

Biogeochemical evidence for environmental changes of Pleistocene Lake Olduvai during the transitional sequence of OGCP core 2A that encompasses Tuff IB (~1.848 Ma)

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ABSTRACT

Olduvai Gorge is renowned for discoveries of hominin fossils and tools in a well-resolved sedimentary context, representing one of the foremost sites in East Africa that has afforded critical evidence of hominin evolution. In 2014, the Olduvai Gorge Coring Project (OGCP) recovered the first deep sediment cores from this location. These cores provide the first opportunity to examine an extensive stratigraphic record from one location and independent of the weathering and related degradation typical of outcrop samples. Samples from these cores have been correlated to Bed I tuffs and basalt marker beds that are well characterized from outcrops within the gorge. This study focuses on the biogeochemical investigation of a ~10 m segment from OGCP sediment core 2A, where age constraints indicate deposition occurred over ~50,000 years (from 1.8055 ± 0.003 Ma to 1.8551 ± 0.013 Ma). The segment includes Tuff IB and IF, which were deposited at a time that prior research indicates represents marked changes in the paleoenvironment at Olduvai, with indications that Paleolake Olduvai may have been completely desiccated by the time Tuff IF was deposited. This environmental change is recorded by the composition of sedimentary organic matter (OM) in terms of bulk organic geochemical properties observed as a decrease in % TOC and $\delta^{13}\text{C}_{\text{org}}$. In addition, temporal variations in source-specific biomarkers (*n*-alkanes, phytane, steradienes, A-norsteranes and alkenones) reflect a shift from a deeper lake setting with a prevalence of aquatic-sourced OM combined with input from terrestrial plant waxes to a more shallow, perennial lake where evidence of burrows and erosional surfaces is associated with microbially degraded OM and intermittent aquatic biomarkers. Thus, variations in biogeochemical proxies complement the sedimentological evidence confirming increased periods of prolonged desiccation of Paleolake Olduvai beginning around the time of Tuff IB deposition.

1. Introduction

The depositional record of Olduvai Gorge, Tanzania, comprises a ~2 Myr sequence of fluvial-lacustrine and volcanic deposits providing an extensive, rich legacy of fossil and archaeological finds, and contributing substantively to the understanding of hominin evolution during a critical period of Earth's climate history (e.g., Hay, 1976;

deMenocal, 2004; Trauth et al., 2005; Trauth et al., 2007; Maslin et al., 2014). In particular, the interval of the Pleistocene from ~2.0 to 1.7 Ma corresponds to a significant change in the climatic coupling of ocean and atmosphere linked to the development of the Walker Circulation (e.g., Trauth et al., 2005; Trauth et al., 2007; Maslin et al., 2014), although there is evidence to suggest that zonal circulation occurred in equatorial regions before this time (Zhang et al., 2014). In East Africa,

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evolutionary developments accompanied the changes in climate during this ~300,000 year interval that are characterized by key evolutionary events including peak diversity among hominin species (Shultz et al., 2012; Maslin et al., 2014), the advent of a marked increase in hominin cranial capacity (deMenocal, 1995, 2011; Shultz et al., 2012; Antón et al., 2014; Maslin et al., 2014, 2015), and notable early hominin migration (Agusti and Lordkipanidze, 2011; Antón et al., 2014; Maslin et al., 2014).

Numerous studies employing various methodologies have sought to better understand the paleoenvironmental context of archaeological occurrences at Olduvai Gorge. Previous research has been based on samples collected from either outcrops or trenches dug into the sides of the gorge, approaches that have both benefits and limitations. One benefit is that outcrops and trenches enable assessment of lateral variations in sedimentology and stratigraphy aided by the substantive range of outcrop/trench locations at Olduvai Gorge with stratigraphic correlation facilitated by the presence of diagnostic marker beds, such as tuffs.

A key stratigraphic unit of Olduvai Gorge, Upper Bed I (e.g., McHenry, 2012; Stanistreet et al., 2018) previously referred to as Bed I (Hay, 1976), contains many archaeological and vertebrate fossil assemblages, including early hominins. These Pleistocene deposits span ~74 kyr, bracketed by the Bed I Basalt and Tuff IF, dated, respectively, at 1.877 ± 0.013 Ma and 1.803 ± 0.002 Ma (Deino, 2012). Other tuffs within the Bed I deposit, such as Tuff IB, 1.848 ± 0.003 Ma (Deino, 2012), provide additional marker horizons for correlation between outcrops and help improve age constraints. The Bed I deposit also contains the “*Zinjanthropus* horizon,” a well-studied stratigraphic interval in which an unusually high volume of hominin artifacts and butchered bones are preserved, suggesting that it represents a time of extensive hominin activity in the gorge (Potts and Shipman, 1981; Blumenschine, 1995; Ashley et al., 2010b; Blumenschine et al., 2012a, 2012b; Njau and Blumenschine, 2012; Driese and Ashley, 2016; Aramendi et al., 2017). The ability to correlate Bed I deposits based on their plentiful fossil assemblages and numerous marker beds has helped make the Bed I deposits the focus of many previous paleoenvironmental reconstruction studies based on samples from outcrops and trenches within the gorge (e.g., Barboni et al., 2010; Albert and Bamford, 2012; Bennett et al., 2012; Stanistreet, 2012; Blumenschine et al., 2012a;

Magill et al., 2016; Aramendi et al., 2017; Albert et al., 2018; Stanistreet et al., 2018). Thus, it has been possible to reconstruct the types of vegetation found within the Olduvai Basin (e.g., Ashley et al., 2010a; Albert et al., 2015, 2018) to help characterize the paleo-landscape encountered by early hominins. Such studies have also provided evidence for temporal variations in the vegetation during deposition of Bed I (e.g., Magill et al., 2013a, 2013b) reflecting changes in the environmental conditions over this time interval. Spatial differences are also apparent with evidence for grassland in one area of the basin (Bamford et al., 2008) while another area contained forest surrounded by bushland during the same time period (Barboni et al., 2010; Albert et al., 2018). Additionally, such local variations in plant communities have been associated with hominin activities (Magill et al., 2016). Collectively, research focused on outcrops and trenches has demonstrated the ability to reconstruct the paleoenvironment encountered by hominins, however efforts to interpret regional characteristics of the paleo-landscape by collating evidence across various sites has challenges related to the inherent localized features in vegetation.

Building a comprehensive understanding of the depositional history of Paleolake Olduvai requires a compilation of findings from multiple sites as no single outcrop or trench within the gorge provides exposures that span the entire stratigraphic record. In addition, biogeochemical studies of sediment samples collected from outcrops and trenches tend to be limited to assessment of robust proxies (e.g., Magill et al., 2013a, 2013b; Driese and Ashley, 2016; Dominguez-Rodrigo et al., 2017) able to survive exposure to the atmosphere. In the case of biomarkers, even those robust enough to survive exposure often still experience some loss due to weathering, thus requiring larger amounts of sample for successful analysis, which typically decreases the temporal resolution. Evaluation of more labile proxies, including those based on biomarkers susceptible to degradation upon exposure to oxygen, requires better preserved sediments. The cores collected by OGCP in 2014, especially sediment core 2A (Fig. 1) which targeted the inferred depocenter of Paleolake Olduvai during Bed I deposition, help achieve this goal because of the sediment sequences containing well-preserved organic matter that enable biomarker analyses to be conducted with high temporal resolution (Colcord et al., 2018).

The fluvio-lacustrine sedimentary sequences recovered by OGCP provide the opportunity to develop climatic and environmental records

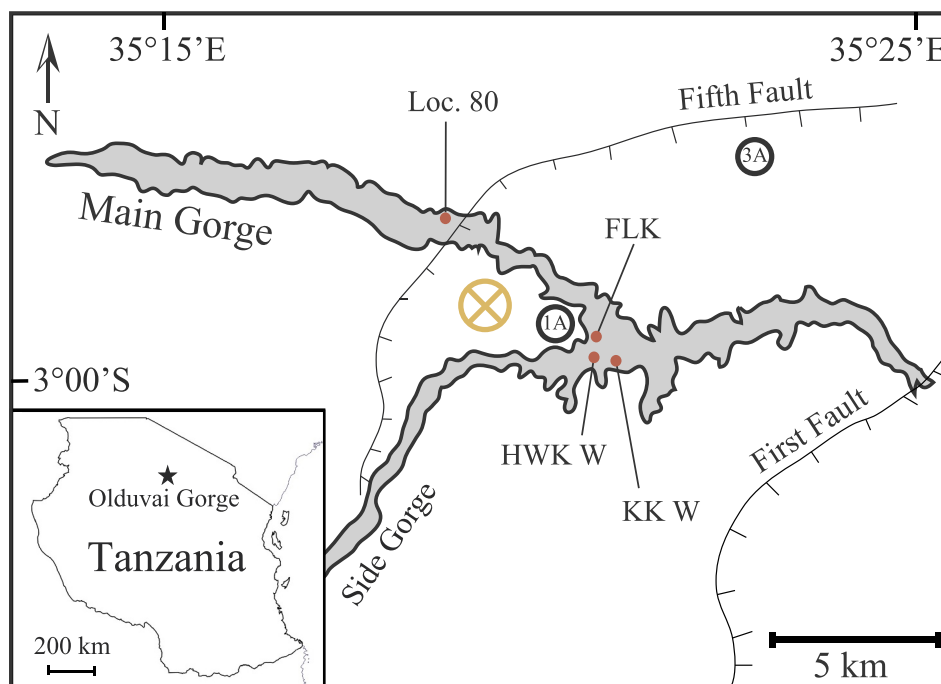


Fig. 1. Map showing the location of Borehole 2A (Orange circle with X in it) and Boreholes 1A and 3A (black circles) in the context of Olduvai Gorge. Also noted on the map are major faults and outcrop/trench sites (red dots): Locality 80, KK W, HWK W and FLK. Inset map showing location of Olduvai Gorge within Tanzania. Modified from Colcord et al., 2018. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

based on biogeochemical proxies that can complement and enhance those determined from analogous studies of outcrops and trenches. The current investigation examines the bulk organic geochemical composition and the distributions of biomarkers in a ~10 m segment of OGCP sediment core 2A (66.3–76.4 m borehole depth), focusing on three specific objectives: (i) elucidating the characteristics of the Paleolake Olduvai depositional setting by profiling diagnostic biomarkers for aquatic biota and terrestrial vegetation, and using biogeochemical proxies to assess temporal variations in the Olduvai paleoenvironment, (ii) identifying biogeochemical evidence of changes in the depositional environment, especially those reflecting transitions associated with the deposition of Tuff IB or in its immediate aftermath, and (iii) assessing temporal variations in molecular signatures from biota that reflect longer-term trends in the evolution of Paleolake Olduvai and the overall environment of the Olduvai Basin.

2. Background

2.1. Study site

Research activities at Olduvai Gorge, located adjacent to the eastern branch of the East African Rift System (EARS) in northern Tanzania (Fig. 1), have yielded numerous discoveries of hominin fossils and stone tools that represent significant scientific contributions to human origins research. Olduvai Gorge exposes outcrops of Pleistocene fluvio-lacustrine deposits that span ~2 Myr (Hay, 1976) and include materials sourced from the Ngorongoro Volcanic Highlands to the east of the gorge where several volcanoes have been active at different times in geologic history. Among these volcanoes, Olmoti has been identified as the likely source of tuffs deposited within Bed I of Olduvai Gorge (Mollet and Swisher III, 2012). Geochemical fingerprinting of tuffs and basalt within the gorge has been instrumental in correlating stratigraphic units and, most recently, helped establish the relationships of OGCP cores to the gorge succession (Stollhofen et al., 2008; McHenry, 2012; Habermann et al., 2016; McHenry et al., this volume; Stanistreet et al., 2019).

The stratigraphic succession in Olduvai Gorge contains multiple episodes of lacustrine deposition during the evolution of Paleolake Olduvai, with some of the most studied lacustrine sediments coming from Bed I deposits. Laminated lacustrine deposits from Bed I found at Location 80 in the gorge have been identified as “central basin” deposits (e.g., Hay, 1976; Hay and Kyser, 2001) (Fig. 1), whereas sediments to the east and west of Location 80 are described as lake margin deposits. There is also evidence, however, that the extent of Paleolake Olduvai varied during Bed I times (e.g., Sikes and Ashley, 2007; Stollhofen et al., 2008; Bamford et al., 2008; Barboni et al., 2010; Stanistreet, 2012; Beverly et al., 2014). Specifically, during Bed I times, Paleolake Olduvai was a broad, mostly hydrologically closed, saline-alkaline lake, with sedimentological evidence indicating a significant drying event in the area during deposition of the later part of Bed I potentially resulting in multiple prolonged desiccation episodes (Hay, 1976; Hay and Kyser, 2001; Sikes and Ashley, 2007; Stollhofen et al., 2008; Bamford et al., 2008; Barboni et al., 2010; Deocampo et al., 2017).

Prior isotopic analyses have indicated that annual rainfall during deposition of Bed I may have been as high as 800 mm/year, especially during wetter seasons (Sikes and Ashley, 2007). The rain shadow effect of the Ngorongoro Volcanic Highlands and the positions of both the Inter-tropical Convergence Zone (ITCZ) and the Congo Air Boundary (CAB) (also known as the Inter-oceanic confluence) affect precipitation levels in this region (Nicholson, 2000). Changes in insolation and the resultant heating of the surface lead to variations in the annual location and extent of the ITCZ and CAB (Nicholson, 2000). Today, the climate at Olduvai Gorge reflects its equatorial location (~3°S) and

concomitant limited fluctuations in temperature, which combine to create an annual weather cycle predominantly controlled by precipitation availability (Nicholson, 2000). Thus, the Olduvai region currently experiences two rainy seasons in a year, a “long rain” from March to May, and a “short rain” from October to December (e.g., Magill et al., 2013b).

2.2. Core sampling

The OGCP collected ~245 m of sediment core from borehole 2A (02° 58' 43.0" S, 035° 19' 25.5" E; Stanistreet et al., 2019). Site 2A was chosen to target the thickest Bed I sequence thought to correspond to the depocenter of Paleolake Olduvai (Stanistreet et al., 2019). This study focuses on a ~10 m segment of sediment core 2A (66.3–76.4 m depth) which includes the critical “*Zinjanthropus* horizon” (Blumenschine et al., 2012a; Magill et al., 2016), which indicates the presence of hominin within the Olduvai Basin during this time. Overall, this section of Bed I in OGCP Core 2A can be correlated to outcrops based on the presence of Tuff IF (~66 m depth) and Tuff IB (~72 m depth) identified within the core segment studied here and further constrained by the presence of the Bed I Basalt (~90 m depth) below (McHenry et al., this volume).

The total recovery for OGCP sediment core 2A was ~94%, with care taken to avoid contamination by lubricants and other petroleum products during and after drilling. After recovery, the core was tubed, sealed, and shipped to the National Lacustrine Core Facility (LacCore) at the University of Minnesota for sampling and storage. Once split, a series of samples spanning 3 cm were collected from the center of the core to avoid potential contamination along the edges. Samples were taken at ~16 cm intervals throughout the 10 m (66–76 m) segment of core 2A for both bulk organic geochemical analyses (< 1 g per sample) and detailed biomarker analyses (< 20 g per sample).

2.3. Biogeochemical proxies

The analysis of organic matter (OM), both autochthonous and allochthonous, preserved in lacustrine sediments provides a well-established proxy for the determination of past climates and environments and identification of how and why changes occurred (e.g. Meyers and Ishiwatari, 1993; Castañeda and Schouten, 2011). Bulk characteristics, such as total organic carbon (% TOC), can provide an indication of the quality of preservation as well as an insight into the productivity of the system. Changes in bulk carbon isotopes ($\delta^{13}\text{C}_{\text{org}}$) aid in reconstructions because they can record evidence for the relative contributions of terrestrial input from C_3 or C_4 vegetation. Carbon isotopes can also help identify sedimentary OM contributions from bacteria (e.g., purple sulfur bacteria; Hartgers et al., 2000) or methanotrophs (e.g., Bian et al., 2001). The distribution of suites of biomarker compounds can be used to monitor environmental changes (i.e. series of steranes such as C_{28} and C_{29} steranes or *n*-alkane homologs). At the same time, the presence of a source-specific organic compound, one with a known source organism, can also provide crucial information as its presence indicates the existence of that organism's habitat (i.e. alkenones produced by haptophyte algae, an aquatic organism, indicates the presence of an aquatic environment). In this study a number of these different proxies are employed to understand the paleoenvironment and how it changed during a critical time at Olduvai Gorge. In terms of methodology the approach is similar to previous research on Bed I core samples (Colcord et al., 2018; Colcord et al., this volume), however the core segment examined here overlies the previously studied Bed I Basalt to Tuff IB segment and contains both the time of the “*Zinjanthropus* horizon” and deposition of marker bed Tuff IF, which defines the top of Bed I.

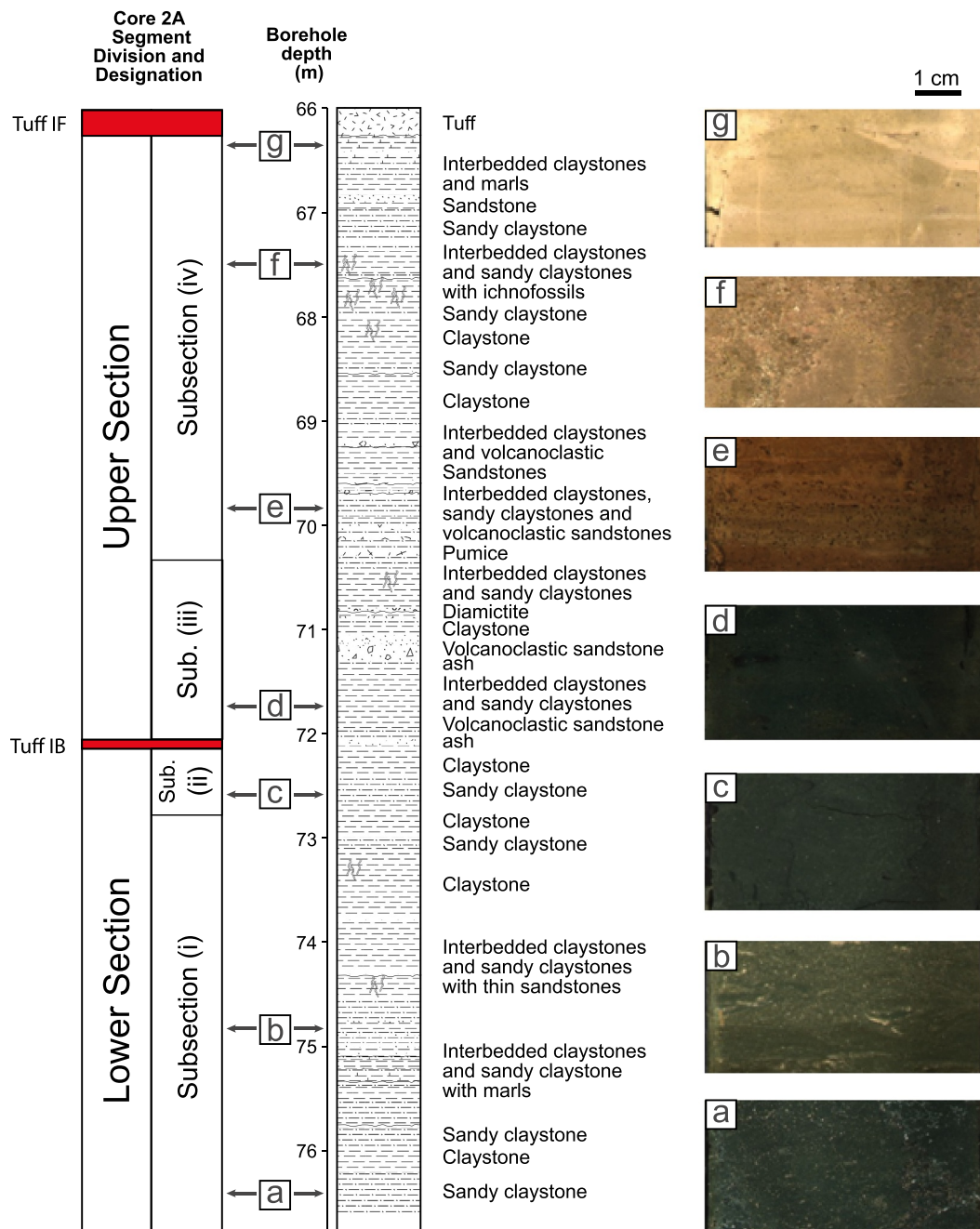


Fig. 2. On the left, an illustration showing how this segment of Core 2A has been divided and to what depths the designations used within this article refer. In the middle, a stratigraphic column is included for this segment of Core 2A, with borehole depth in meters to the left of the stratigraphic column and descriptions to the right of it. On the right of the figure are images of the core corresponding to sample locations, each has been identified with a lower-case letter, that letter is used in Figs. 3, 4, and 5 to indicate the samples associated which each as well as on the stratigraphic column of this figure, arrows indicate from the position of each image within the core segment. Red boxes indicate the locations of Tuff IF (1.803 ± 0.002 Ma) and Tuff IB (1.848 ± 0.003 Ma) within the core. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Methods

3.1. Core description

The visual characteristics of this ~10 m segment of core 2A (66.3–76.4 m depth; Fig. 2) reveal its natural division into two distinct parts. The sediment below Tuff IB, designated here as the Lower Section (72.2–76.4 m), comprises an alternating sequence of smectitic claystone and sandy claystone, with occasional thin marls below 75.4 m succeeded by intercalated thin sandstones (74.8–75.4 m). The Lower Section contains comparatively few instances of root traces/burrows

and erosion surfaces and no evidence of either in situ or reworked volcanic deposits (Stanistreet et al., 2019). The division between the two parts of the core segment is marked by Tuff IB (~72.2 m). The sediment between Tuffs IB (~72.2 m depth) and IF (66.0–66.3 m depth), designated here as the Upper Section (66.3–71.7 m), contains a series of volcanoclastic sandstones intercalated with dominantly claystones/sandy claystones toward the base (68.6–72.1 m depth), followed by clay-rich sediments varying from smectitic claystones to sandy claystones with marls toward the top of the section (66.3–68.6 m depth). The sediments in the Upper Section are generally characterized by red/tan colors, except for several centimeters above Tuff IB,

designated here as Subsection (iii), where the core color is very dark, appearing almost black and resembling the Lower Section, before grading into increasingly lighter colors found in Subsection (iv). In addition, within the Upper Section are multiple horizons with ichnofossils as well as numerous erosion surfaces. Images from the core segment (Fig. 2) place these descriptions in a stratigraphic context.

3.2. Chronology

Three key marker beds (Bed I Basalt, Tuff IB, and Tuff IF), previously dated from outcrops (Deino, 2012), were identified within OGCP core 2A via geochemical fingerprinting (Stollhofen et al., 2008; McHenry, 2012; Habermann et al., 2016; Stanistreet et al., 2019). Linear extrapolation between these three dated horizons indicates that the examined ~10 m (66.3–76.4 m depth) segment of Core 2A represents ~50,000 years (1.803 ± 0.002 Ma to 1.8551 ± 0.013 Ma). In addition, the marker beds enable sediment accumulation rates to be calculated as 62 cm/kyr for the Lower Section by using linear age interpolation and assuming constant sedimentation between the Bed I Basalt at ~90 m (1.877 ± 0.013 Ma) and Tuff IB at ~72 m (1.848 ± 0.003 Ma). For the Upper Section, applying the same approach employing the ages for Tuff IB at ~72 m (1.848 ± 0.003 Ma) and Tuff IF at ~66 m (1.803 ± 0.002 Ma) yields a sediment accumulation rate of 13 cm/kyr.

3.3. Bulk organic geochemical analyses

Samples (< 1 g per sample) were stored frozen and freeze dried prior to treatment with excess 1 N HCl to dissolve carbonate. Once dissolution was complete, each sample was rinsed to attain neutral pH and then again freeze dried. Samples were analyzed at Indiana University's Stable Isotope Research Facility (SIRF) via elemental analysis – isotope ratio mass spectrometry (EA-IRMS) (e.g., Colcord et al., 2018) to determine percent total organic carbon (%TOC) and the carbon isotopic composition of bulk organic matter ($\delta^{13}\text{C}_{\text{org}}$). Carbon isotope values were normalized to the Vienna Pee Dee Belemnite (VPDB) standard, using acetanilide ($-29.53\text{‰} \pm 0.01$) and ethylene diamine tetraacetic acid ($-40.38\text{‰} \pm 0.01$) standards provided by Dr. A. Schimmelmann of Indiana University.

3.4. Biomarker analyses

In total, 54 samples (< 20 g per sample) were selected for biomarker analyses from the ~10 m segment of core 2A, 25 samples from the Lower Section and 29 samples from the Upper Section. Samples were packed in 66 ml cells, extracted at 100 °C and 1200 psi using 9:1 (v:v) dichloromethane/methanol in three 15-minute cycles, using an Automated Solvent Extractor (ASE). The resulting total lipid extract (TLE) for each sample was separated through two rounds of column chromatography, first silica gel and second via alumina columns, eluting sequentially. Complete details of the extraction method can be found in the Supplemental material. The apolar and ketone fractions were dried under nitrogen, dissolved in an appropriate amount of hexane (ranging from 250 to 1000 μl) based on %TOC, and analyzed via Gas Chromatography by Quadrupole Time-of-Flight Mass Spectrometry (GC-QTOF-MS) for identification and quantification of organic compounds at Indiana University's Mass Spectrometry facility. Quantifications utilized a squalane standard provided by A. Schimmelmann of Indiana University. The detection limit for all biomarker measurements was determined as 0.01 $\mu\text{g/gC}$; hence, lack of a data point in core profiles indicates that the specific compound was below the detection limit.

4. Results and interpretation

4.1. Chronology

The Lower Section, comprising over four meters of sediment from below Tuff IB (72.2–76.4 m), spans ~7100 years, based on the assumption of continuous sedimentation and a linear interpolation between marker beds. Thus, the calculated sediment accumulation rate (~0.062 cm/year) means that each 3 cm biomarker subsample from the Lower Section spans ~50 years, with an average of < 300 years estimated between samples. The Upper Section comprises over five meters of sediment between Tuff IF and Tuff IB (66.3–71.7 m), and corresponds to a time span of ~40,500 years, again assuming continuous sedimentation and linear interpolation between marker beds. The resulting sediment accumulation rate is therefore lower, ~0.13 mm/year, and means that each 3 cm biomarker subsample from the Upper Section spans ~225 years, with an average of > 1000 years between samples. These assumptions do not account for near-instantaneous events, notably ash layers, nor for possible hiatuses, which are likely to exert a significant effect on the age model. However, the age interpolation places constraints on the approximate timespan represented by each sample and the time interval between individual samples. The calculated rates illustrate the marked difference between sediment accumulation during deposition of the Lower and Upper Sections, which is pertinent to interpretations of biogeochemical records for this section of OGCP Core 2A.

Visual inspection of the cores indicates that this ~10 m segment of core 2A contains a number of depositional hiatuses, indicated by soil development. The approximations of sediment accumulation rates for the Lower Section and Upper Section of this segment are therefore minimum values, which clearly fail to account for variations over time but allow downcore data to be plotted against time. This approach affords a more accurate representation of temporal variations (Fig. 3B) than plots against depth (Fig. 3C), and better illustrates that the Lower Section provides a higher resolution record, albeit for a much shorter time interval.

4.2. Depositional setting

The dominant lithology of gray-olive colored “waxy” claystones in the Lower Section matches previous descriptions (Hay and Kyser, 2001; Ashley and Hay, 2002) attributed to sediments deposited in the center of Paleolake Olduvai which was interpreted to be a playa lake. By contrast, the sediments from the Upper Section parallel the description of deposits from the margin of the lake (Ashley and Hay, 2002; Stanistreet, 2012), as this sequence of claystone varies in color from olive-brown-yellow. Thus, the lithologic descriptions of the ~10 m segment of OGCP core 2A are consistent with the general interpretation that the depositional setting for the Lower Section was a deeper lake where oxygen levels were low (dysoxic), while the depositional setting of the Upper Section was that of a shallower lake, where subaerial exposure was more likely to occur.

The prevalence of sandstones, sediment hues indicative of oxidation, and the frequent occurrences of roots/burrows, soil development, and erosion surfaces indicate a shallower lake environment during the deposition of the Upper Section, characterized by multiple episodes when core site 2A was completely dry for a period of time. This culminated at the time of Tuff IF (Stollhofen et al., 2008; Bamford et al., 2008), which is thought to have been deposited when the lake was virtually empty. In addition to these visual indications of a shallower lake environment, evidence for the progradation of the Olmoti Fandelta into the Olduvai Basin has been previously noted (Hay, 1976; Stanistreet, 2012) and more recently identified in OGCP Boreholes 1A and 3A (Stanistreet et al., 2019; Stollhofen et al., this volume). The

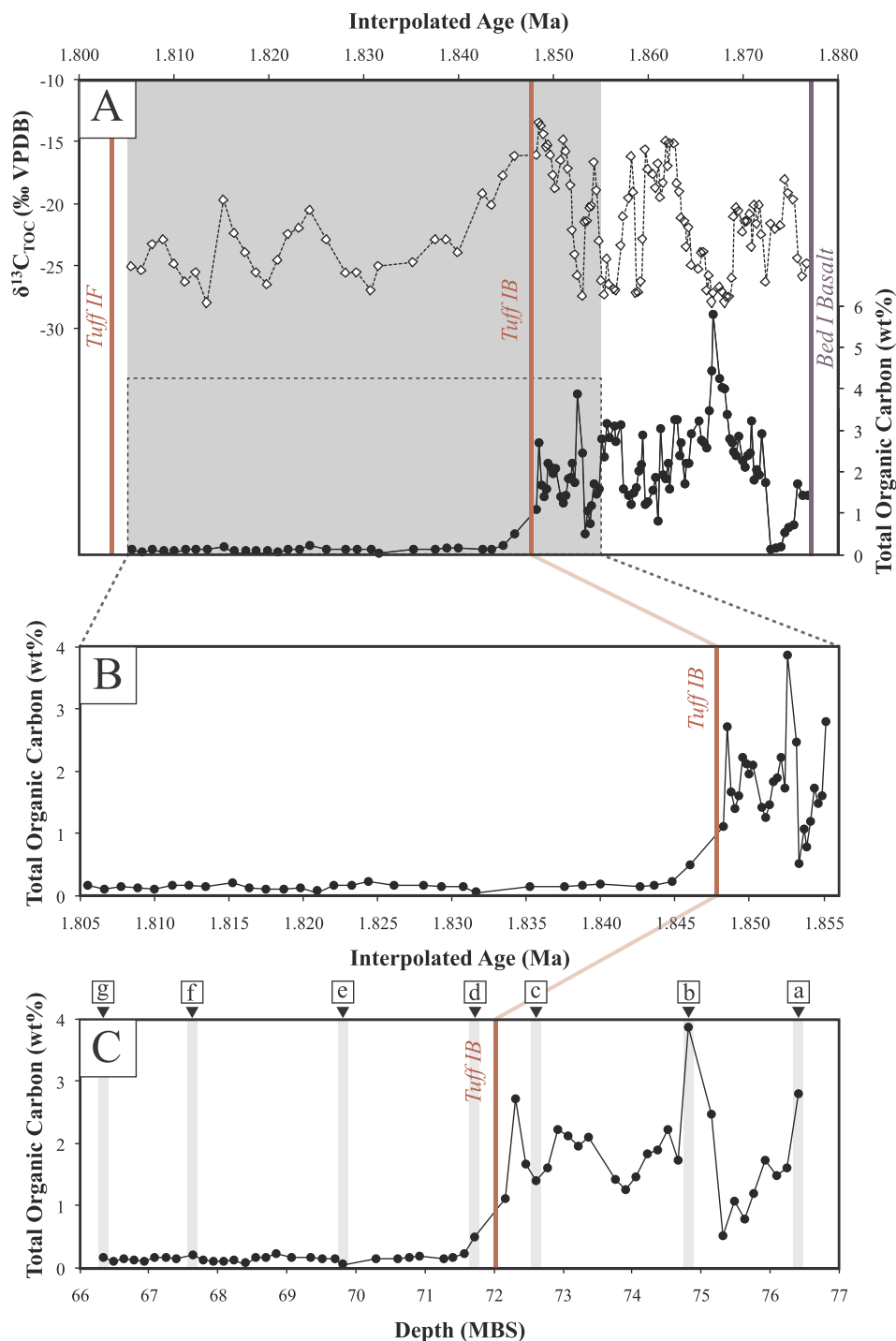


Fig. 3. Bulk organic geochemistry results. (A) Showing bulk $\delta^{13}\text{C}_{\text{TOC}}$ and Total Organic Carbon (wt%) plotted by age for an extended portion of Core 2A, includes data previously published in Colcord et al., 2018. Tuff IF (1.803 ± 0.002 Ma) and Tuff IB (1.848 ± 0.003 Ma) have been indicated with red lines, and Bed I Basalt (1.877 ± 0.013 Ma) with a purple line. The segment of Core 2A focused on for this study has a gray background. The dashed box indicates the focus of plot B. (B) % TOC for the study segment of Core 2A, plotted by age. Tuff IB is indicated by the continued red line. (C) Again, TOC for the study segment of Core 2A, this time plotted by depth. Tuff IB indicated by the continued red line. Above plot C, black triangles pointing to gray shaded areas that contain the data points corresponding to the images on Fig. 2, identified by lower case letters, for example: (a) on the graph points to the sample collected from location (a) on Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Upper Section should be visualized as the most distal toe end of the westward prograding fan-delta body (Stanistreet et al., 2019). Periods of subaerial exposure of lake beds alternated with wetter intervals with more water in the lake, during which the lake expanded and claystone deposition occurred. The trend toward drier conditions in this segment of OGCP core 2A corresponds with the interpretation proposed by several other researchers (e.g. Hay, 1976; Hay and Kyser, 2001; Ashley and Hay, 2002; Stollhofen et al., 2008; Barboni et al., 2010; Stanistreet, 2012; Deocampo et al., 2017) that the interval between deposition of Tuff IB and Tuff IF, and particularly just prior to Tuff IF, was characterized by repeated prolonged desiccation events and lake regression, up to complete drying of the lake.

4.3. Bulk organic geochemistry

Total organic carbon (TOC wt%) varies between the Lower and Upper Section (Table 1) as the amount of preserved organic matter (OM) decreases markedly during the interval of Tuff IB deposition, Subsections (ii) and (iii) (Fig. 3). The average % TOC for the Lower Section and Upper Section are 1.8% and 0.15%, respectively. The range of values for these two parts of the core segment differ by almost an order of magnitude (approximately 10×) (Table 1), with the minimum value for the Lower Section (0.5–3.9%) corresponding to the maximum value for the Upper Section (0.05–0.5%). The values for the Lower Section are comparable to those of the underlying lacustrine deposits in OGCP core 2A that extend down to the Bed I basalt (Colcord et al.,

Table 1

Results of the bulk organic geochemical and biomarker analyses for both the Upper Section and Lower Section. Averages and ranges for biomarkers do not include samples that were below the detection limit of 0.01 µg/gC.

	Upper Section (66.3–71.7 m)		Lower Section (72.2–76.4 m)	
	Average	Range	Average	Range
Bulk organic geochemistry				
Total C _{org} (%)	0.15	0.05 to 0.50	1.80	0.50 to 3.90
δ ¹³ C _{org} (‰)	−23.4	−28.0 to −16.2	−18.9	−27.5 to −13.5
Biomarkers				
Alkenones (µg/g C)	7.26	0.09–48.5	77.6	0.09–319
A-norsteranes (µg/g C)	0.97	0.04–4.29	12.5	0.12–35.6
Steradienes (µg/g C)	0.08	0.06–0.14	11.5	0.03–50.8
Phytane (µg/g C)	2.49	0.05–15.8	3.86	0.19–13.9
n-C ₁₇ (µg/g C)	2.63	0.15–9.55	5.22	0.32–21.0
Carbon preference index (CPI)	2.1	1.1–3.5	4.0	2.8–5.1
Dominant source of n-alkanes	Microbial/terrestrial		Terrestrial/mixed	
Core descriptions				
Claystone color		Tan/red		Gray/black
Roots/burrows/bioturbation		Frequent		Uncommon
Volcanic deposits		Reworked & in situ		None

$$\text{CPI} = [\text{C}_{23} + 2 * (\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31})] / [\text{C}_{33} + 2 * (\text{C}_{24} + \text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32})]$$

2018) and indicate an environment conducive to OM preservation. The marked decrease in % TOC values for the Upper Section reflects an environmental change that resulted in a significant decline in the supply of OM and/or enhanced post-depositional degradation of OM. Indeed, the Upper Section has % TOC values similar to those reported from outcrop samples of the same stratigraphic section of Bed I lacustrine sediments (0.1–0.9% TOC; Magill et al., 2013a). Thus, the occurrence of claystone throughout the Upper Section, combined with colors indicative of subaerial exposure and % TOC values comparable to outcrops, provide evidence that this depositional sequence from OGCP core 2A was oxidized and portions exposed prior to burial. This level of degradation suggests that, similar to what has been inferred from outcrop samples, the more labile biomarkers are likely poorly preserved in the Upper Section. However, in the Lower Section the % TOC values are markedly higher than those reported from outcrop samples of the same stratigraphic section (Magill et al., 2013a) and similar to those reported for a ~10 m segment of core underlying the one studied here (76.4–89.8 m; Colcord et al., 2018), which showed good OM preservation.

The range of δ¹³C_{org} values for the Lower Section is comparable to that observed in the underlying lacustrine sequence (OGCP core 2A, 76.4–89.8 m; Fig. 2; Colcord et al., 2018), which can be attributed to temporal changes in the proportions of OM contributions from C₃ and C₄ plants as previously reported for outcrop data from Olduvai Gorge (Magill et al., 2013a). Within the sequence the maximum and minimum δ¹³C_{org} values are broadly comparable to end-member for C₄ and C₃ plants (e.g., Tipple and Pagani, 2007), which suggests that δ¹³C_{org} values for the Lower Section are largely unaffected by microbial alteration processes, especially in soils that can preferentially degrade the C₄ plant signatures (e.g. Wynn and Bird, 2007). Additionally, the δ¹³C_{org} values of the Lower Section show rapid, sub-Milankovitch shifts between C₃ versus C₄ dominance, again consistent with the underlying lacustrine sequence (OGCP core 2A, 76.4–89.8 m; Fig. 2; Colcord et al., 2018). The δ¹³C_{org} values decrease in the aftermath of Tuff IB, Subsection (iii) (Fig. 3) and then vary in the −20‰ to −28‰ range in Subsection (iv), albeit with fluctuations recorded at markedly lower temporal resolution than that of the Lower Section. The lower temporal resolution likely explains the lack of observable sub-Milankovitch shifts during the Upper Section.

4.4. Biomarker composition

The primary focus for investigations of biomarkers in the chosen

segment of OGCP Core 2A was to determine the composition of aliphatic hydrocarbons, complemented by assessment of alkenones. This should enable the identification of OM sources and thus provide an interpretational framework of the depositional environments of Paleolake Olduvai. Additionally, the assessment of how biomarker abundances and distributions vary throughout the section seeks to identify and understand the likely influences behind temporal variations in the depositional environment. In particular, a key aim is to find evidence among these data for environmental changes to the lake setting associated with the deposition of Tuff IB and reflected in the sediment record. Consequently, aspects of the data are presented in terms of the characteristics of biomarkers representative of specific sources of OM in the Lower and the Upper Section, and comparisons of occurrences and abundances in both parts. OGCP core 2A provides the opportunity for investigation of labile components not preserved in time-equivalent outcrop samples wherein only more robust compounds survive.

4.4.1. Aquatic biomarkers

Several of the biomarkers identified in the core segment can be attributed unequivocally to organisms living in an aquatic environment. Here, we focus on three suites of such source-specific aquatic biomarkers: (i) alkenones sourced by haptophyte algae (e.g., Marlowe et al., 1984; Longo et al., 2006; Theroux et al., 2010; Nakamura et al., 2014), (ii) A-norsteranes attributed to inputs from sponges (van Grass et al., 1982; Bohlin et al., 1982), and (iii) C₂₈ and C₂₉ steradienes derived from algal sterols (e.g., Gagosian and Farrington, 1978; Cornford et al., 1979; McEvoy and Maxwell, 1983; Brassell, 1992; Dumitrescu and Brassell, 2005). These three series of compounds were present in all 25 samples from the Lower Section, but occurred sporadically in the Upper Section; alkenones and A-norsteranes were only detected in 8 and 14, respectively, of the 29 samples and in 12 samples from the Upper Section none of the three series of aquatic biomarkers was detectable. The average concentrations of alkenones and A-norsteranes were roughly an order of magnitude (approximately 10×) higher in the Lower Section (Table 1) with few samples from the Upper Section containing significant amounts (> 1.0 µg/gC; Fig. 4). For steradienes the contrast between the Lower Section and Upper Section is more pronounced, with uniformly low amounts when detected in the latter.

The intermittent presence of aquatic biomarkers in the Upper Section is consistent with the sedimentological interpretation of a shallower lake. The % TOC contents and core coloration suggest, coupled with evidence from burrows and other sedimentary features, that

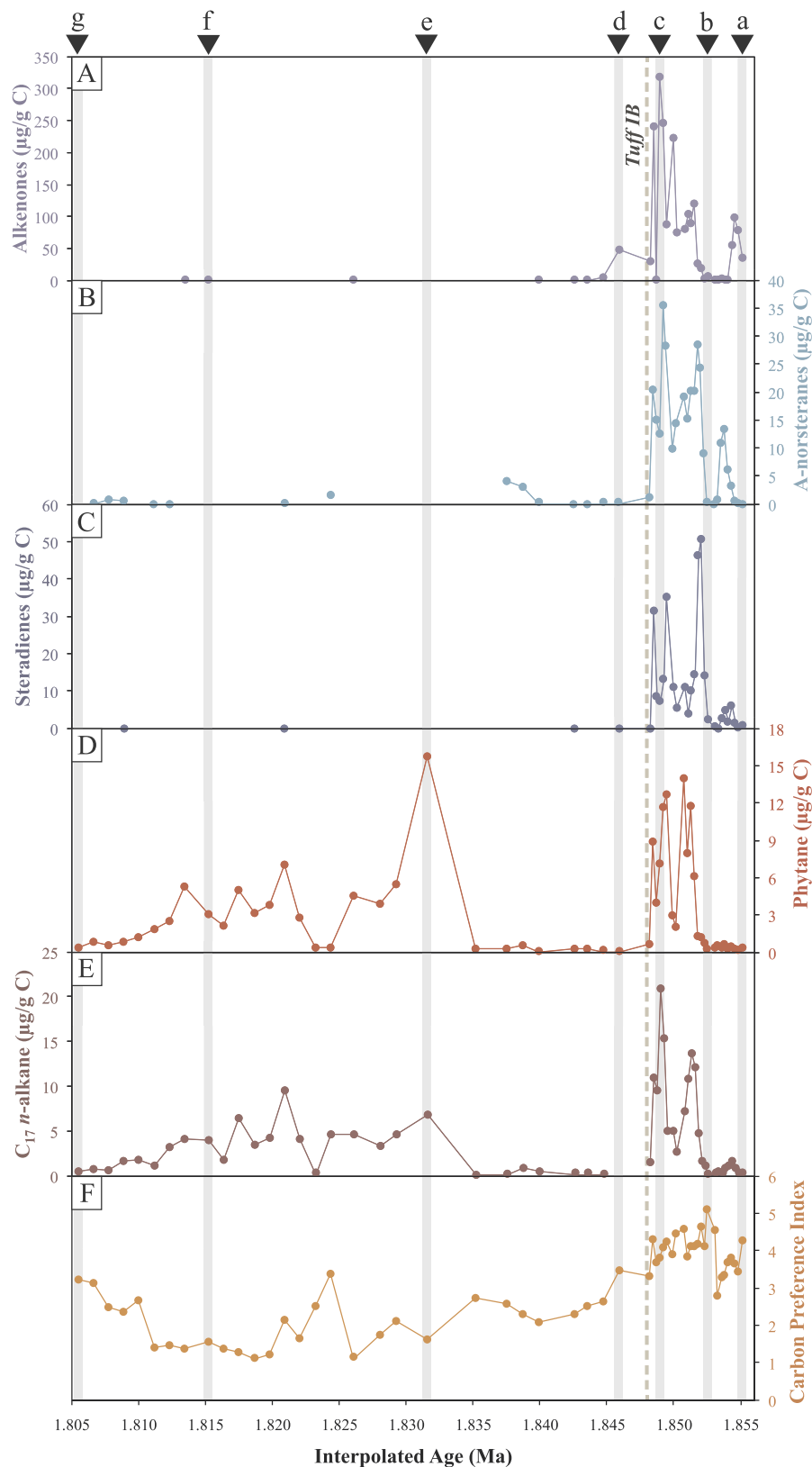


Fig. 4. Biomarker results for 66.3–76.4 m borehole depth of OGCP Core 2A. Plots A, B, C, D and E are typically attributed to aquatic producers, and F as indicative of microbial influence with lower CPI values suggesting increased microbial influence. All biomarker concentrations have been normalized to grams carbon extracted and all data points represent values greater than the detection limit of 0.01 µg/gC. (A) Combined alkenones ($C_{37:3} + C_{37:2} + C_{38:3} + C_{38:2}$) produced by haptophyte algae (Longo et al., 2006). (B) Combined a-norsteranes (C_{27} and C_{28} a-norsteranes) indicates the presence of sponges in the system (Bohlin et al., 1982; van Grass et al., 1982). Combined steradienes ($C_{28} \Delta^{4,22} + C_{28} \Delta^{5,22} + C_{29} \Delta^{4,22} + C_{29} \Delta^{5,22}$) produced by algae (Cornford et al., 1979; McEvoy et al., 1983; Dumitrescu and Brassell, 2005). (D) Phytane is produced from phytol or by archaea, specifically halophiles (Grossi et al., 1998; Schouten et al., 2001; Rontani and Bonin, 2011). (E) C_{17} n-alkane is produced by algae and by cyanobacteria (Gelpi et al., 1970; Brassell et al., 1978; Cranwell et al., 1987). (F) Carbon Preference Index (CPI) = $[C_{23} + 2 * (C_{25} + C_{27} + C_{29} + C_{31})] / [C_{33} + 2 * (C_{24} + C_{26} + C_{28} + C_{30} + C_{32})]$ from Bray and Evans (1961). At the top of the figure are black triangles pointing to gray shaded areas that contain the data points corresponding to the images on Fig. 2, identified by lower case letters, for example: (a) on the graph points to the sample collected from location (a) on Fig. 2.

the sediments from this interval experienced prolonged exposure to the atmosphere that would have caused some degradation of OM and its constituent biomarkers. Thus, the low concentrations of aquatic biomarkers preserved in the Upper Section may reflect either limited production of these compounds in the lake and/or poor preservation because of post-depositional exposure and degradation.

The distributions of alkenones (C_{37} alkadien-2-ones and alkatrien-2-ones; C_{38} alkadien-3-ones and alkatrien-3-ones) resemble those of Group II haptophytes that are found in contemporary saline/alkaline environments rather than the Group I haptophytes associated with freshwater ecosystems (e.g., Longo et al., 2018). Consequently, it is likely that the species of haptophytes in Paleolake Olduvai persisted

during episodes of enhanced salinity and alkalinity associated with lake shallowing and desiccation. However, the occurrence of A-norsteranes derived from sponge sterols is consistent with the presence of sponge spicules in outcrop samples (Albert et al., 2015, 2018) and indicative of a dominantly freshwater environment. There are a few instances during the Upper Section where both alkenones and A-norsteranes are observed in the same sample. One possible explanation is that the freshwater sponges are living in freshwater environments outside of the lake (i.e. wetlands) and sponge OM brought into the lake system via runoff.

Of the aquatic biomarkers found in the Upper Section, the steradienes occur in the fewest number of samples. It is possible that the algae, perhaps diatoms, producing the sterols that serve as the steradiene precursors were, for some reason, less viable in the more shallow, perennial lake environment of the Upper Section. Again, it is important to remember that samples from the Upper Section appear to have been degraded and that the extent of degradation likely varies between the different biomarkers. Thus, it is possible that the aquatic biomarkers discussed here could have existed during times when, due to poor preservation, no measurable amounts remain within the sample.

The concentrations of all three series of aquatic biomarkers in the Lower Section attest to significant, albeit variable, productivity in Paleolake Olduvai. This variability likely reflects changes in climate, more specifically changes in precipitation amount, associated with Milankovitch scale precession cycles, as observed in the underlying lacustrine sediments (OGCP core 2A, 76.4–89.8 m; Fig. 2; Colcord et al., 2018). The lack of synchronicity in their fluctuating abundances illustrates that the different source organisms exhibit varied responses to changes in the lake environment, reflecting its dynamic behavior.

4.4.2. Microbial biomarkers

Evidence for microbial sources of OM is provided by the presence of various biomarkers, including n -C₁₇ likely derived from cyanobacteria (e.g., Gelpi et al., 1970; Brassell et al., 1978; Cranwell et al., 1987) and phytane likely formed from phytol via phytanes or contributed directly by archaea, notably halophiles (e.g., Grossi et al., 1998; Schouten et al., 2001; Rontani and Bonin, 2011). These two compounds are biomarkers biosynthesized by primary producers but microbial contributions are also represented by components formed via degradation of OM. Such microbial contributions are often reflected in n -alkane distributions dominated by shorter-chain homologs, with low odd/even predominance (e.g., Brassell et al., 1978; Castañeda and Schouten, 2011).

Microbial biomarkers, unlike the aquatic biomarkers, could be readily quantified in all samples from both the Lower Section and Upper Section with one exception, the sample immediately above Tuff IB, in which the C₁₇ n -alkane was below the detection limit. The average value and range of concentrations for both n -C₁₇ and phytane (Table 1) were higher in the Lower Section than in the Upper Section, typically by a factor of about two, but the difference was far less than that observed for aquatic biomarkers. The profiles of n -C₁₇ and phytane show greater similarity (Fig. 4) than the various aquatic biomarkers, suggesting that similar environmental conditions may have favored their source organisms, cyanobacteria and archaea, or that the circumstances leading to their preservation during OM degradation were comparable. Both the average and the range of Carbon Preference Index (CPI) values for the Lower Section were higher than those for the Upper Section (Table 1) and is attributed to a pronounced terrestrial input of plant waxes. The Upper Section contained a greater proportion of shorter-chain, even-numbered homologs, likely the result of bacteria associated with the degradation and oxidation of OM.

4.4.3. Discrimination of n -alkane sources

There appear to be three principal sources of n -alkanes within both, the Lower Section and Upper Section, namely contributions from: (i) plant waxes, dominated by higher, odd-numbered homologs (n -C₂₇, n -C₂₉, n -C₃₁, and n -C₃₃), (ii) aquatic sources, including macrophytes and

cyanobacteria, that produce shorter-chain, odd-numbered homologs (n -C₁₇, n -C₁₉, n -C₂₁, and n -C₂₃), and (iii) microbial degradation of OM, characterized by shorter-chain, even-numbered homologs (n -C₁₆, n -C₁₈, n -C₂₀, and n -C₂₂). The relative proportions of these three sources can be expressed in a ternary diagram, where each apex represents the specific range of n -alkanes representative of each source (Fig. 5). Using this approach, the Lower and the Upper Section largely separate into distinct fields. The Lower Section varies in its relative proportions of terrestrial vegetation (~30–70%) and aquatic producers (~10–50%), accompanying a more uniform range of microbial contributions (~20–40%). By contrast the majority of the Upper Section is dominated by microbial contributions (~50–90%), with varying proportions of n -alkanes from terrestrial sources (~0–40%) but more consistent amounts representing aquatic sources (~10–25%). A smaller group of samples from the Upper Section plot in a cluster showing much lower microbial contribution (25–35%), higher terrestrial vegetation contribution (55–75%), and limited contributions from aquatic producers (< 20%). Thus, the distinction in the characteristics of the OM between the Lower and the Upper Section is well delineated by this representation n -alkane sources, reflecting the change from a signal dominated by terrestrial and aquatic producers to one characterized by the predominance of OM affected by microbial degradation.

5. Discussion

5.1. Transition of depositional paleoenvironments before and after Tuff IB

The Lower Section is characterized by a prevalence of aquatic biomarkers augmented by contributions from terrestrial vegetation that reflects a productive lake environment in which OM is well preserved, as recorded by high % TOC values. The sediments from the Upper Section are red/tan in color, low in % TOC, and contain biomarkers that attest to microbial degradation of the sedimentary OM. The Upper Section has a lower sediment accumulation rate and includes numerous horizons with roots and burrows, erosional surfaces, and possible paleosols. Collectively, this evidence is consistent with the development of a shallowing lake that during wetter conditions, such as those found in the Lower Section, had deep enough waters that were likely dysoxic, allowing for better preservation of more labile compounds such as alkenones, A-norsteranes, and steradienes, then later during drier conditions, such as those of the Upper section, shallower, more oxygenated water resulted in decreased OM preservation and therefore the loss of many biomarker signals.

The critical question for this segment of core 2A is what altered the depositional environment, causing the observed change in sediment characteristics. Based on comparison to previous analyses of the lacustrine sediment underlying the Lower Section (OGCP core 2A, 76.4–89.8 m; Fig. 2; Colcord et al., 2018), Milankovitch scale precession cycles are the driving force behind changes in climate and precipitation, which in turn are responsible for the varying abundances and biomarker distributions recorded in the Lower Section. After the Bed I Basalt there is an absence of volcanic material preserved within core 2A until the deposition of Tuff IB. This period of apparent volcanic quiet has also been shown in seismic survey to be the time of greatest subsidence (Stanistreet et al., 2019). This contributes to the idea that during the Lower Section the system was much simpler, with climate as the primary driving force behind changes in the sediment record. It appears that around the time of Tuff IB deposition climate is no longer the only dominant factor and the system becomes far more complex, with influences from volcanic activity, a decrease in subsidence, and climate possibly all reflected in the sedimentary record.

Previous research has focused on the impact of climate during the time between Tuff IB and Tuff IF, here referred to as the Upper Section, and based on a variety of paleoenvironmental indicators has identified an overall drying trend during this time (e.g. Bonnefille, 1984; Kappelman, 1986; Plummer and Bishop, 1994; Hay and Kyser, 2001;

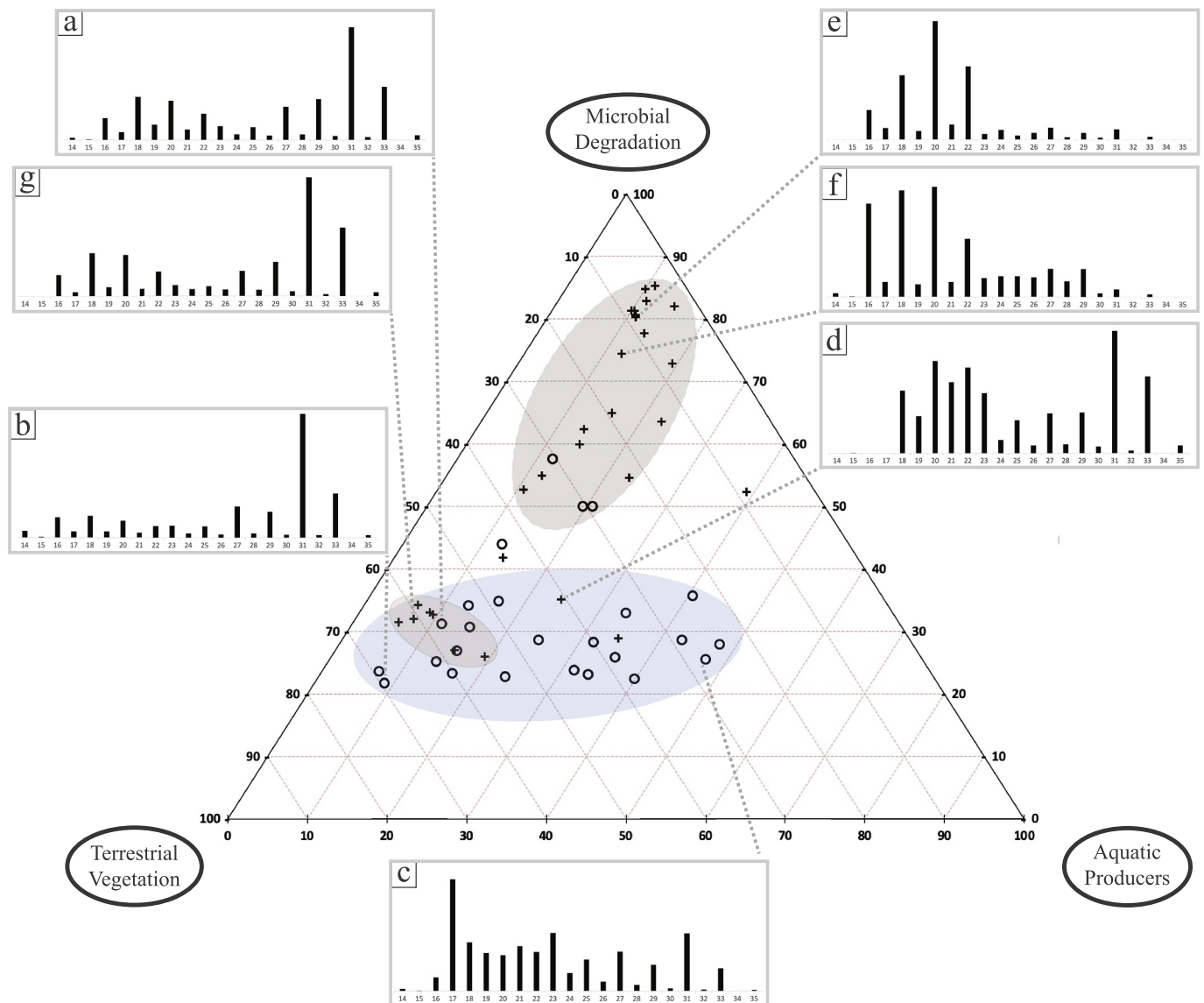


Fig. 5. A ternary plot of *n*-alkane distributions. The Lower Section samples are indicated as (o) and Upper Section as (+). The majority of Lower Section samples fall within the blue shaded region. The majority of Upper Section samples fall within the larger brown shaded region of samples more influenced by microbial degradation, with another cluster of samples in the smaller brown shaded region of primarily terrestrially influenced *n*-alkane distributions. *n*-Alkane chain lengths of *n*-C₁₆, *n*-C₁₈, *n*-C₂₀, and *n*-C₂₂ comprise the “Microbial Degradation” endmember. The “Aquatic Producer” end member is comprised of *n*-C₁₇, *n*-C₁₉, *n*-C₂₁, and *n*-C₂₃, while the “Terrestrial Vegetation” end member includes *n*-C₂₇, *n*-C₂₉, *n*-C₃₁, and *n*-C₃₃. *n*-Alkane distributions (μg/gC) are plotted and identified by lower case letters in the upper left corner, corresponding to those samples pictured in Fig. 2. Numbers along the x-axis indicate the different *n*-alkane chain lengths, and y-axis is increasing abundance, each plot is normalized to the major *n*-alkane in each sample. Dashed lines connect the plot of distribution to where on the ternary diagram that sample is plotted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Sikes and Ashley, 2007; Bamford et al., 2008, and Ashley et al., 2010a). While the overall climate of the Olduvai Basin appears to have been drying during this time, there is evidence, supported by the biomarker findings of this study, for the existence of freshwater, likely groundwater, supported wetlands during times of aridity (Ashley et al., 2010a, 2010b; Barboni et al., 2010; Bamford, 2012; Blumenschine et al., 2012a, 2012b; Magill et al., 2016; Albert et al., 2018). Indeed, phytolith data suggest that there were forests and bushland supported by groundwater/springs/freshwater systems in different parts of the landscape at this time (Barboni et al., 2010), and there is both evidence of freshwater and preserved marshland vegetation buried by Tuffs IB, IC, and ID at KK W just east of FLK (Bamford, 2012) between Tuffs ID and IE at HWK W (Albert et al., 2018) and evidence of freshwater wetlands around the FLK Peninsula during *Zinjanthropus* times (1.84 Ma; Blumenschine et al., 2012a; Magill et al., 2016).

Recent examination of data from OGCP Boreholes 1A and 3A indicate that the Olmoti Fan-delta originated with the Olmoti eruption that produced Tuff IB (Stanistreet et al., 2019). Progradation of the Olmoti Fan-delta would have increased sediment supply to the Olduvai Basin as well as altered the topography (Stanistreet et al., 2019). However, seemingly contrary to this idea, preliminary chronology shows a decrease in the sediment accumulation rate after the deposition of Tuff IB in this segment of core 2A, indicating additional factors are likely contributing to the sedimentary record. Sediment deposition requires sediment transport, so the decrease in sediment accumulation may be due to a climate driven decrease in precipitation or a redistribution of drainage patterns from the prograding Olmoti Fan-delta, both could cause less runoff transporting sediment within the basin. Additionally, tectonics and a decrease in subsidence offer additional, non-climate driven explanations. In the end, the most likely explanation

in such a complex system is that a combination of these and potentially other, more secondary, factors are all coming into play.

Maximal subsidence has been identified from around the time of the Bed I Basalt and continuing throughout the deposition of the lacustrine sediment underlying the section examined here (Stanistreet et al., 2019). It has also been suggested that a reduction in subsidence was likely during the time between Tuff IB and IF, which would have decreased the accommodation space and when combined with increased sediment availability and infill due to the progradation of the Olmoti Fan-delta into the basin, could have produced a shallowing of Paleolake Olduvai (Stanistreet et al., 2019). However, this theory does not account for the impact of climate, which previous studies have shown affected Paleolake Olduvai (Colcord et al. 2018, this volume). The potential decrease in subsidence, formation and progradation of the Olmoti-Fan delta, and continuation of the previously identified precession driven wet-dry cycles likely all contributed to the shallowing of this lake system.

The bulk organic geochemical and biomarker data supports an increase in system complexity, from a subsiding basin with a deeper lake where sediment deposits record changes driven by climate in the Lower Section to a system showing ever increasing shallowing with periods of prolonged desiccation, and that is no longer controlled by climate alone, but by a number of factors, in the Upper Section. However, due to the unknown impact of poor preservation, which may have removed some if not all of the more labile biomarkers, there is a limit to what can be inferred from the biomarkers deposited during the Upper Section. Future research using other cores collected by OGCP from Olduvai, including core 1A (Fig. 2) will likely be able to provide a better sense of the changes in the extent of the lake by providing more lateral information.

5.2. Environmental impact on hominin evolution

The dark, organic rich sediments comprising the Lower Section were deposited in a dysoxic lake during a time when changes were driven largely by Milankovitch scale precession cycles, and were succeeded in the Upper Section by a sequence of oxidized red/tan claystones containing multiple erosion surfaces and horizons with roots and burrows that depict a shallower lake affected by multiple factors including decreased subsidence, infill from the progradation of the Olmoti Fan-delta system, (Stanistreet et al., 2019; and or Stollhofen et al., 2019), and climate, an overall more complex depositional environment. The biogeochemical data reflect this change in terms of the preservation of OM and the abundance of aquatic and microbial biomarkers. Hominins in this environment would have experienced dynamic changes in the landscape, albeit on multi-generational timescales, possibly affecting the availability of water and food resources in this lacustrine setting. Some were driven by regional climatic patterns, notably Milankovitch-scale variations in precipitation (e.g., Magill et al., 2013a; Colcord et al. 2018, this volume) because they are recorded on a continental scale, whereas others are more localized, especially the shallowing and oxidation of sediments within Paleolake Olduvai after Tuff IB, due to a number of factors including infill from the prograding Olmoti Fan-delta, potential redistribution of drainage pathways, decreased subsidence, and climate related changes. Thus, the lake conditions during deposition of the Lower Section could have helped sustain a diversity of hominins in East Africa, while subsequent prolonged desiccation events may not have supported such diversity. The environmental conditions within the Olduvai Basin during the Upper Section likely favored specific lifestyles better capable of surviving under drier conditions (Van der Merwe et al., 2008; Cerling et al., 2011; Magill et al., 2016). Additionally, the shallow lake present during the deposition of the Upper Section may have provided hominins access to certain materials for stone tool production such as the quartzites of Naibor Soit, which would have been less accessible during high lake stands (Blumenshine, 1995; Reti, 2016). Current theories of evolution do not typically consider

variations in both regional climate and environmental changes as well as the effect that more local water-catchment-scale changes may have had on specific populations inhabiting an area. This examination of ~10 m of core 2A shows that multiple factors were likely influencing and changing the paleo-landscape around Paleolake Olduvai beginning around the time of Tuff IB deposition.

6. Conclusions

Examination of a ~10 m sequence of OGCP core 2A (66.3–76.4 m), which includes the dated marker beds Tuff IB and IF, reveals a time of transition and increased shallowing, oxidation, and likely prolonged desiccation of Paleolake Olduvai sediments. Chronology based on linear interpolation between the three dated marker beds shows a marked decrease in sediment accumulation rate in the Upper Section of the core compared to the Lower Section. The Lower Section of this core segment reveals good OM preservation, enabling examination of more labile biomarkers typically not preserved in outcrop samples. Biogeochemical analyses of the Lower Section indicate the depositional environment throughout this time consistently corresponds with the characteristics of the lake depocenter, providing sparse evidence for drying episodes. Around the time of Tuff IB deposition, the environment transitions into a shallower lake recorded by evidence of increased periods of prolonged desiccation throughout the Upper Section. The presence of root traces, bioturbation, erosional surfaces, paleosol development, and sediment coloration typical of subaerial oxidation combined with low % TOC values, a marked decrease in the concentrations of more labile biomarkers, and a corresponding increase in evidence for microbial degradation all provide evidence for poor OM preservation during this time. Throughout the Upper Section, the core location indicates an increase in the frequency of prolonged desiccation events with both sediments and their biomarker compositions attesting to depositional facies more indicative of a lake margin environment. Overall, the biomarker compositions help define the stark difference in the lake environment before and after Tuff IB as indicated by the *n*-alkane distributions, which show a balance of OM inputs from aquatic and terrestrial sources replaced by a dominance of homologs attributed to microbial degradation. The results from this study are consistent with the idea that around the time of Tuff IB deposition Paleolake Olduvai experienced a shallowing of the lake attributable to a number of factors: (i) basin infill likely influenced by the progradation of the Olmoti Fan-delta, (ii) a decrease in water supply to the lake due to reconfigured drainage patterns, (iii) a decrease in precipitation associated with Milankovitch scale precession cycles, and (iv) decreasing subsidence.

Evidence for the depositional setting of Paleolake Olduvai derived from biogeochemical analysis of this ~10 m segment of OGCP core 2A suggests that hominins would have encountered a persistent deep lake prior to the environmental transition that occurred around the time of Tuff IB. Subsequently, prolonged desiccation episodes occur more frequently and this radical transition in the environment of Paleolake Olduvai would likely have had an effect on the water and food resources available for use by hominins in the region. The shallowing of the lake at this time may also have provided hominins access to additional resources, such as the quartzites of Naibor Soit, that were inaccessible at higher lake levels. In summary, the OGCP cores afford unprecedented opportunities to decipher evidence for environmental changes recorded in the sedimentary sequence of Paleolake Olduvai, including those associated with deposition of Tuff IB.

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Appendix A. Supplementary data

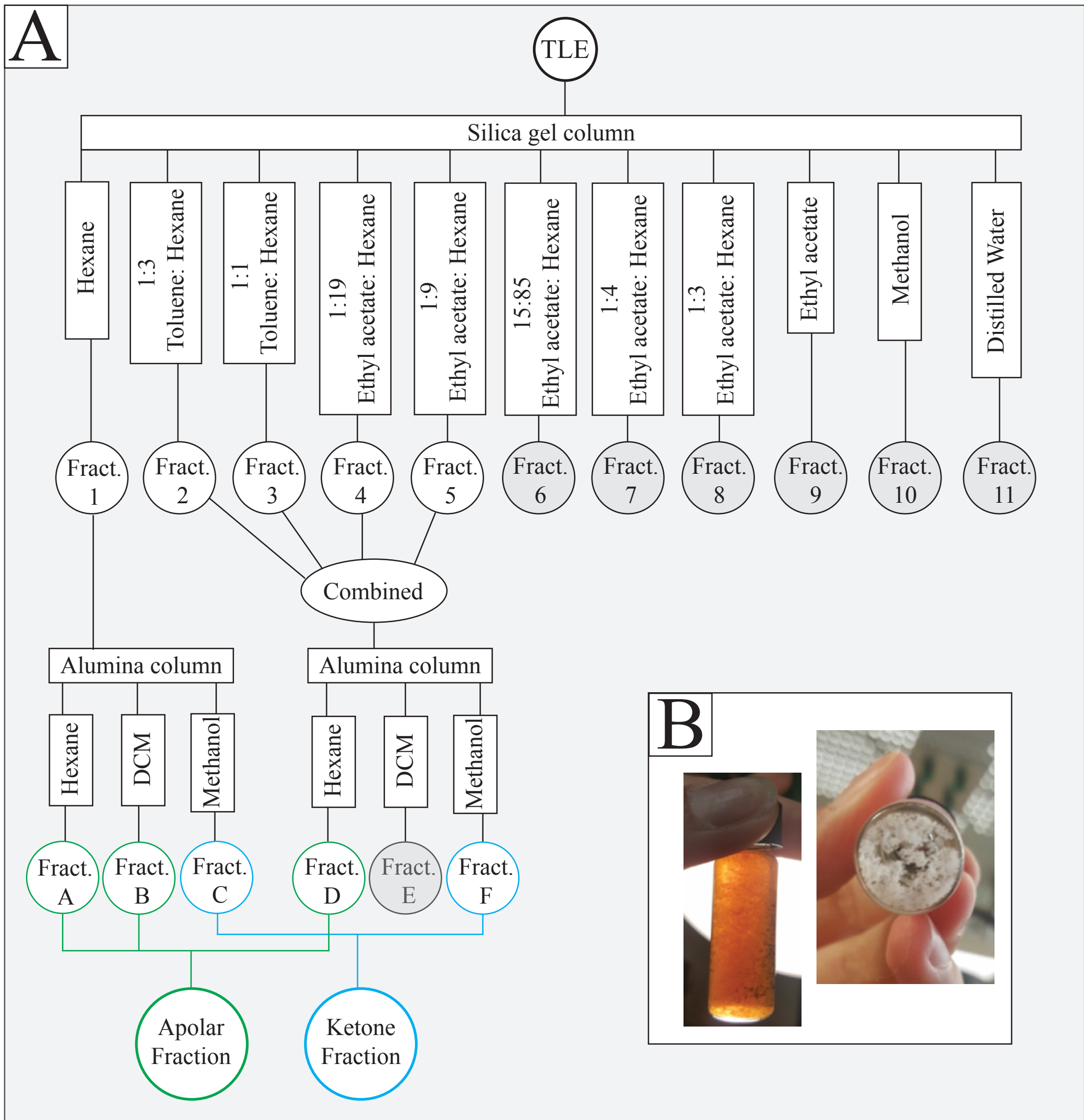
Supplementary data to this article can be found online at <https://doi.org/10.1016/j.palaeo.2019.109267>.

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The next two pages are the supplemental information files



Supplemental figure 1

SUPPLEMENTAL METHODS

Prior to separation an unidentified flocculate was observed forming when TLEs were concentrated from ASE vials into 4 ml. Multiple attempts were made to re-dissolve the material including different solvent and temperature, methanol and heat could re-dissolve the material however upon cooling the material returned. NMR was used in attempt to identify the substance but to no avail. It is likely this substance is some form of extracellular polysaccharide, however as this was not the intended focus of this study, no further resources were dedicated to determining its identity. It was thought that column chromatography would help remove some of this material.

TLEs were first separated via silica gel chromatography with sequential elution from apolar to polar over 11 fractions, 4 ml of each solvent was used, one to put the sample on the column and 3 to flush through. The goal of this first separation was to separate possible target compound classes and ideally remove enough of the flocculate to allow gc-qtof-ms analysis. Unfortunately, the silica gel columns did not remove enough of the flocculate and it was decided that alumina columns would be used in a second round of separation. Additionally, it was determined that separation could be further refined by combining some of the fractions. The final method developed is illustrated in Supplemental Figure 1.