidate for exclusion. All dates in the age-depth model that pass the chi-squared test ($> 95\%$) were accepted. Unless otherwise stated, all reported ages referring to the Smith Mountain Lake stratigraphy are Bayesian modeled calendar ages derived from OxCal P_Sequence modeling; calibrated radiocarbon ages are reported separately in Table 1.

Laser granulometry

Laser granulometry was conducted at the Department of Geology and Environmental Geosciences, College of Charleston. Approximately 0.3 g of each sample was analyzed for particle size using a CILAS 1180 laser particle size analyzer. Prior to analysis, samples were pretreated with 30% hydrogen peroxide (H_2O_2) to remove humic material and then soaked in a 50 g/L sodium metaphosphate solution to disperse clay aggregates. The CILAS 1180 measures particle sizes ranging from $0.04\text{ }\mu\text{m}$ to 2.5 mm, providing a continuous distribution of grain sizes across 100 size bins. GRADISTAT v. 8.0 was used to produce summary statistics of particle size data [85].

Single Particle Inductively Coupled Plasma Time-of-Flight Mass Spectrometry (SP-ICP-TOF-MS)

Particle extraction

For particle extraction, 100 mg of sediment samples were suspended in 10 mL of ultrapure water (UPW, Millipore Advantage System, Merck Millipore, Darmstadt, Germany) in 15 mL acid-washed plastic centrifuge tubes. The sediment suspensions were vortexed using a vortex mixer (Scientific Industries, G560, USA), followed by 15 minutes of batch sonication (Branson 2800, 40 kHz, Danbury, CT, USA) to disperse the particles. After sonication, the samples were left undisturbed for 24 hours to allow larger particles to settle. The top 5 mL supernatant was then transferred into acid-washed 15 mL centrifuge tubes and stored in a refrigerator at $4\text{ }^\circ\text{C}$ before single particle-inductively coupled plasma time-of-flight mass spectrometry (SP-ICP-TOF-MS) analysis. Just before SP-ICP-TOF-MS analysis, the samples were diluted 5000-fold in UPW, and the suspensions were sonicated both before and after dilution to enhance particle dispersion and minimize settling during analysis.

Particle composition on a single-particle basis

The elemental composition of individual particles was determined by SP-ICP-TOF-MS (TOFWERK, Thun, Switzerland), following methods described in our previous studies [86–88]. Samples were introduced into the ICP using a 2DX autosampler (Element Scientific, Omaha, United States) and a MicroMist U-series Nebulizer (Thermo Scientific, USA) connected to a Quartz Cyclonic Spray Chamber (Meinhard, USA) and then into the ICP torch. The SP-ICP-TOF-MS operating parameters and monitored isotopes together with their mass detection limits are detailed in Supplementary Tables S8 and S9, respectively.

Element-specific instrument sensitivities were measured in triplicate with multi-element solutions prepared from a mixed multi-element ICP certified reference standard (0, 1, 2, 5, and 10 $\mu\text{g/L}$ multi-element standard, diluted in 1% HNO_3 , BDH Chemicals, Radnor, PA, USA). Transport efficiency was calculated using the known size method with certified 60-nm Au ENMs (NIST RM 8013 Au, Gaithersburg, MD, USA) and a series of ionic Au standards (BDH Chemicals, West Chester, PA, USA) [89].

A 4.5% H_2/He gas mixture was used as collision gas to eliminate or minimize interferences, optimized specifically for $^{56}\text{Fe}+$ and $^{28}\text{Si}+$ signals. Data processing, including signal thresholding (using the Poisson algorithm [90]) and split event correction, was conducted using TOFPilot (Version 2.11.3, TOFWERK, Thun, Switzerland). The mass and size detection limits assuming pure metal and metal oxide phases are provided in Supplementary Table S9. All samples and UPW blanks were analyzed in triplicates, and data was acquired for 200 seconds per replicate. After confirming the reproducibility of single particle elemental composition and number concentrations among replicates, the data from the three replicates were combined to achieve comprehensive analysis due to limited detection events of certain elements.

SP-ICP-TOF-MS measurements quantify changes in elemental mass concentrations but do not, by themselves, establish particle provenance; interpretation relies on stratigraphic coherence and association with independent high-temperature proxies.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

Laser ablation on microspherules and MDPs was conducted at the Center for Elemental Mass Spectrometry (CEMS), University of South Carolina. Element concentrations were determined using a Photon Machines UV-Eximer 193 nm laser ablation system with a HELIX 2 sample cell in a He atmosphere, coupled to a Thermo ELEMENT 2 High-Resolution ICP-MS. Microspherule concentrations were determined by spot ablation with a 25 μm spot at 8 Hz and $\sim 11 \text{ J/cm}^2$ fluence. Relevant laser and ICPMS parameters can be found in [91]. Microspherules and MDPs were handpicked and mounted on glass slides with tape. Each spot was ablated for ~ 17 seconds. Tests were conducted to determine the potential overlap of the beam with the tape and the signals generated by ablating tape or glass slide. Each ablation spot data was manually screened for the potential of the beam to obliterate the specimen and hit the underlying tape. In those cases, only the portion of the signal from the unknown spot was used for reduction. We monitored masses ^{23}Na , ^{27}Al , ^{25}Mg , ^{29}Si , ^{43}Ca , ^{47}Ti , ^{51}V , ^{53}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{85}Rb , ^{88}Sr , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{98}Mo , ^{99}Ru , ^{101}Ru , ^{103}Rh , ^{105}Pd , ^{106}Pd , ^{137}Ba , ^{139}La , ^{140}Ce , ^{146}Nd , ^{149}Sm , ^{157}Gd , ^{163}Dy , ^{167}Er , ^{172}Yb , ^{178}Hf , ^{185}Re , ^{192}Os , ^{193}Ir , ^{195}Pt , ^{208}Pb , ^{232}Th , ^{238}U . Data reduction was performed manually following [91]. We used a combination of laser ablation standards and reference materials (NIST 612, BCR-2G) to quantify the Relative Sensitivity Factors (RSF) in silicate oxide-bearing

samples, as well as fragments of meteorites Hoba and Filomena and NIST SRM 1263 (Cr-V-steel alloy) to quantify the metal content in MDPs and the platinum group elements. For the silicate-rich samples, we assumed that the sum of the major cation oxides (MgO , FeO , CaO , TiO_2 , MnO , Al_2O_3 , Na_2O , SiO_2) was 98%, assuming that the rest of the analytes, including elements we did not analyze such as volatiles made the difference to the 100%. This protocol allows us to calculate the SiO_2 in wt% of the unknown, which then becomes the internal standard to calculate the rest of the analytes against the silicate standards listed above. For the MDPs, we summed the V, Cr, Mn, Fe, Ni, Co, Cu, and Zn metal content to 100% and used Fe as the internal standard, assuming no oxides, consistent with the SEM work reported earlier. The USGS Reference material BIR-1G was run as unknown to monitor precision and reproducibility against the preferred values; the data and the detection limits of the method are in Supplementary Table S10.

Magnetic susceptibility

Magnetic susceptibility (MS) is a property of sediments that measures the susceptibility of minerals to an induced magnetic field. For a given sample, sediment MS is an indicator of the combined strength of the magnetic minerals, such as magnetite and magnetite, present in the sample. In geoarchaeological contexts, MS can indicate paleoclimate [33], site formation processes, anthropogenic or natural firing [34], and often serve as a proxy for particle size [36]. The changes in MS over time allow for inferences to be made and hypotheses formulated as to the processes involved in the observed pattern of variation and allow for comparisons of stratigraphy between sites.

A ZH Instruments SM-30 magnetic susceptibility meter was used to collect *Volume Susceptibility K* of 27 samples collected at 1 cm intervals from Smith Mountain Lake site 44PY152. The readings were made on plastic sampling bags of sediment. A drift-corrected average of three readings was recorded for each sediment sample. The SM-30 has a 50 mm diameter pickup coil, an operating frequency of 8kHz, and a sensitivity of 1×10^{-7} SI Units.

A Bartington MS2B meter was used to collect *Mass-Corrected Susceptibility X* of 27 samples collected at 1 cm intervals from Smith Mountain Lake site 44PY152. The readings were made on $2 \times 2 \times 2 \text{ cm}$, 8 cc plastic cubes containing sediment centered in a 33 mm diameter instrument cavity. The MS2B operates at a low frequency (LF) of 0.465kHz $\pm 1\%$ and a high frequency (HF) 4.65kHz $\pm 1\%$. The amplitude of the applied field is 250uT peak $\pm 10\%$. The noise floor is $< 2 \times 10^{-5}$ SI Units. The sensitivity is 1×10^{-6} SI Units.

Total organic carbon, nitrogen, and soot

Organic carbon and total nitrogen were isolated in each sample. Dried and ground sediment samples from each depth interval were placed in ashed (450 $^\circ\text{C}$ for 4 hours) glass scintillation vials and acidified dropwise with 2 N HCl until effervescence ceased. Samples were then dried at 60 $^\circ\text{C}$ until the weight stabilized after which a small amount of each residual sample

was placed in a 5 mm × 9 mm tin capsule, weighed, and crimped. Samples were sent to the stable isotope facility at UNCW or the University of Florida to quantify OC and TN abundance and the isotopic signature of each element ($\delta^{13}\text{C}_{\text{OC}}$, $\delta^{15}\text{N}_{\text{TN}}$). The standard deviation of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements on isotopic standards interspersed with all samples were better than 0.2 and 0.5‰, respectively.

Soot was isolated from the residual OC using chemo-thermal oxidation (CTO-375; Gustafsson et al., 1997) [27]. Non-soot OC is oxidized thermally by placing each sample in an ashed aluminum foil pan and heating at 4 degrees/min 375 °C for 24 h. Soot carbon abundance and isotopic values were determined in a manner similar to that of OC.

Stable C and N isotope analysis of sediments

Homogenized sediments were transferred to tin capsules and combusted in a Costech 4010 elemental analyzer interfaced with a Thermo Delta V Plus stable isotope mass spectrometer at the University of North Carolina Wilmington (UNCW). Carbon and nitrogen isotopic signatures ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of the samples were expressed in the standard delta unit notation (δ) as $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$ (‰) = $[(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$, where R is $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$, respectively. Repeated measurements of USGS 40 and 41 glutamic acid standards indicate that the precision of these analyses is better than 0.5‰.

Mercury (Hg)

All mercury (Hg) analyses were performed at the Geochemistry of Ancient and Modern Environmental Systems (GAMES) Laboratory at the College of Charleston. Briefly, samples were dried in a gravity oven at low temperatures to minimize Hg volatilization. Samples were then lightly ground and homogenized using a mortar and pestle. Approximately 50–100 mg of each powder were added into a nickel measuring boat and then placed into a DMA-80 evo (Milestone, Inc., Shelton, CT). Samples were heated in stages to 750°C, and volatilized Hg was collected by gold amalgamation and measured via spectral analysis. The raw Hg data were calibrated using international reference standards (CRM DORM-5 and CRM TORT-3). The average concentration of CRM TORT-3 was 291.7 ng/g (± 8.8 ng/g; $N = 18$). The average concentration of CRM DORM-5 was 315.2 ng/g (± 2.6 ng/g; $N = 9$). Approximately 1/3 of the samples were replicated at least two times, and the average 2-sigma standard deviation of these replicate analyses is ± 0.5 ng/g, with a range of 0.1 to 1.0 ng/g.

X-RAY POWDER DIFFRACTION (XRD)

Select Fe-rich magnetic grains (Supplementary Figure S28) were prepared for XRD analysis using a Bruker D8 Advance® diffractometer with methods described in Schroeder [92]. Grains were mounted on “zero-background” plates, which are polished single quartz crystals cut 6° of the c -axis to direct substrate response away from the detector and minimize noise. The sample was rotated at 15 rpm, which, at angles below 15° 2 θ , causes some cropping of the signal by the sample holder.

Reasonable signal to noise (>1) was returned below 60° 2 θ to make peak assignments for matching with XRD patterns in the International Centre for Diffraction Data (ICDD) powder diffraction database (PDF) PDF4+.

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SUPPORTING INFORMATION

SI. Supporting information. Additional figures, tables, and methods. (PDF) <https://zenodo.org/records/19667623>.

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DATA AVAILABILITY

All data generated or analyzed during this study are included in this published article and Supplementary Information.

SAMPLE AVAILABILITY

Samples from 44PY152 are mostly depleted, but limited amounts may be available from the Corresponding Author.

AUTHOR CONTRIBUTIONS

All authors reviewed and approved the manuscript. Author C.R.M. designed the study; C.R.M., J.A.M.G., W.C., M.A.L., A.W., M.J.D. wrote the paper; C.R.M., J.A.M.G. and W.C. designed and conducted the fieldwork, and M.B., M.B., T.A.F., S.M., C.S.L., T.R.T., M.S.H., V.A., K.A.L., M.A., P.A.S., A.T., J.J., and M.J.D. contributed data and technical analysis for the paper.

POTENTIAL CONFLICTS OF INTEREST

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