The Younger Dryas black mat from Ojo de Agua, a geoarchaeological site in Northeastern Zacatecas, Mexico

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New explorations in the desert of northeastern Zacatecas, in central-northern Mexico, revealed dozens of archaeological and geoarchaeological sites. One of them, Ojo de Agua, contains the remains of a Pleistocene spring-fed hydrographic system located at the southeastern end of a large elongated endorheic basin. The locality yielded a particularly dark, highly organic stratigraphic layer commonly known in the Americas as Black Mat (BM), exposed on the natural profiles of a creek, but not associated with cultural materials. Several radiocarbon assessments confirmed the formation of the Ojo de Agua Black Mat during the Younger Dryas chronozone, with ten calibrated results clustering between 12,700–12,100 cal BP. This multi-proxy study confirmed the peculiarity of the deposit and found similarities and differences with other contexts of Younger Dryas age. The Ojo de Agua Black Mat (stratum C2) is far richer in charcoal specks than the related strata, but lacks phytoliths, diatoms or ostracods. No further biological remains were found in it, except for intrusive capillary roots. Clearly water-lain in a shallow pond, the stratum qualifies as a clayey silt with an acidic-to-neutral pH. Rich in heavy metals and with high contents of titanium, the Ojo de Agua Black Mat yielded significant indicators of intense wildfires during the Younger Dryas, but produced no carbon spherules or nanodiamonds supposedly linked to the impact theory.

1. Introduction

The archaeology of early prehistoric occupations faces evident difficulties when working in regions with no previous geoarchaeological work, like northern Zacatecas, Mexico. Lacking chronostratigraphic markers for key Quaternary geo-climatic events is working in darkness, especially during initial archaeological surveys. Without investing time and resources in dating methods, it is still difficult to recognize the Pleistocene-Holocene transition on stratigraphic profiles, visually. Learning to read the end of the Ice Age when working in the field means learning where to look for early human occupations. But can systematic
exploration identify reliable chronostratigraphic markers of regional validity, able to discern between Pleistocene and Holocene deposits and guide future geoarchaeological research in the region? Our working hypothesis departed from a positive answer.

This paper reports the discovery of a black mat layer of Younger Dryas age in Mexico, derived from geoarchaeological investigations conducted within a large-scale project directed by the first author, in a remote and never-studied-before region in the northeast of the State of Zacatecas, Northern Highlands, on the Tropic of Cancer (Fig. 1). Since 2010, the project focused on an area with high potential for the study of hunter-gatherer societies, cultural diversity and geo-climatic dynamics along the Pleistocene-Holocene continuum (Ardelean, 2013; Ardelean and Macías-Quintero, 2016; Macías-Quintero, 2017). Intentionally looking for easy-to-see potential stratigraphic markers on naturally-formed profiles, the explorers discovered a black silty layer commonly known in Americas as “black mat” (BM).

Recent investigations pointed at specific stratigraphic and pedogenic horizons related to the Pleistocene-Holocene transition in the north, west and center of the country, but those layers could only reveal their chronological relevance after specialized laboratory analyses, lacking the physical attributes of a good visual guide for archaeologists (see paleosols in Sonora, northwestern Mexico; Cruz-y-Cruz et al., 2014, 2015). A batter case has been recently presented by Israde-Alcántara et al. (2017), with several dark-colored strata found in different regions of Mexico, dating to the Younger Dryas chronozone, some of them qualifying as black mats themselves. The sound investigations recently undertaken at the Clovis-age archaeological site of El Fin del Mundo in Sonora and neighboring areas yielded many relevant aspects of archaeological and geoarchaeological relevance, such as diatomite layers with organic lenses, but not a proper stratum similar to a black mat (Sánchez et al., 2014).

Since the original discovery at the Murray Springs archaeological site in Arizona (Haynes and Huckell, 2007), black mats used to be perceived as an ideal stratigraphic indicator for the end of the Pleistocene and an argument in favor of a global manifestation of the Younger Dryas. Although several authors showed that black mats could reflect diverse events from very different moments during the Quaternary (Quade et al., 1998; Pigati et al., 2012; Harris-Parks, 2014), many archaeologists understood them as synonymous to Younger Dryas. When Ardelean and Macías-Quintero first saw the black stratum at Ojo de Agua in 2010, they felt they had discovered the first “proper” BM in Mexico and a recognizable chronostratigraphic marker for the Pleistocene-Holocene transition.

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Fig. 1. Location map. The site is situated in the central-northern region of Mexico, in the northeast of the State of Zacatecas, less than 100 km north of the Tropic of Cancer (a). The Pleistocene spring-and-pond system of Ojo de Agua lies in the highlands closing the southeastern end of the Concepción del Oro endorheic basin (b), in a narrow passage between two sierras, El Astillero and Borrada (c).
This study seeks response to a series of inquiries derived from that discovery. Did the Ojo de Agua BM form during the Younger Dryas? How does it compare to other similar strata reported elsewhere in North America? Can science learn paleoclimatic information from this particular stratum? Finally, can the Ojo de Agua BM be considered relevant to the study of early prehistoric human occupations on a regional scale?

2. Geographical settings and context of the Mexican black mat

Among the thirty-five new archaeological, paleontological and geoarchaeological sites discovered during intensive archaeological surveys between 2010 and 2012 in the study area, a few locations yielded proper Pleistocene sediments, whose age was initially suggested by stratigraphic observations and later confirmed by direct dating. One of the most important is Ojo de Agua, a small locality in the sierra, at the southeastern end of the Concepción del Oro endorheic basin in Northern Zacatecas, part of the Northern Highlands (Fig. 1). The site is visible today as eroded, carbonate-rich deposits containing extinct fauna bones (Figs. 2 and 3). It sits along a geological fault on the western edge of a narrow high plain, in a gorge formed between the Borrada and Astillero Mountains, whose drainage system contributed to the endorheic, half-graben basin from the southeast. Thick, greenish hydrothermal deposits mark the older, deeper phases of the still ponds on the lower sections of the local geology (Fig. 4).

Ojo de Agua stands at an altitude of 1948 m.a.s.l, as a shallow depression surrounded by low hills, alluvial fans and gentle slopes. The landscape is an arid semi-desert, with steep, rocky alluvial fans and terraces with shallow, underdeveloped and eroded litosols, covered predominantly by desert shrubs (Larrea sp.), Joshua trees (Yucca spp.), mesquite trees (Prosopis sp.), and varieties of agave (Agave lechuguilla). On the eastern higher terrace, deeper Holocene soils are suitable for maize cultivation. The area has a dusty surface, and the white and yellowish carbonates eroded in a stepped formation alongside creeks and gullies, each step being a remnant of an Ice Age stratum (Figs. 2 and 3). Gullies and arroyos are typical formations in arid landscapes, and this site has both, exposing stratigraphic profiles.

Ojo de Agua’s short and narrow gully is located along the western edge of the deposits, where sediments meet the base of the hill slope. It commences as a shallow ditch in the south, reaching 3 m deep towards the center, where black-and-white alternating deposits yielded Ice Age megafauna remains and motivated initial exploration of the site (Fig. 3). The larger arroyo, in the east of the deposits, is where the Younger Dryas BM was found. Up to 30 m wide, the arroyo is meandering and single-coursed, with few alluvial islands and bars. Its western profile is taller, up to 6 m (Fig. 4), while the eastern one is lower and eroded. The gully and the arroyo do not share the stratigraphy, and correlations are difficult to establish. Also, the stratigraphic sequence is not alike on the two banks of the main arroyo. The two Holocene-age drainages formed over distinct, non-contemporary components of the Pleistocene landscape. The arroyo cut through more recent strata, while the gully exposed sediments older than 25,000 cal BP (Fig. 3b; see details in Ardelean, 2013).
3. Younger Dryas and black mats

3.1. General remarks about the Younger Dryas

The Younger Dryas (YD) was the last episode of a series of fast-developing climatic events during the Terminal Pleistocene following the Late Glacial Maximum. With it, the Ice Age reached its terminus point. The YD officially marks the end of the Pleistocene and the beginning of the Holocene, globally (Head and Gibbard, 2015; Ardelean, 2016). During the YD chronozone (12,800 ± 11,700 cal BP), the climate witnessed a return to almost full-glacial conditions, a "cold spell" that installed suddenly and finished in an abrupt manner (Mercer, 1969; Harvey, 1989; Berger, 1990; Peteet, 1995). The causes that may have led to a sudden and millennium-long descent of global temperatures puzzled scientists for many years, and a variety of hypotheses arose from the debates. Among them, the fresh-water discharges into the Northern Atlantic as an effect of the melting of continental ice caps, leading to changes in the behavior of ocean currents (Broecker, 2006, 2010; Broecker et al., 1988, 2010), and the impact theory, which suggests a cosmic impact that unleashed abrupt global changes that cooled the planet (Firestone et al., 2007; Kennett et al., 2008; Holliday and Meltzer, 2010; Kenzie et al., 2014; Istrate-Alcántara et al., 2012). In America, the study of the YD was especially important because it had long been considered contemporary with the initial stages of human peopling of the continent (Haynes, 2006, 2008; Meltzer and Holliday, 2010; Holliday et al., 2011; Ballenger et al., 2011; Eren, 2012).

3.2. The Younger Dryas in Mexico

Studies about the YD in Mexico are scarce, and there were impressions that the cold reversal did not manifest at all in Mexican territories. Scholars assumed that the YD had to be tracked mainly through glacial advances, a paradigm that prevented researchers from conducting a sustained search for different paleoclimatic, multi-proxy signatures in tropical regions. Early in the history of Mexican prehistoric archaeology and paleoenvironmental studies, Sokoloff and Lorenzo (1953) emphasized that there was no evidence for any significant climate change or cooling reversal for the Basin of Mexico corresponding to the YD. Heine (1994) observed that the glacial advances there manifested before and after the YD chronological interval, but no data supported cold peaks during that time. Vázquez-Selem and Heine (2004) suggested that a local, Mexican glacial maximum had occurred not in parallel with the known Late Glacial Maximum (LGM), but well after its climax.

In northern Mexico, Ortega-Ramírez et al. (2004) identified humid conditions for the Late Glacial in the Babicora Basin, with a switch to dry climate and a change in vegetation cover around 11,000 RCYBP. Shortly after, the region returned to wetter and cooler conditions, seemingly in relationship to the YD. Pollen also shows wetter and cooler values at the onset of the cold interval, with shallow lakes suggested by diatom studies and a progressive installation of deserts and succulents after the YD (Metcalfe et al., 2000). The most recent studies performed in the northwestern region of Sonora managed to identify a series of paleosols associated with a succession of climatic events that developed during the Late Pleistocene and after (Cruz-y-Cruz et al., 2014, 2015). However,
the information obtained from those horizons remains within the expected margins of paleoenvironmental variation during the Pleistocene-Holocene transition.

Other investigations performed in Mexico went on the path of the impact theory and searched for indicators related to a potential catastrophic event that may have caused or contributed to the climate reversal (Israde-Alcántara et al., 2012). The most recent study shows a significant incidence of micro-spherules and other proxies suggesting a possible meteoric impact in several Younger Dryas black mats located in exposed profiles and deep cores at several lacustrine sites in Mexico (Israde-Alcántara et al., 2017).

3.3. Characteristics of the black mats

In general terms, the words “black mat” refer to a distinctive, organic-rich, black-colored layer, clearly highlighted visually by contrast with the associated stratigraphy, and causally related to formation processes in valley bottoms, ancient ponds, high water tables and spring-fed systems (Quade et al., 1998; Haynes, 2008; Pigati et al., 2009; Harris-Parks, 2014; Rachal et al., 2016). Such black strata have been found in distant places, such as the Venezuelan Andes (Mahaney et al., 2011) or around the Red Sea (Botz et al., 2007). The principal inconvenience of black mats, at least in America, is that they seem to have formed principally in pond-related contexts and rarely in areas where dry soils dominated the ancient landscape, meaning they have limited potential as chronostratigraphic markers for the purpose of archaeological investigations (cf. González-Hernández, 2017).

The black mats, in the wider acceptance of the term, were not exclusive to the YD, although mostly related to it (Quade et al., 1998; Harris-Parks, 2014; Rachal et al., 2016). According to this more inclusive posture, the formation of a BM would not relate to a single specific event, but to episodes of higher organic productivity around ancient springs and a rise in the level of groundwater with the establishment of reducing conditions, phenomena that happened repeatedly during the Quaternary. The BM-related radiocarbon dates reported by Quade et al. (1998) from a variety of sites fall in two large categories: one between 11,800-6300 RCYBP and a second one from 2300 RCYBP to the present. The hiatus in between is probably explained by the warm and arid conditions established during the Alithermal warm period in North America. Most black mats cluster around approximately 10,000 RCYBP (about 12,000 cal BP), still coinciding with the YD and maintaining a relative potential as a chronostratigraphic marker for the Pleistocene-Holocene transition.

The BM studies started in 1966, when geoarchaeologist C. Vance Haynes first identified such a stratum on the exposed profiles of Curry Draw, at the Murray Springs archaeological site in southern Arizona (Haynes and Huckell, 2007). The black layer formed on top of the Clovis-age occupation at the site (“Clovis” is the best-known Terminal Pleistocene archaeological culture in North America, developing roughly between 13,500—12,800 cal BP). In an epoch of drought, the mammoth remains and Clovis artifacts were quickly covered by the BM layer, due to a sudden installment of swampy conditions related to an abrupt raise in the water table (Haynes, 1991, 2007a,b).

The Murray Springs BM is a highly organic silty clay, mainly formed of montmorillonite. About 2—10 cm thick, it thins upslope and becomes thicker in the depressions. “It has a distinct, sharp, basal contact across variable lithologies and usually breaks cleanly
away from the underlying surface (…)” (Haynes, 2007d: 240). It may split into stringers, separated by white marls, indicating fast fluctuating episodes of variation in the pond’s depth. The “original” BM presents a fine angular blocky-to-granular structure, with a waxy, sticky consistency. The sediment pedds are coated with filaments of calcium carbonate and, occasionally, with “filaments of a white leathery fungus that upon drying can be mistaken for a carbonate coating” (Haynes, 2007b: 45). No macroscopic remains of plants were visible in that BM (Haynes, 2007d: 240; Rogers, 2007), although intruding capillary roots of recent age can appear in some cases (Quade et al., 1998).

The BM at Murray Springs has been securely dated to the Younger Dryas, its radiocarbon age falling between 9700 RCYBP at the top to 10,800 RCYBP at the bottom (Haynes, 2007b,c). In spite of doubts about the accuracy of the radiocarbon dating of black mats in relationship to a variety of factors that may affect their isotopic content, laboratory results showed that the humic fraction was secure for dating, as it originated in primary organic matter, not in contaminating sources (Quade et al., 1998).

Quade et al. (1998) reported that the black mats of the Great Basin contained a main mineral fraction, principally carbonates from the subjacent limestone beds, plus a mixture of quartz and biotite. As noticed by Harris-Parks (2014), the content of calcium carbonates varies widely between 0 and 51%. At Murray Springs, the samples contained carbon (4.6%) and hydrogen (1.3%), with small amounts of oxygen and negligible traces of nitrogen. Spectroscopy showed that the main fraction was composed of Si, Fe and Al, with smaller amounts of Mg, K and Ca. The samples were free of gypsum, weak in sulfate, with 0.18% of phosphorus and an acidic pH of 6.7 (Rogers, 2007; Haynes, 2007d).

Quade et al. (1998) observed the organic concentration was higher in the upper layers of a BM, where the reducing conditions favored the formation and preservation of primary organic material, while in the older part of the strata the organics were eliminated by the oxidizing capacity of groundwaters. Black mats include around 0.5–4% of primary organic matter, reaching up to 8–10% (Haynes, 2008; Botz et al., 2007). Harris-Parks (2014) concluded that the organic content oscillated between 0.4 and 21.8%. At Murray Springs, this rarely surpasses 1–2% (Stankiewicz and Tegelaar, 2007).

The distinctively black color of this peculiar type of deposit is a debated characteristic. Often, there was little evidence of undegraded plant remains, charcoal, wood or roots (Leenheer, 2007), while the “loss on ignition” (LOI) analyses yielded low organic content (Rogers, 2007). However, the presence of aromatic molecules possibly indicates burned wood, the nitrogen compounds may suggest a bacterial or fungal origin, while the aliphatic components may derive from algae remains and spores. Biochemical signatures inferred as presence of algae became a widely-known explanation for the pitch-black color (Leenheer, 2007; Stankiewicz and Tegelaar, 2007; Haynes and Rogers, 2007). More recent comparative investigations suggest that the black color was more likely caused by high concentration of organics produced by herbaceous plants, rather than fungi (Harris-Parks, 2014).

In many cases, black mats were associated with relatively diverse malacological material. The analyses identified principally terrestrial snails, followed by aquatic taxa, with a notorious absence of aquatic ostracodes. The Pupillidiae snail family seemed dominant, with a diversity of Gastrocopta and Verrigo species, some of them diagnostic of the Pleistocene (Mead, 2007; Quade et al., 1998).

4. Methods and analyses

Preliminary and still incomplete laboratory analyses on the Ojo de Agua BM had already been presented in two dissertations (Ardelean, 2013; González-Hernández, 2017). The present study is a full reassessment and a more thorough version of the previous approaches, including: archaeological and geoarchaeological explorations both on the surfaces and by controlled excavations; direct observations, profile cleaning, strata description and detailed sampling of a defined column on the western profile of the Ojo de Agua arroyo; radiocarbon (AMS) dating in different labs and on different sample components; geochemical studies; micromorphology; elemental composition (inductively coupled plasma mass spectrometry or ICP-MS, energy-dispersive X-ray spectrometry or EDS, X-ray diffraction or XRD, X-ray fluorescence or XRF); magnetic susceptibility; phytoliths; flotation; charcoal particles; electronic microscopy; diatoms; malacology. A more detailed presentation of the methods and analyses is available as Supplemental Material.

5. Results

5.1. The archaeological and paleontological record

Despite sustained archaeological investigations, Ojo de Agua and its black mat could not be conclusively related to ancient human presence, although the rest of the endorheic basin proved surprisingly rich in hunter-gatherer prehistoric sites (Ardelean, 2013; Gibbons, 2014; Ardelean and Macías-Quintero, 2016; Huerta-Arellano, 2016; Macías-Quintero, 2017). The site only produced surface materials, mainly Late Holocene lithic types. The only possible artifact potentially related to the Pleistocene strata was found on surface eroding from the western banks of the gully: a tabular limestone nodule with marginal flaking scars and impact traces on edges (Ardelean, 2013: 389, fig. 247). The only clearly Pleistocene materials are the megafaunal remains lacking indicators of cultural modification. The finds consist of bone fragments and dental pieces embedded in naturally exposed profiles, others than the BM one. The majority represent mammoth (Mammutus columbi) tusk fragments, molars and fragmented long bones. Other genera of extinct herbivores are present, such as American horse (Equus sp.) and tapir (Tapirus sp.), forming a relatively diverse assemblage with potential for paleoenvironmental inferences.

5.2. The stratigraphy of the Ojo de Agua arroyo

The Ojo de Agua BM appears on the western bank of the main arroyo, in a section about 80 m long (Fig. 4). The 5.8 m sedimentary sequence consists of a succession of lacustrine sandy silts to fluviolacustrine silty sands, interrupted by a black, organic-rich silty clay, 10–15 cm thick, at a depth of 3.00 m (Figs. 5 and 6). The black stratum (C2, BM), mainly composed of brittle powdery black clays with very fine silts, is bracketed by two, 20 cm thick calcium carbonate strata, indicating a seasonally oversaturated pond (Unit C). Below the BM, strata in Unit D are composed of pseudostratified fine silt calcium carbonates with abundant travertine clasts. At the center of the stratigraphy, strata grouped within Unit B, corresponding to the very end of the Pleistocene and the Early Holocene, display a continuous succession of organic layers and black-and-white laminae indicating a period of intense fluctuations of water levels, just as those visible on the pre-LGM profiles excavated on the gully (Figs. 3b and 5). Silts in this unit are poorly sorted. In transitional contact overlaying the silty units, there are 2 m of sandy silty deposits (Unit A), showing at the center several paleochannels filled by angular gravels less than 7 cm in diameter. Minor formations, including cross-bedding and flat lamination, are common towards the top of the sequence, with main clastic components comprising fine-to-medium sand deposits, mainly...
Fig. 5. The Ojo de Agua main arroyo stratigraphic profile studied for this paper. Left: The 5.8 m tall lithological column depicting the four main geological units and showing the available radiocarbon dates to the left. The detail of Unit C, containing the Younger Dryas deposit, is shown in Fig. 6. Center: Magnetic susceptibility (XFD%) behavior of the stratigraphy, emphasizing a notorious peak for the black mat, contrasting with the rest of the strata. The XFD% values are indicators of the presence of ferrimagnetic superparamagnetic (SP) minerals. Right: The clean profile that represented the base for our analyses and provided the majority of the samples. The black mat is clearly visible at the center of the stratigraphy.

Fig. 6. Lithology of Unit C containing the black mat (BM) and related strata. Unit C1: calcium carbonate facies; Unit C2 (BM): organic marshy facies; Unit C3: calcium carbonate facies. To the right, a table showing some of the results discussed in the paper. The black mat stands out as rich in organic matter and charred plant remains. For the data in the last column, see Fig. 7.
composed of calcium carbonate grains of high textural maturity. At the very top, eolian sediments reflect the aridization of the region during the recent stages of the Holocene.

5.3. Radiocarbon dating results

Several radiocarbon (AMS) assessments were performed successfully on samples from the BM, as well as on two of the overlying buried paleosols (Table 1; Fig. 5). We obtained ten radiocarbon dates for the Ojo de Agua BM, from different fractions of the deposit, in three different laboratories. They all confirm the Younger Dryas age of the stratum, with the calibrated values concentrating in the earlier half of the cold interval (2σ range: 12,700–12,100 cal BP). The dates are consistent between laboratories and between different components of the same sample. When different fractions were dated, the results were almost identical. The two AMS dates for the overlying paleosols (the last two rows in Table 1) are consistent with each other in vertical succession, and slightly younger than the BM, situating those horizons in the initial stages of the Early Holocene.

5.4. Laboratory analyses

5.4.1. Paleobotanical remains

There were no phytoliths at all in the BM samples, despite repeated replications of the analyses. The same was valid for pollen and botanical macro-remains, during preliminary testing (except charcoal). Fine fragments of capillary roots can be found in the BM, though. They are visible macroscopically and float when the sediment is soaked. They can be considered intrusive material, from overlying paleosols. The cellular structure of the remains is highly visible and the specimens did not refract under X-polarized light, so most likely the botanical fragments were not fossilized.

5.4.2. Charcoal particles

Charcoal particles settled in the Ojo de Agua pond before, during and after the YD (Fig. 6). Before the formation of the BM, stratum C3 received concentrations of 74 mpc/cm³. The BM (C2) doubles the values, at 147 mpc/cm³. Above C2, the black and white lenses show received concentrations of 74 mpc/cm³. The BM (C2) doubles the concentration of charcoal. Potassic and plagioclase feldspars are among the main constituents of the BM, together with quartz grains and lithic particles ranging from coarse silt to medium-sized sand (0.03–0.3 mm). Quartzes are mono-crystalline, sub-rounded with low sphericity, while the feldspars are rounded with medium sphericity. The visible feldspars are anorthite. The material is bound with low sphericity, while the feldspars are rounded with medium sphericity. The visible feldspars are anorthite. The material is bound together by calcareous cement (<10%). Additional components are represented by hematite, muscovite and black particles or specks that could be related to the burned organic material confirmed by other analyses. Algae presence was confirmed, as well. The textured particles are fragments of charcoal, while the solid pieces are “glasslike carbon.” Both can be interpreted as indicators of fire (Fig. 8).

5.4.3. Malacology and microfossils

There were no ostracods, gastropods or bivalves in the BM samples from Ojo de Agua, but relatively abundant in the adjacent layers (Fig. 6). Below the BM, strata in Units C3 and D proved rich in gastropod taxa: *Pisidium compressum*, *Retinella electrina*, *Succinea avora*, *Deroceras aestigma*, and *Vertigo ovata*; additionally, one bivalve (*Gyrulus parvus*) and one ostracod (Candonina sp.). There were also mineralized microvertebrate remains. Above the BM, stratum C1 showed fewer taxa, a significant drop in gastropods and only one ostracod (Candonina sp.). Diatoms were absent from all samples.

5.4.4. pH

The tests indicated slightly acidic to neutral pH values of 6.8 for most BM samples from Ojo de Agua. In strata below the BM, pH was 7.3, while in layers above it reached 7.6.

5.4.5. Sediment fractions

This BM could be defined as silt (65.06%), followed by clay (34.36%), with low amounts of sand (0.59%). The reference “BM-like” deposits excavated along the gully (Fig. 3) and those from the underlying greenish strata (Unit D) showed more sand in composition (at least 3%), suggesting higher energy environments.

5.4.6. Micromorphology

The results indicate a water-lain sediment, with moderately-to-poorly sorted composition. In some sectors, a slight lamination suggests the sedimentation was episodic. The matrix of the BM is silty clay (>30%). This is a phyllosilicate or layered alumino-silicate, proving that the black mat has genetic relationship with the hydrothermal deposits underneath. Important amounts of sericite-type mica are reported from the matrix, derived from the weathering of plagioclase feldspars. Potassic and plagioclase feldspars are among the main constituents of the BM, together with quartz grains and lithic particles ranging from coarse silt to medium-sized sand (0.03–0.3 mm). Quartzes are mono-crystalline, sub-rounded with low sphericity, while the feldspars are rounded with medium sphericity. The visible feldspars are anorthite. The material is bound together by calcareous cement (<10%). Additional components are represented by hematite, muscovite and black particles or specks that could be related to the burned organic material confirmed by other analyses. Algae presence was confirmed, as well. The textured particles are fragments of charcoal, while the solid pieces are “glasslike carbon.” Both can be interpreted as indicators of fire (Fig. 8).

Table 1

<table>
<thead>
<tr>
<th>Laboratory/method</th>
<th>Sample number</th>
<th>Sampled layer/dated fraction</th>
<th>Depth from surface (m)</th>
<th>Radiocarbon age (RCYBP)</th>
<th>Calibrated age calBP, 2σ (OxCal 4.2, intCAL13)</th>
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<tr>
<td>UNAM, Mexico/AMS</td>
<td>LEMA 422.1</td>
<td>Black mat UPPER part/humic acids</td>
<td>3.10</td>
<td>10,397 ± 30</td>
<td>12,140–12,095</td>
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<tr>
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<td>LEMA 422.2</td>
<td>Black mat UPPER part/charcoal</td>
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<td>10,438 ± 35</td>
<td>12,528–12,119</td>
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<tr>
<td>University of California-Irvine/AMS</td>
<td>UCIAMS-125805</td>
<td>Black mat, bulk/acid insoluble 1</td>
<td>3.30</td>
<td>10,414 ± 30</td>
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<td>Black mat, bulk/sample/base soluble</td>
<td>3.30</td>
<td>10,525 ± 25</td>
<td>12,582–12,417</td>
</tr>
<tr>
<td>University of California-Irvine/AMS</td>
<td>UCIAMS-125824</td>
<td>Black mat, bulk/residue</td>
<td>3.30</td>
<td>10,495 ± 20</td>
<td>12,564–12,403</td>
</tr>
<tr>
<td>Beta Analytic/AMS</td>
<td>Beta-350198</td>
<td>Black mat, bulk/total organic content</td>
<td>3.30</td>
<td>10,500 ± 50</td>
<td>12,270–12,220</td>
</tr>
<tr>
<td>University of California-Irvine/AMS</td>
<td>UCIAMS-125825</td>
<td>Black mat LOWER part/humic acids</td>
<td>3.20</td>
<td>10,659 ± 30</td>
<td>12,600–12,659</td>
</tr>
<tr>
<td>Beta Analytic/AMS</td>
<td>Beta - 399510</td>
<td>Above BM, Paleosol B1/humic acids</td>
<td>2.00</td>
<td>9520 ± 30</td>
<td>11,070–10,705</td>
</tr>
<tr>
<td>UNAM, Mexico/AMS</td>
<td>LEMA 507.1.1</td>
<td>Above BM, Paleosol B5/humic acids</td>
<td>2.60</td>
<td>9810 ± 50</td>
<td>11,317–11,166</td>
</tr>
</tbody>
</table>

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5.4.7. Total organic carbon (TOC), Total Inorganic Carbon (TIC), loss on ignition (LOI)

TOC and TIC analyses, involving the “loss on ignition” method, were performed on the three main strata: the pre-BM top layers of Unit D, the BM (Unit C2) and the post-BM transition of Units C1 to B (Figs. 5 and 6). The highest inorganic contents were observed in...
Unit D, reaching values of 35.55% (weight %). In the BM, the inorganic carbon falls to 8.72%, while the overlying strata show 28.21%. More evident is the behavior of the organic carbon (TOC), measuring 2.87% in Unit D, 9.19% in the YD (C2) deposit, and dropping to 4.17% at the base of Unit B. Certain BM samples, in separate assessments, showed increased values of around 12.9% of organic content, more elevated than expected.

5.4.8. Magnetic susceptibility
The raw results of the initial magnetic susceptibility tests had suggested there was low probability for significant burning in the BM. The situation changed and became better understood when the XFD ratio was used. XFD is the result of the porcentual difference between the magnetic susceptibility measured at low frequencies (470 kHz) and high frequencies (4700 kHz) (Fig. 5, center). Values higher than 10% indicate the presence of very fine supermagnetic grains. The results show low XFD values in the sub-BM layers, but increasing in the form of a protruding peak inside the BM, which confirms the existence of fine magnetic materials in the YD silty matrix. In strata above the BM, the concentrations of fine-sized supermagnetic materials return to sub-BM levels.

5.4.9. Heavy metals content
The BM has the highest content of heavy metals in relationship to the reference samples. The high values are likely an effect of metal-rich water table rises during the deposition interval. The iron (Fe) content is significantly high in all comparative samples: 4939.2 ppm in the BM, 4709.85 ppm in the hydrothermal deposit underneath (Unit D), and 3921.65 ppm in the pre-LGM black layers in the test excavations. The BM also rated high in Zn (68.75 ppm), Cu (272. ppm) and Pb (15.8 ppm).

5.4.10. Manganese content
The BM yielded low levels of Mn (42.4 ppm), much lower than the 202.55 ppm obtained for the greenish strata below. The black color is apparently not related to the Mn content, with the Fe content potentially contributing more to this characteristic.

5.4.11. Phosphate content
In comparison to the reference samples, repeated analyses of BM samples yielded the lowest values of total P (396.37 µg/g) and inorganic P (306.54 µg/g), and yet higher than the reference frames for organic phosphate (92.71 µg/g). This is consistent with a higher concentration of organic matter in the BM.

5.4.12. Mineralogy
The X-ray diffraction (XRD) qualitative analysis showed that the major element in the BM was quartz, followed by traces of albite, calcite and muscovite. Supra-BM layer C1 contains montmorillonite, while the sub-BM unit C3 includes cristobalite. The X-ray fluorescence (XRF) indicates that the main grain composition of the whole sequence is calcium carbonate and silica, with plagioclases and barium as secondary materials. The difference between the top (C1) and bottom (C3) units bracketing the BM (C2) consists of an increase of CaO at the bottom (31.13%), and an increase in Al₂O₃ (6.79%), Fe₂O₃ (1.20%) and TiO₂ (0.41%) at the top. The BM itself is characterized by FeO (4.18%), TiO₂ (1.36%), SiO₂ (52.30%) and very small amounts of CaO (6.45%). Forty-one trace elements were identified by inductively coupled plasma mass spectrometry (ICP-MS). The BM sample was analyzed in parallel with two reference samples from the older strata exposed in the western gully. The results showed titanium was dominant as the main trace element, with values in excess of 3700 ppm, joining Fe as a principal component. Other high values were observed for barium, vanadium, strontium, selenium, copper or lithium. The high values of Cu, Pb and Zn revealed by this method are consistent with the results of the heavy metal analysis. The incipient observations made by electronic microscopy (SEM) confirm the presence of these dominant elements, such as iron, titanium and selenium. The energy-dispersion X-ray spectroscopy (EDS) results are in concordance with other analyses: the dominant elements in the BM are titanium (29.68%, in weight %), iron (30.23%), and oxygen (28.74%), with Si, Al, Ca, Mn and C as accessory components (Figs. 6 and 7).

6. Discussion
New black mats dating to the YD interval are being discovered in other parts of the continent (Rachal et al., 2016; Israde-Alcántara et al., 2017). The finds at Ojo de Agua indicate the phenomena responsible for such geological signatures were widely extended geographically. In an eloquent study, Harris-Parks (2014) analyzed 25 black mats from localities in the southwestern United States, many of them related to early human occupations. The results define the black mats as sediments and paleosols formed in spring-related moist contexts, establishing a classification with four main categories (labeled I,II, IIb, and III). ‘Type I’ is defined by a “massive to layered, blocky structure, composed of finely fragmented opaque organic matter, little mineral component, phytoliths abundant”, with black opaque micromass. Its genesis occurs in contexts with shallow standing water affected by abrupt periods of desiccation that would cause peat-like accumulations of organic matter (Harris-Parks, 2014: 39, Table 1).

Except for the absence of phytoliths and pollen in our samples, the Ojo de Agua BM corresponds to Harris-Parks’ Type I: water-lain in a spring-fed pond, with 9.19–12.9% of organic content versus 8.72% of inorganic carbon; a structure of angular blocks; abundant organic matter from decomposed vegetal material; a high count of vegetal charcoal specks. Its microcomponents are almost entirely opaque finely fragmented fitoclasts. In thin sections, the organic matter does appear reddened on the edges and most samples yielded elements keeping intact cellular structures.

The YD-age BM from Murray Springs is also classified as Type I by Harris-Parks. The reason to insist on the Murray Springs case is because it is more familiar and better known to archaeologists doing prehistory-related work in our regions of study, and we used to face legitimate questions from colleagues regarding similarities between the Mexican BM and the Arizona ones. It is difficult to establish a comprehensive comparison based on absolute values. No matter how similar the formation processes may have been, it cannot be expected for sites situated thousands of km apart to yield identical results. Differences stand out easily: the Mexican BM contains considerable amounts of charcoal specks, algae remains have been observed but not in relevant amounts, phytoliths and gastropods are absent, and so are indicators of human activity. Nevertheless, the Ojo de Agua deposit belongs to the same specific topological conditions that favored the formation of BM during the YD in desiccated marshy ponds. It is still premature to perform reliable comparisons between the Ojo de Agua BM and the other cases of dark strata recently reported by Israde-Alcántara et al. (2017) for several lacustrine localities in Mexico. But, considering the reassessments and synthesis performed by Harris-Parks (2014); the Ojo de Agua BM displays major geological and chemical attributes of a “type I black mat”, taxonomically similar to Murray Springs.

Across the entire stratigraphic column, repeated indicators of fires suggest the presence of vegetal fuel mass in the area, and the highest values come from the BM stratum, with 147 mpc. The abundance of charcoal specks indicating vegetation around the spring marks an interesting contradiction with the lack of pollen
and phytoliths in the black layer, but consistent with a period of drought that desiccated the pond, transformed it into a swamp, and dried the surrounding vegetation (grasses and pines), causing wildfires. Although one of the co-authors has been actively involved in the study of the extraterrestrial impact theory (Israde-Alcántara et al., 2012, 2017), the purpose of the present study was not to corroborate that particular explanation. The Ojo de Agua BM has not produced relevant data supporting the impact theory, so far. Nevertheless, the large burning of biomass clearly visible in the samples was most likely linked to an anomalous event, showing large amounts of windblown burned material as a product of extensive fires in a dry environment.

This distinctive black layer is rich in organics, possibly as a result of the rapid death and breakdown of large quantities of floral species, due to a rapid climatic deterioration at the end of the YD, and successive burning. The results also show no human influences on its deposition, because specific signatures (such as organic phosphates) were not present. The BM seemingly formed from sudden natural events, like a particular combination of underground water table oscillations, atmospheric precipitation and temperature and the color could be attributed to a burning episode. A plausible idea, though, is that the depositional sequence in Ojo de Agua arroyo has been very fluid since its formation, with a highly variable water table over time, which caused large amounts of post-burial mixing and leaching of physical and chemical properties through the layers. This would justify further analyses, more micromorphology assessments and additional plant micro/macro-fossil work, in order to determine the nature of the organic material present.

There are no diatoms anywhere in the stratigraphic sequence, although the presence of a small lake is evident. Geochemical analyses show an environment dominated by the chemical precipitation of calcium carbonate in conditions of supersaturated alkaline water propitiating the formation of travertinous deposits. The very low magnetic susceptibility values of sediments previous to YD indicate very low fluviatile detritic input in a system fed by constant hydrothermal spring flow. The BM does not contain either ostracods or gastropods, but they are present in strata above and below C2. Gastropods are mainly represented by Succineidae family, small land snails that prefer humid conditions, like marshes. Deroceras aenigma also lives in environments with permanent humidity. Ostracod records include only one freshwater species (Candona sp.) in layers overlying the BM, but increase to at least five taxa in strata below. The lack of malacological material parallels the total absence of phytoliths. However, there were variations in the pH of the BM. Those may be related to specific and variable concentrations of organics and carbonates or salts in different samples, suggesting that the geochemistry of a BM layer may not be homogenous across the deposit. The same may be valid for other measurements.

During the YD, conditions changed drastically showing an increase in fine silty clay and particles rich in charcoal including plant tissues and Ti, Fe, and K as major cations. The diluted conditions, together with fires around the basin, indicate a humid and fine detrital marshy environment. The marsh or shallow lake was interrupted by wildfires that stopped carbonate sedimentation and produced infilling of the lake, which became a shallow pond.

The BM is followed in time by relatively stable climate phases, with the incipient formation of soils during the Early Holocene (Unit B). Above them, at the top of the profile, the succession of eolian sediments (Unit A) speaks of the progressive aridization of the region. Two AMS dates obtained from two of the overlying strata show that the sedimentation of the following 1 m above the BM occurred very fast, within about 1000–1500 radiocarbon years after the deposition of stratum C2 (Table 1). The AMS dates obtained for two of the paleosols in Unit B correspond to periods immediately after the end of the YD chronozone. These dates are in consonance with the solid radiocarbon values obtained for the BM itself. During the early stages of the Early Holocene, after the termination of the YD, the environment seems to have been stable and relatively humid at Ojo de Agua. The aridity manifested in the top 2 m of the stratigraphy suggests dramatic climate changes that may have occurred after the so-called Altithermal, once the Middle Holocene started.

Cultural material and megafauna remains are not present at all on the stratigraphic sequence containing the BM. Early human presence has been confirmed throughout the endorheic basin, but people did not make use of this geographic spot precisely during the deposition of the studied sediments or they simply did not leave materials inside the pond. From another perspective, the fire markers seen in the BM could hypothetically relate to anthropic activities, as suggested by others, elsewhere (Piperno and Jones, 2003). Fragmented skeletal parts of extinct species are relatively abundant, but only in strata of considerable age, older than the Late Glacial Maximum. As a hypothesis for future work, the iconic Pleistocene megafauna may have already disappeared from the region before the YD.

We chose the path of repeated replication of radiocarbon dates on different sediment fractions by independent laboratories because we sought an irrefutable argument in favor of the YD age of the layer. Several causes can be invoked when speaking about the potential contamination with old or young carbon of contexts like this, located in depressions and vulnerable to hydrological mechanisms. Our dates indicate that all organic components of the Ojo de Agua BM are of the same age, meaning that our deposit is chronometrically “healthy”. More studies on such deposits will probably confirm that the particular signatures of natural processes and climatic conditions related specifically to the Younger Dryas do give this type of BM the potential to be considered a chronostratigraphic marker for the Pleistocene-Holocene Transition.

7. Conclusion

Repeated radiocarbon assessments confirm that the Ojo de Agua BM dates to the YD interval. This Mexican BM is a sediment, as there are no conclusive indicators of pedogenesis for it to be considered a paleosol. The results of the analyses are similar to other cases in North America and situate the Ojo de Agua example in Harris-Parks’ Type I category. The role potentially played by algae in the formation and coloration of the Zacatecas case has not been positively evaluated yet, but an abundant organic content derived from the decomposition of vegetal matter and a considerable amount of vegetal charcoal specks indicate the existence of anomalous events at the onset or during the YD interval and offer clues to the physical and geo-chemical particularities of the black layer. Significant and abrupt water table oscillations occurred in the Zacatecas spring-fed system in YD times, leading to the formation of highly organic deposits of soaked mud in place of previously opulent ponds.

The presence of primary structures, charcoal fragments, gastropods and ostracods along the main stratigraphy at Ojo de Agua confirm the existence of a shallow water body, at the end of the Pleistocene, fed by a thermal spring surrounded by abundant cold-adapted grasses and coniferous trees. This landscape was interrupted by sudden events during the YD climate reversal and the pond transformed into a muddy marsh that witnessed significant burning of biomass. Such episodes of intense fires have been observed in numerous other sites in distinct environments, often associated to charcoal flecks and soot blown in form wildfires. Other proxies such as spherules were not present in our sedimentary sequence, possibly because of a quick oxidation of Fe in an
arid environment, but further analysis of the BM is needed in order to test this assumption. After the YD, the deposits reflect periods of stability with soils being formed. The marsh was gradually replaced by a fluvial system of low energy. Later into the Holocene, the environment became more alluvial, supporting coarser gravels in minor fluvial channels. At the top of the column, alternating thin beds of fine eolian sediments show the final aridization of the region.

The Ojo de Agua black mat forms part of an important stratigraphic sequence that provides valuable insights to the ancient landscape of a region that had never been studied before. The true potential of such a distinctive black layer can only be understood after more studies are performed and similar cases discovered. It is true that a BM like this has limited use as a regional marker because its genesis is strictly related to very specific niches, while its chronological significance is much more diluted than previously thought. Nevertheless, it is important to keep exploring the potential of YD black mats as a valuable aid in the understanding of regional Quaternary geology and paleoclimatology within the context of the investigation of early human occupations.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.quaint.2017.08.069.

References

