ARCHAEOLOGY

Paleoindian ochre mines in the submerged caves of the Yucatán Peninsula, Quintana Roo, Mexico

Brandi L. MacDonald[1]*†, James C. Chatters[2,3]*†, Eduard G. Reinhardt[4]*†, Fred Devos[5], Sam Meacham[5], Dominique Rissolo[6], Barry Rock[7], Chris Le Maillot[5], David Stalla[8], Marc D. Marino[1,9], Eric Lo[6], Pilar Luna Erreguerena[10]

Copyright © 2020 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).

Investigations in the now-submerged cave systems on the Yucatán Peninsula continue to yield evidence for human presence during the Pleistocene-Holocene transition. Skeletal remains are scattered throughout the caves of Quintana Roo, most representing individuals who died in situ. The reasons why they explored these underground environments have remained unclear. Here, we announce the discovery of the first subterranean ochre mine of Paleoindian age found in the Americas, offering compelling evidence for mining in three cave systems on the eastern Yucatán over a ~2000-year period between ~12 and 10 ka. The cave passages exhibit preserved evidence for ochre extraction pits, speleothem digging tools, shattered and piled flowstone debris, cairn navigational markers, and hearths yielding charcoal from highly resinous wood species. The sophistication and extent of the activities demonstrate a readiness to venture into the dark zones of the caves to prospect and collect what was evidently a highly valued mineral resource.

INTRODUCTION

By the end of the Pleistocene, humans had migrated to and inhabited the area of Quintana Roo, located on the eastern Yucatán Peninsula, Mexico (*1*–*3*). This karstic landscape is characterized by a large limestone platform punctuated by a now-submerged system of caves. The cave systems were dry and accessible from the Last Glacial Maximum (LGM) until the middle Holocene transition {>13,000 to 8000 calibrated years before present (cal B.P.) [9 to 8 thousand years (ka)]}, after which time most of the caves flooded during sea-level rise, resulting in a unique and well-preserved paleorecord. In the cave systems of Quintana Roo, the remains of at least 10 individuals dating to the Pleistocene-Holocene transition have been reported (*1*, *2*, *4*, *5*); most of these represent persons who had entered when the caves were dry and accessible. However, the reasons why people persisted in their underground exploration of these places have been largely unknown. Previous suggestions have included temporary shelter, access to fresh water, ritual, or intentional burial of human remains (*1*, *6*, *7*), although none are firmly substantiated by available archaeological evidence.

Here, we present uniquely preserved evidence indicating that people were exploring underground cave systems to prospect and mine red ochre, an iron oxide earth mineral pigment used widely by North America's earliest inhabitants (text S1). Red ochre is the most commonly identified inorganic paint used throughout history worldwide (*8*, *9*). Considered to be a key component of human evolutionary development and behavioral complexity, ochre minerals were collected for use in rock paintings, mortuary practices, painted objects, and personal adornment for millennia. Red ochre use is a common characteristic of North American Paleoindians and is found associated with human remains (*10*, *11*), mobiliary art, toolkit caches (*12*), ochre grinding stones, ochre-processing areas (*13*), hide tanning, or other domestic or utilitarian contexts, including a component of grease, mastic, and hafting adhesive (*14*). One instance of ochre quarrying activity has been proposed at the Powars II site (Wyoming), yet evidence for intensive mining activity (i.e., pits and trenches) remains uncertain (*15*–*17*). Whether ochre procurement or use by Paleoindian groups and their Old World predecessors constitutes evidence for ritual behavior or utilitarian purposes remains an ongoing anthropological discussion (*12*, *18*), yet consensus suggests that the two are not mutually exclusive (*19*, *20*). Despite the ubiquitous and sustained use of ochre among Paleoindian peoples, there is virtually no archaeological evidence available concerning ochre prospection and mining methods in the Americas.

RESULTS

Sites in three now-submerged cave systems along the eastern coastline of Quintana Roo, referred to here as Camilo Mina, Monkey Dust, and Sagitario, including the section called La Mina, contain evidence for ochre mineral prospection and extraction (Fig. 1). All sites are presently located within 8 to 10 km inland of the present-day coastline (Fig. 1A). On the basis of the bathymetric profile, the shore would have been ~1 km farther away during the terminal Pleistocene. Qualitative and geochemical analysis of ochre from all three sites indicates that they include high-purity iron oxides and that the material from La Mina and Camilo Mina, in particular, is conducive to the production of a vibrant, fine-grained red mineral pigment (Fig. 1B, text S2, fig. S1, and table S1). We focus the bulk of our presentation here on Sagitario and the La Mina section (Fig. 1, C and D),

[1]Archaeometry Laboratory, University of Missouri Research Reactor, Columbia, MO 65211, USA. [2]Applied Paleoscience, Bothell, WA 98011, USA. [3]DirectAMS, Bothell, WA 98011, USA. [4]School of Geography and Earth Sciences, McMaster University, Hamilton, ON L8S 4K1, Canada. [5]Centro Investigador del Sistema Acuífero de Q Roo (CINDAQ A.C.), Puerto Aventuras, Q Roo, Mexico. [6]Qualcomm Institute, University of California, San Diego, La Jolla, CA, 92093-0436, USA. [7]Department of Natural Resources and the Environment, University of New Hampshire, Durham, NH 03824, USA. [8]Electron Microscopy Core, University of Missouri, Columbia, MO 65211, USA. [9]Department of Anthropology, University of Arkansas, Fayetteville, AR 72704, USA. [10]Instituto Nacional de Antropología e Historia, Mexico City, DF, Mexico.
*Corresponding author. Email: macdonaldb@missouri.edu (B.L.M.); paleosci@gmail.com (J.C.C.); ereinhar@mcmaster.ca (E.G.R.)
†These authors contributed equally to this work.

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024

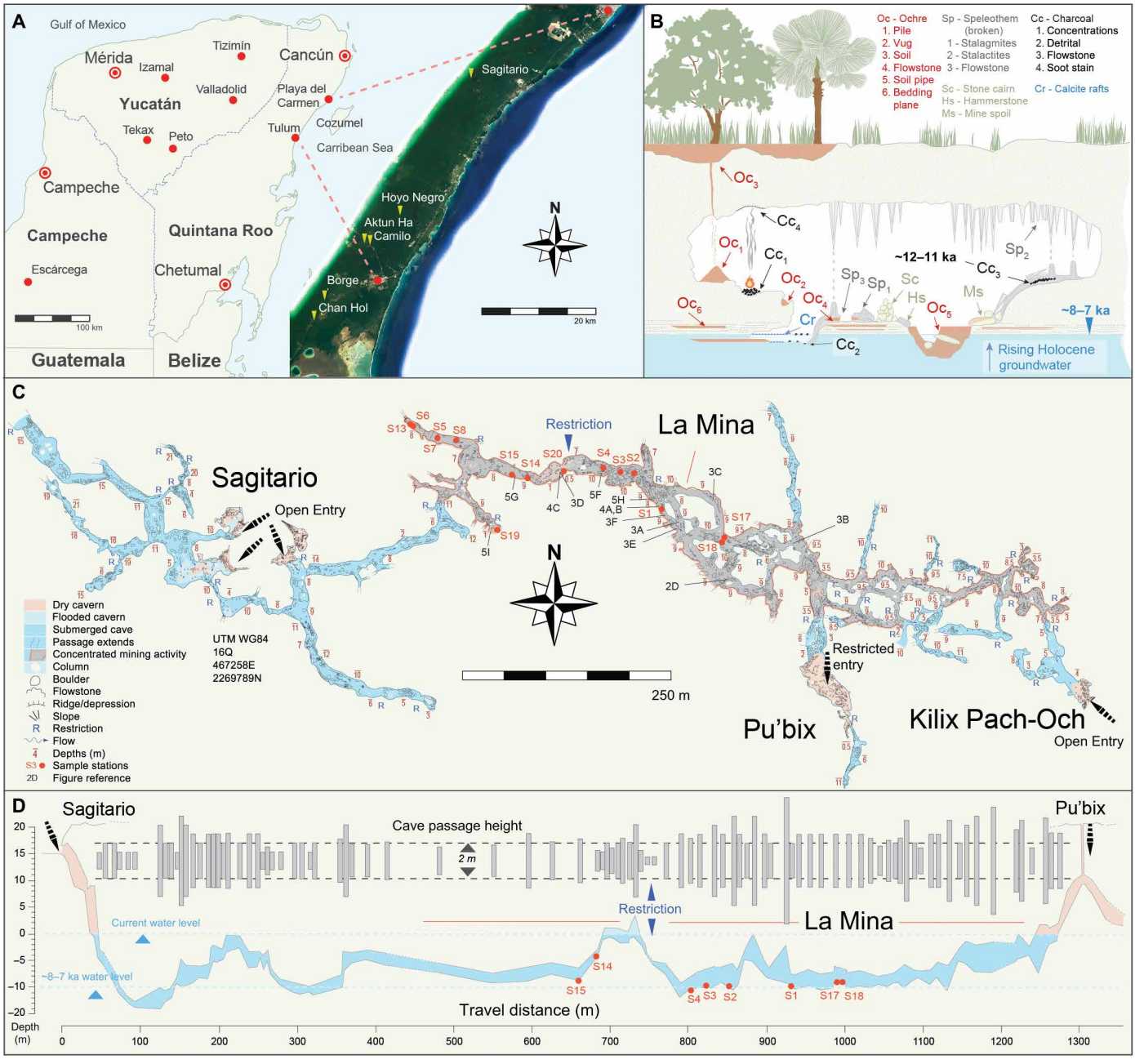


Fig. 1. La Mina site context. (**A**) Regional overview of study area. La Mina is situated within the Sagitario cave system, while Camilo Mina is located in Sistema Camilo. Monkey Dust is part of the Borge section of Sistema Dos Pisos. Hoyo Negro and Chan Hol are sites of key importance in Paleoindian archaeology in this region (*1*, *2*). Satellite image modified from Google Earth Imagery (*41*). (**B**) Conceptual cross-section showing relationship between geomorphic and cultural features observed in La Mina, Camilo Mina, and Monkey Dust cave systems, including ochre deposits, speleothem and flowstone, mining spoil, charcoal and soot deposition, hammerstone artifacts, hearth features, and calcite rafts. (**C**) Map of Sagitario and La Mina showing the configuration of the cave system and its geomorphic features, with the location of sample stations and key features. La Mina is defined as areas of concentrated mining activity within Sagitario. (**D**) Cave profile from the Sagitario and Pu'bix cave entrances showing cave bottom and ceiling heights at survey stations on the main cave line. Profile path is denoted by the restriction between Sagitario and La Mina sections of the cave and sample stations. Horizontal distance (in meters) is measured as the length of the survey line over the irregular topography of the cave and thus represents an overall travel distance for human movement rather than horizontal distance. Cave passage height along the profile shows the restricted nature of the mine site and the difficulties accessing and removing ochre from this location.

which is the subject of most intensive study and the locality with the richest evidence for ochre prospecting and mining. Camilo Mina and Monkey Dust also demonstrate characteristics of ochre prospecting and mining, consistent with those observed in Sagitario, and are the subject of future study. We demonstrate here that subterranean ochre prospection and mining was not limited to a single location and may have been a regional-scale activity that was sustained over multiple generations.

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024

Navigating, prospecting, and ochre mining at La Mina

To date, more than 7000 m of the Sagitario cave system has been explored and mapped. Ochre mining is confined to the area referred to as La Mina, a ~900-m-long series of anastomosing tunnels situated largely east of the restriction that separates La Mina from Sagitario (Figs. 1C and 2, A to C). Before the inundation of the cave by postglacial sea-level rise, the ochre miners used one of three surface entry points, Entrada Pu'bix, Entrada Sagitario, or Entrada Kilix Pach-Och (Fig. 1C) (*1*, *7*, *21*, *22*). All mining activity is located well into the dark zone of the cave. The nearest light is the narrow, chimney-like Entrada Pu'bix, at least 200 m from the closest mining activity. At its farthest, natural light is more than 650 m away. From any of the three possible entrances, the passages leading to and in the immediate vicinity of the mined area are generally wide (>20 to 25 m), often with a short ceiling clearance (1 to 2 m) (Fig. 1D). Several narrow passages with tight restriction points necessitated careful navigation to access La Mina. One length of passage to the east of Entrada Pu'bix was at one time completely obstructed by a dense concentration of stalactites and stalagmites. These speleothems were broken out wide and high enough to allow movement of people and ochre between the mining area and the surface (Fig. 2A and fig. S7).

Evidence of human activity in La Mina is abundantly clear (Figs. 2D and 3, A to F). Broken speleothems and stacked piles of debris lie everywhere. The passageways from both surface entrances are marked with cairns of shattered flowstone (Fig. 3B) and broken stalactites, evidently used as navigational markers directing the miners to the ochre pits (Fig. 3, C and D). To date, we have documented 155 cairn features and 166 locations with broken speleothems (Fig. 1C). One example includes two cairns straddling a narrow path, one of which includes a standing, ochre-stained stalagmite fragment (Fig. 3E). Another example includes a cairn beside a fire-reddened hearth area (Fig. 3F and fig. S4). Broken lengths of speleothem, used opportunistically as expedient hammerstones (Fig. 3A), and shattered piles of flowstone evident of ochre prospecting (Fig. 3E) are scattered along the 900 m of passageways. Lengths of flowstone floor along the edges of mine pits and large stalagmite bases used in cairn construction are visibly scalloped by conchoidal fracturing (Fig. 3, B to D). Broken stalagmite bases are carefully stacked on the tunnel floor. Where it was too thick to break, the flowstone has been deeply undermined (Fig. 2D). Piles of mine spoil line the cave walls, overlying the flowstone floor (Fig. 2E). Stalactites and "soda straws" that once draped the ceiling above are broken away, and their remaining stumps were stained black. Pits and trenches from which the ochre was last extracted span the entire breadth of the cave floor, while older pits are filled with rubble discarded from continuous digging. These pit features are often more than 50-cm deep, where ochre minerals had been removed from what appear to be soil-pipe and detrital flowstone ochre deposits (Fig. 1B and fig. S2, B and C). In other areas, small patches of flowstone are broken out, yet no digging occurred beyond exposure of the substrate, as though these were failed prospects. The site appears much as it was when abandoned. Throughout most of the mine, no more than a light dusting of fine sediment or scattering of calcite rafts covers artifacts and archaeological features.

It is reasonable to suggest that the ochre from La Mina was targeted, in part, for its mineral properties. The color, texture, and overall quality of ochre pigments are attributable to characteristics such as iron oxide content (purity), grain size, and the presence and quantity of other mineral impurities. Ochre samples were collected from multiple locations throughout La Mina (Fig. 1A) and from terra rossa soils (text S3) from the surface near the entrance of Sagitario. They were analyzed to determine their elemental, mineralogical, and morphological properties (see text S2 and fig. S1D). Results showed that the ochre from La Mina was vibrant red, high in iron oxide purity (~60 to 80% by mass), with fine-grained pigment particles (<1 μm) and low amounts of mineral impurities. In contrast, the iron-enriched terra rossa soils from the surface were low in iron oxide purity (~8.0% by mass), low in color intensity, and dominated by impurities of coarse-grained quartz, boehmite, and almandine particles (>50 μm; text S2, fig. S1, table S1, and data S1). Of the samples we have collected to date, the composition and texture of the terra rossa soils surrounding Sagitario would not be an optimal choice for the production of pigment, especially when one considers the high-purity ochre that was readily available in the cave systems below. The ochre from La Mina is arguably a ready-made paint, which may be one of the reasons why these individuals went to such efforts to collect it.

Estimating the amount of ochre removed from La Mina is complicated by the variability in the source deposits (see text S3 for expanded discussion). To date, we have identified 352 individual disturbance features (e.g., pits, trenches, beds, and lenses) along the ~900 m of mining activity, where many, if not most, would have been filled with ochre. These pits are often intercut and contiguous for up to ~75- to 100-m-long sections of the tunnels. However, the volume and size of each mine pit is not necessarily equal to the amount of ochre retrieved. Evidently, not all of the pits contained exploitable ochre deposits. Many of the ochre formations at La Mina are the result of "soil pipes" that were originally paleosols bedded within the limestone stratigraphy. These were subsequently exposed in the cave bottom during speleogenesis (see Fig. 1B). These paleosol units are often irregular in dimension and may have contained additional fragments of limestone. The ochre deposit sometimes appears to have been quite thick. For example, the mined deposit from a pit in Sagitario (La Mina) was up to 1 m thick. A thin covering of ochre staining along the pit walls illustrates the extent of the original fill, which transitions to a clean limestone above the cave bottom. Pits such as these may not have necessarily required extensive breakup of limestone or flowstone. In contrast, some ochre lenses that were interbedded between flowstone layers were generally thin (~1 to 5 cm), with variable geometries and extents (tens of centimeters to several meters in length). Extracting ochre from those thin beds required considerable effort to break and remove the thick layers of flowstone, and we frequently see tens of meters of cave floor dug out from wall to wall. These irregularities inhibit our ability to provide an accurate estimation of the total amount of ochre removed from La Mina over the period of its use. Yet, the combined volume of flowstone and speleothem that was broken and removed, and the probable amount of ochre extracted from the viable deposits along the ~900-m length of the mining area debris field, is considerable.

Dating human activities at La Mina

People could not possibly have reached the mined passageways and pursued their work in the dark zone of the cave without fires for illumination. We identified numerous concentrations of charcoal (Figs. 2A and 4A) and patches of fire-reddened stones and earth along the tread-worn floor between the Sagitario cave entrances and the ochre mining area of La Mina (Figs. 2 and 3F and fig. S3). In

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024

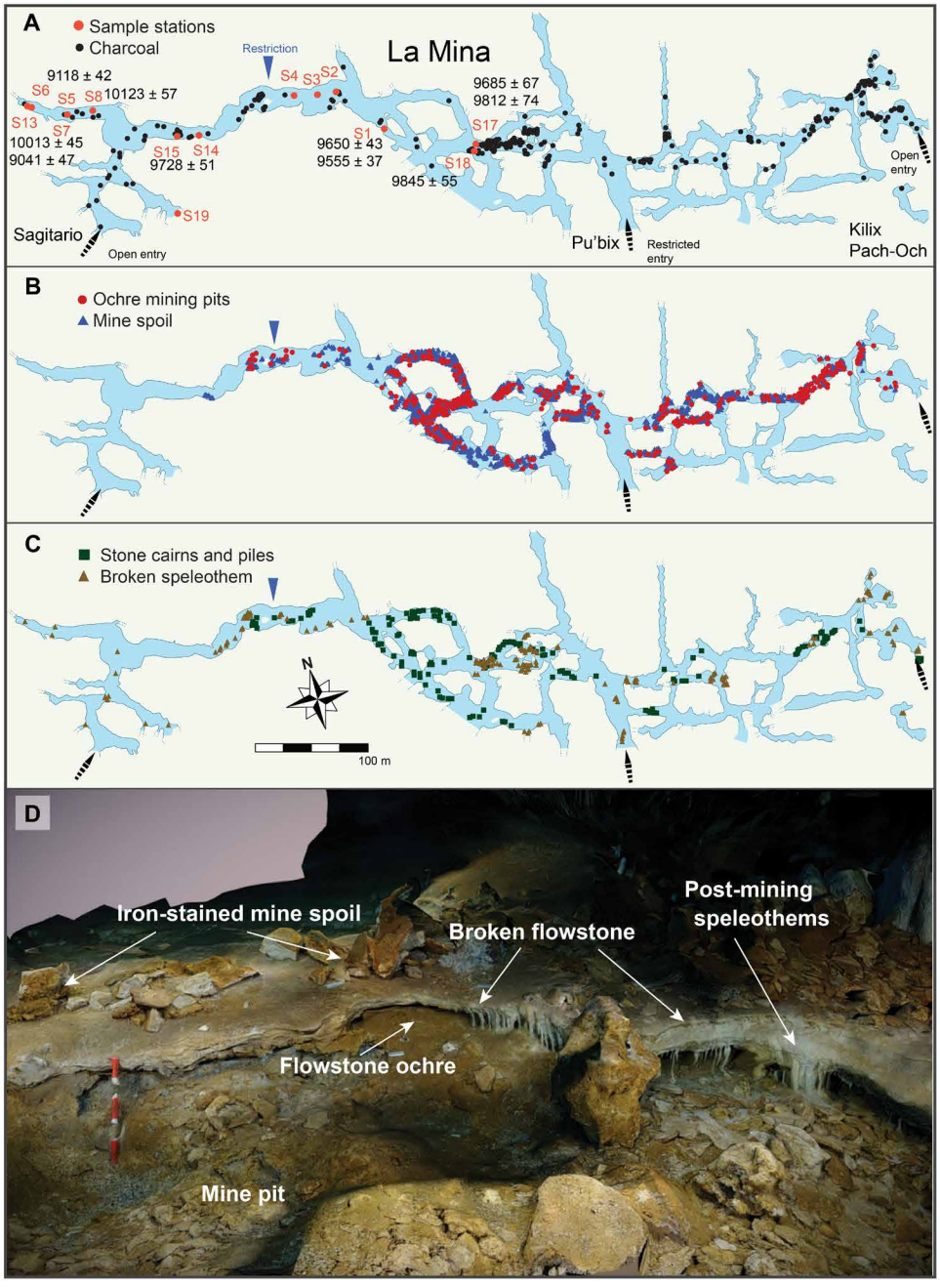


Fig. 2. Overview of cultural features at La Mina. (**A**) Distribution of charcoal concentrations and sampling locations (ochre, charcoal, and calcite raft). (**B**) Distribution of ochre mining pits and mine spoil. To date, 352 disturbance features have been mapped. (**C**) Distribution of stone cairns, rubble piles, and broken speleothem. (**D**) Mine pit showing associated cultural and geomorphic features found in La Mina [see Fig. 1C for location; frame grab from structure from motion (SFM) three-dimensional (3D) model of the cave floor]. Photo credit (for original photography used to produce 3D model shown in 2D): F. Devos (CINDAQ) and S. Meacham (CINDAQ).

some cases, the ceiling above these charcoal-bearing features is still visibly blackened, evidently by the soot that would have issued from the small fires.

We established the age and duration of mining activities in La Mina and Sagitario by a combination of radiocarbon dates on charcoal and calcite rafts, the presence of postmining calcite formations, and the documented regional record of postglacial sea-level rise. Charcoal is a difficult medium for dating in the submerged caves of Quintana Roo because it may be produced by forest fires, then deposited by wind and rain, and remobilized repeatedly by floods during major storm events or, ultimately, by rising sea level. Archaeologists have often interpreted instances where charcoal concentrates in small catchment basins and litters cave floors as prima facie evidence of human activity (*6*, *23*, *24*). However, the mere presence of charcoal concentrations is insufficient to make this inference. Before submerged-cave charcoal can be interpreted as anthropogenic, it is necessary to

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024

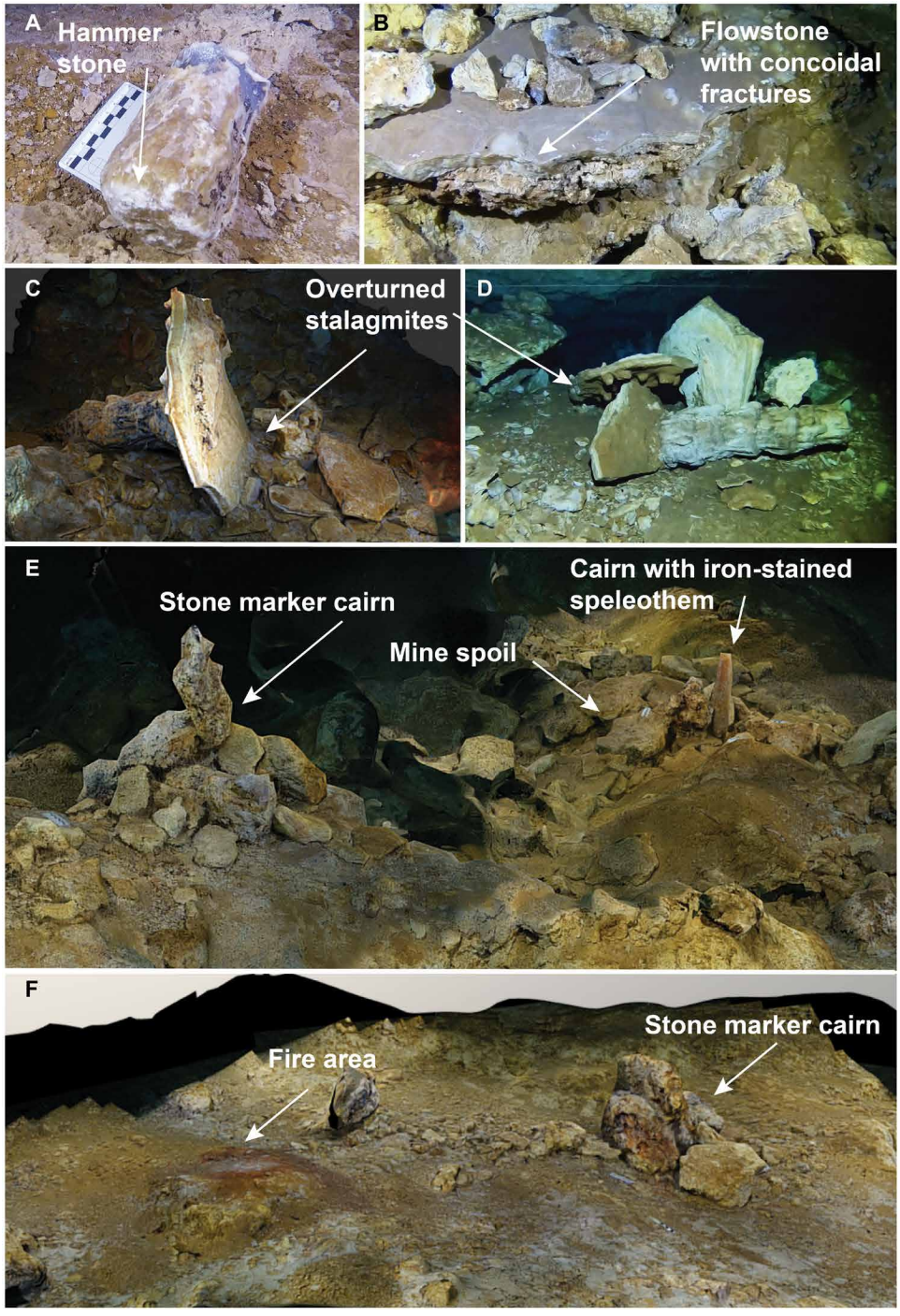


Fig. 3. Selected details of cultural features at La Mina. (**A**) Hammerstone made from a selection of speleothem. (**B**) Conchoidally fractured flowstone floor. (**C**) A tipped stalagmite showing a series of conchoidal fractures around flowstone of its base. Similar fractures can be seen in the stalagmite bases shown in (D). (**D**) A carefully stacked pile of three broken stalagmites. (**E**) Two cairns with elongated central stones. Note that the background cairn supports an ochre-stained segment of stalagmite (see Fig. 1C for locations). (**F**) Pairing of a burned surface and limestone cairn. See also fig. S3. Images in (A), (B), and (D) are digital still images captured by camera. Photo credit: F. Devos, CINDAQ. Images in (C), (E), and (F) are grabs from SFM 3D models of the cave floor. Photo credit [for original photography used to produce 3D model shown in (C), (E), and (F)]: S. Meacham (CINDAQ).

establish that the sample materials are artifacts, that is, that they are representative of human activity and distinct from the products of natural processes. At La Mina, there is an abundance of fire-reddened deposits indicative of in situ burning, which would be compelling in this context, but for administrative reasons, we have not yet had an opportunity to sample all examples of those features. To establish that the charcoal samples were artifacts, we identified splits of individual charcoal fragments to genus level (text S4 and fig. S4) and

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024

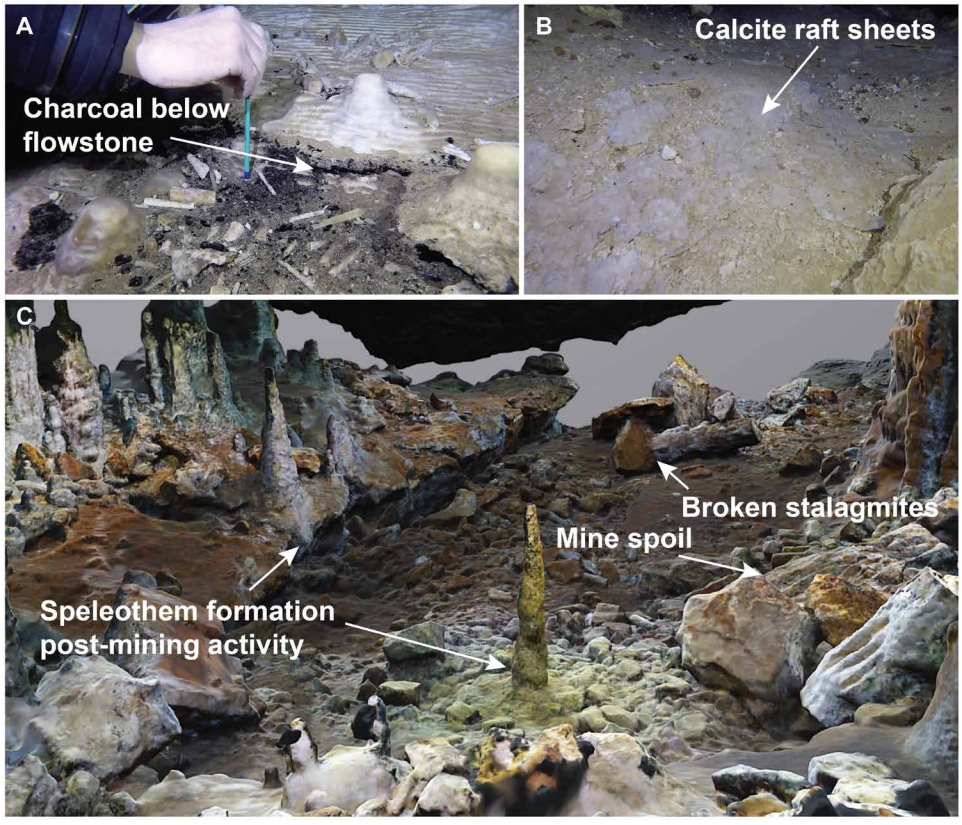


Fig. 4. Dating features. (**A**) Charcoal concentration from sample station S1. The charcoal is sealed above and below by flowstone indicating that it was deposited before the cave was flooded. (**B**) Sheet calcite rafts deposited in an area of mining activity and below a limestone overhang. Note the large size of rafts (10 to 20 cm in diameter) and sheet-like distribution on cave bottom (S1, B9; Fig. 2C, table S1, and fig. S2A). See text S3 for explanation of calcite rafts. (**C**) A 3D model showing the relationship between a mine pit and a large stalagmite formed on pit floor (right) and a second stalagmite with flowstone formed over the broken edge of the undermined floor. The speleothems indicate that they formed in a dry cave for a relatively long time after the mining activity had ceased, reinforcing the ~12 to 10 ka radiocarbon age. Note the stack of three tipped stalagmite bases in the distance that is also shown in Fig. 3D. Photo credits: F. Devos (CINDAQ).

compared the results with identified splits of dated charcoal from nearby Hoyo Negro [see figure 1 in (*1*)]. Hoyo Negro is an immense, 30- to 55-m-deep, 60-m-diameter underground collapse chamber littered with charcoal, which has been continuously sampled and dated since 2011 (*1*, *3*). Samples from Sagitario and Hoyo Negro fall within the same age range (Table 1). Charcoal in Hoyo Negro may be considered at least predominantly naturally deposited and is thus a suitable proxy for establishing whether the La Mina charcoal concentrations are natural or anthropogenic.

We found that all identifiable fragments of La Mina charcoal from all sampling in Sagitario were produced from highly resinous trees known to burn long and bright, referred to colloquially as "torchwood," "candlewood," and "copal" (Table 1). All of these specimens exhibit markedly expanded voids in the vascular ray structure produced by exploding gasses, indicating combustion under intense heat (fig. S4 and text S4). In contrast, the dated charcoal specimens from Hoyo Negro are from a wide variety of nonresinous woods and include only one specimen of copal. Subsequent identification of a larger sample of wood from Hoyo Negro did include candlewood and torchwood, but all specimens of resinous woods lacked the explosive voids, indicating that the Hoyo Negro specimens burned more slowly in a lower oxygen environment. From this pattern of species representation and combustion features, we are confident that the samples from Sagitario are not the result of natural deposition of ambient charcoal, but rather represent wood burned to light the mining activity. This conclusion is supported by the cave profile (Fig. 1D), which shows that it is highly unlikely that any of the dated samples in Sagitario could have washed to their locations. In addition, five of the dated charcoal specimens from Sagitario (La Mina) were collected from deposits situated beneath flowstone that formed after the charcoal was deposited (e.g., Fig. 4A), which would have prevented the transport of charcoal as groundwater flooded the cave at ~7 to 8 ka during Holocene sea-level rise.

The calibrated radiocarbon ages of charcoal from La Mina and the nearest Sagitario sample (see ST-15, shown in Fig. 2A) cluster between 11.4 and 10.7 ka (Table 1), which appears to have been the primary period of mining in the western portion of the cave system. Samples from the small side tunnel of Sagitario (see ST-5, ST-7, and ST-8, shown in Fig. 2A) form two age groups, one between 12.0 and 11.3 ka and another between 10.4 and 10.1 ka, potentially representing multiple periods of ochre exploitation spanning up to 2000 years.

The Paleoindian age of La Mina is corroborated by the timing of the flowstone formation and of the submergence of the cave by sea-level rise. At multiple locations, flowstone can be seen encrusting mined surfaces (Figs. 2D and 4C); sheets of flowstone cap most of the charcoal concentrations that were sampled and dated (Fig. 4A).

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024

Table 1. Radiocarbon ages and taxonomic identification of charcoal from Sagitario (La Mina), Camilo Mina, Monkey Dust, and Hoyo Negro.

Site sample	Station	Depth (m)	Identification (common name)	D-AMS #	^{14}C age (yr B.P. ± 1σ)	Age cal yr B.P. (2σ)
Sagitario (La Mina)						
P06	7	10.7	*Bursera* spp. (torchwood)	30619	10,013 ± 45	11,720–11,290
P07	5	11.0	*Bursera* spp.	30620	9,118 ± 42	10,400–10,210
P10	7	11.0	*Protium copal* (Copal)	20621	9,041 ± 47	10,280–10,150*
P14	8	11.0	*Protium* copal	30623	10,123 ± 57	12,020–11,410
P15	20	8.9	*Amyris* spp. (Candlewood)		Undated	
P16	15	9.2	*Amyris* spp.	30624	9,728 ± 51	11,240–10,870
P11	1	9.0	*Amyris* spp.	27467	9,650 ± 43	11,200–10,790
P12	1	7.8	Unidentifiable	27468	9,555 ± 37	11,090–10,720
P13	1	9.3	*Protium copal*	30622	9,685 ± 67	11,230–10,790
P21	17	9.3	Unidentifiable	30625	9,812 ± 74	11,410–11,080*
P22	18	8.9	*Protium copal*	30626	9,845 ± 55	11,390–11,180
Hoyo Negro						
111204-10		27	*Zanthozylon spp.*	17932	9,549 ± 42	11,090–10,710
150515-3d		42	*Protium* spp.	34148	9,581 ± 36	11,110–10,750
150515-6d		42	*Clusia* spp.	95812	9,565 ± 40	11,100–10,740
150515-6e		42	*Ficus* spp.	34146	9,600 ± 45	11,150–10,760
171128-12		46	*Non-resinous*	26516	9,313 ± 36	10,650–10,410
171128-16		45	*Ficus* spp.	26517	9,478 ± 39	11,070–10,590
171128-25		40	*Zanthozylon* spp.	27543	9,744 ± 41	11,240–11,110
171128-34a		41	*Ficus spp.*	34995	9,570 ± 37	11,100–10,740
181120-10a		43	*Brosimium or Bursera* spp.	31578	9,650 ± 45	11,110–10,730
181120-23a		44	*Metopium brownei*	31580	9,277 ± 46	10,580–10,290
181120-23b		44	*Non-resinous*	31581	8,982 ± 54	10,240–9,920
150515-6		42	*Bursera* spp.	Association†	~9,600	~11,200–10,700
171128-16b		45	*Swientenia spp.*	Association	~9,500	~11,070–10,590
171128-25b		40	*Amyris* spp.	Association	~9,750	~11,240–11,110
181120-8		41	*Brosimium* spp.	Context‡	10,500–8,800	~11,700–9,900
Camilo						
S11		23.3	Not identified	34386	9,850 ± 41	11,330–11,200
S15		23.4	Not identified	34385	9,644 ± 40	11,090–10,710
Monkey Dust						
S5a		7.5	Not identified	34384	10,146 ± 45	12,030–11,510

*Excluding low percentage outliers of probability curves. Retain > 92% probability. †These are age estimates based on ages of other charcoal fragments in the same collection unit, as presented for samples 150515-6d and 150515-6e. This is true also for the two samples below, which come from collection units 171128-16 and 17128-25, for which estimates are based on dates for 171128-16a and 171128-25a, respectively. ‡Age estimate is the interval between the maximum and minimum documented ages of organics in the site.

This indicates that these mined areas had been abandoned for many years before the submergence of Sagitario. Calcite rafts that formed when the cave bottom was flooded with Holocene sea-level rise (Fig. 4B and text S2) produced dates between 8020 and 7760 cal B.P. (table S2), consistent with evidence from Hoyo Negro that sea level surmounted 9 to 11 m below modern sea level between 8.0 and 7.0 ka. Groundwater levels in the region track sea level closely (*7*, *21*, *22*), so water levels in the Sagitario system and Hoyo Negro, 8 and 6 km inland, respectively,

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024

should be equivalent. Therefore, our evidence indicates that mining activities in this system were abandoned well before 8.0 ka.

Camilo Mina and Monkey Dust

Two additional sites, Camilo Mina and Monkey Dust, show characteristics of ochre prospecting and mining similar to La Mina, confirming that it is not an isolated discovery (Fig. 5). Both sites are located within 30 km south-southwest of Sagitario and Hoyo Negro (Fig. 1A). Evidence of mining in Camilo Mina, a much wider and more accessible system than Sagitario, is found in an immense, broad chamber referred to as the "Grand Canyon," which lies ~670-m penetration distance from Cenote Muchachos. Here, the cave floor is systematically potholed with rounded depressions ~1 to 2 m in diameter and of a consistent depth (Fig. 5D), indicating that the miners sought a particular stratum within the limestone, specifically the bedding plane-type ochre seen in Fig. 5E. The ochre beds at Camilo Mina are only a few centimeters thick and are found within an intertidal lithographic limestone with preserved laminated bedding and mud cracks. As observed at La Mina, large chunks of flowstone spoil and broken limestone fragments are stacked around the pits or lie piled in older, adjacent depressions. Cairn features mark the passages leading to the mining area. In our explorations thus far at Camilo Mina, we have not observed any charcoal concentrations lying below flowstone. We attribute this, in part, to the overall lack of stalactite and stalagmite formation due to the size and shape of the Grand Canyon chamber. At 24 m below surface, the Grand Canyon is twice the depth of La Mina and therefore must have been exploited before 9.0 ka, when sea-level rise would have flooded the bottom of the cave (*7*, *22*). Charcoal samples that were collected from areas adjacent to cultural features (i.e., cairns and mining pits) yielded radiocarbon dates similar in age to La Mina. Their association with the mining activity strongly suggests an anthropogenic origin (Table 1). We expect that further exploration at Camilo Mina will reveal additional cultural features and associated charcoal for dating.

In Monkey Dust, a series of rock cairns seemingly leads to an area where ochre deposits occur as cone-shaped piles on the cave floor, having filtered through the cave ceiling from the surface (Fig. 5, A and B). These are a minimum of ~370-m penetration distance from entrance. There is circumstantial evidence of ochre prospecting and mining activity here, such as broken speleothems, stone cairns, and charcoal concentrations adjacent to large piles of ochre, yet the activities are not obvious because an extensive blanket of flowstone overlies most features. However, many of the cairns and thick, localized concentrations of charcoal that lie below flowstone are strongly indicative of human presence (Fig. 5C). The charcoal collected from below the flowstone deposits at Monkey Dust (~380-m penetration) is similar in age to samples from La Mina and Camilo Mina. Had we not first seen such conspicuous evidence for ochre mining at La Mina and Camilo Mina, we might not have recognized the significance of comparable features at Monkey Dust.

DISCUSSION

The submerged caves of Quintana Roo continue to yield evidence for intensive human use during the Pleistocene-Holocene transition. To date, that evidence has consisted almost solely of remains of individuals who died while navigating the cave passages. For nearly two decades, their reason for being there has remained unclear. Evidence from La Mina, Camilo Mina, and Monkey Dust demonstrates that at least one of the reasons people probed deep into those caves was to prospect for and mine ochre. At La Mina, this activity took them through naturally darkened passages, encountering overhead hazards and narrow restrictions well into the dark zone of Sagitario, up to at least 650 m from natural light. Evidence from elsewhere in Sagitario, Camilo Mina, and Monkey Dust caves suggests that once one ochre deposit was exhausted by mining activity, others were continuously sought out. It is clear by the amount of disturbed flowstone debris and the obvious effort expended to prospect and remove the ochre that it was considered an important mineral resource. Unfortunately, the dearth of contemporaneous aboveground archaeological sites in Quintana Roo limits our determination of how the ochre was used. There are several possibilities to consider, none of which are mutually exclusive. As previously noted, interpretations of Paleoindian ochre use in other regions of North America often categorize them into "utilitarian" or "ritual-symbolic" contexts (*12*, *19*). Experimental studies and archaeological evidence have demonstrated that ochre could have had practical or medicinal value as antiseptic (*25*), as sunscreen (*26*), for therapeutic consumption or geophagia (*27*), for hide tanning (*13*, *28*, *29*), for tool hafting (*30*, *31*), as a repellent of vermin (such as ticks or lice), or for purging parasites (*25*, *32*). For instance, the ochre from La Mina and Camilo Mina is notably high in arsenic, approaching up to 4000 parts per million (ppm) at some localities, which would have been more than sufficient to repel pests.

Elsewhere in North America, ochre is also a prominent feature in ritual and symbolic contexts such as mortuary practices, ritual caches, or decoration of mobiliary art (see text S1). At the outset of our study, we had considered the potential that the ochre mining at La Mina was ritually motivated. Yet, we have not identified any direct evidence in the mining areas or near the cave entrances (dry or flooded) that would support such an interpretation at this time. Certainly, during the rich archaeological record of the later pre-Classic and Classic Maya periods, the ritual use of caves in the Yucatán Peninsula is well documented (text S5). The Maya actively used caves for ritual and mortuary purposes (*33*–*35*), as well as a critical source of water (*36*). They also exploited caves as geological resources, intensively mining red and white pigments (*37*, *38*) as well as taking speleothems and other stone for ceremonial or symbolic purposes. While we do not discount the possibility that the ochre mining at La Mina was ritually motivated, our study has not yet identified strong evidence to support this interpretation.

The knowledge, time, and effort evident in the prospecting and extractive process, and the distance that people traveled into the Sagitario and Camilo cave systems to begin finding ochre as long ago as 12 ka, demonstrates that this was likely not the first time people extracted cave ochre in Quintana Roo. They were already familiar with the resource potential of the caves and had been actively seeking ochre there. The death as much as 12,800 years ago of Naia, the young woman found in Hoyo Negro, 600-m penetration distance within a tunnel system (*1*), indicates that cave exploration, and perhaps ochre extraction, began in Quintana Roo soon after humans first arrived on the Yucatán Peninsula. From the evidence we have so far, this activity appears to have ceased by around 10,000 cal B.P., at least in La Mina, Camilo Mina, and Monkey Dust, well before rising sea levels submerged the ochre deposits. This activity may have persisted longer in other caves, such as Chan Hol, where possibly anthropogenic concentrations of charcoal are reported to

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024

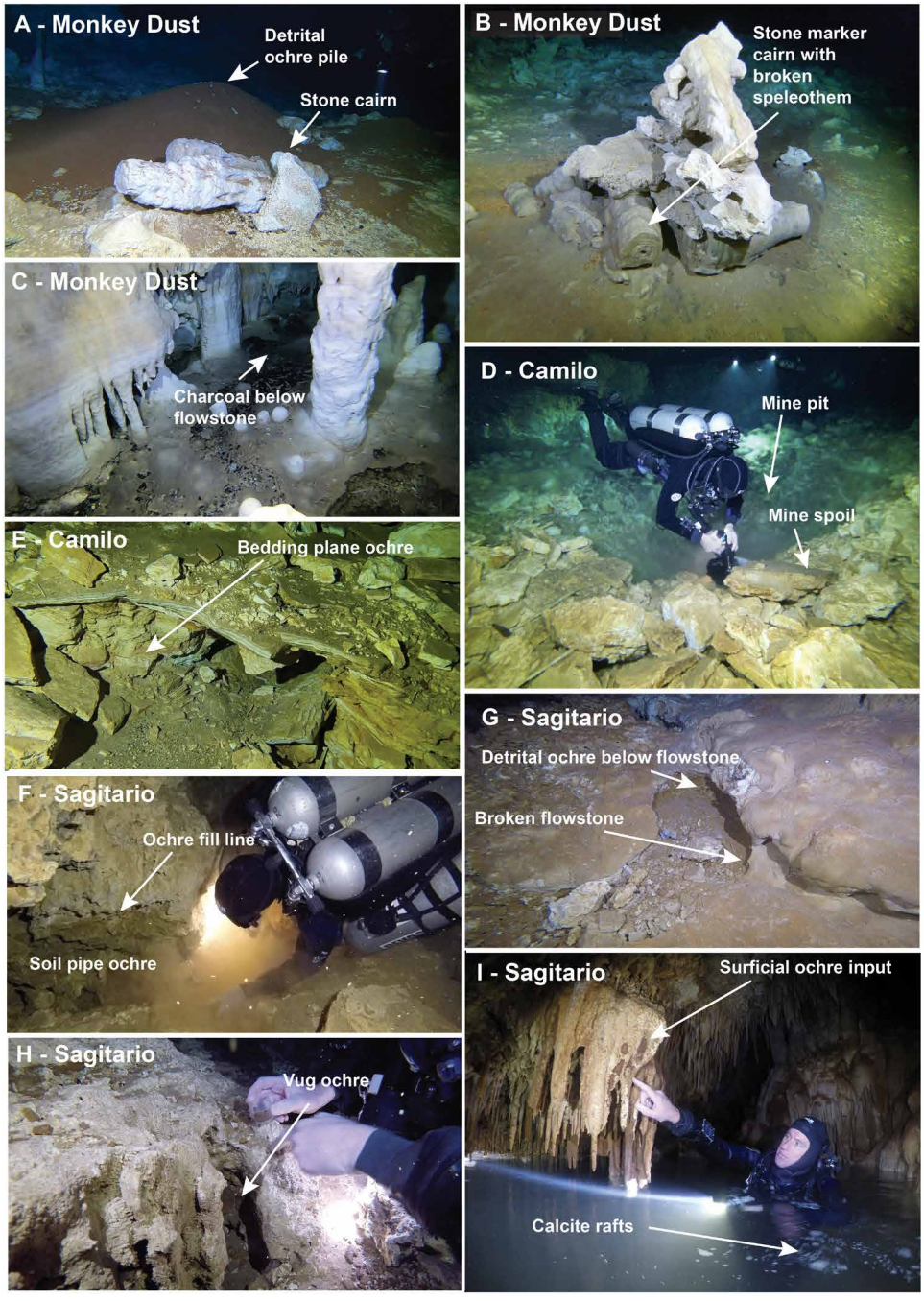


Fig. 5. Additional mine features in Sagitario and other cave systems. (**A**). Detrital ochre pile in Monkey Dust and adjacent marker speleothem. The source of the ochre is an overhead dissolution pipe (~10 to 20 cm in diameter), which has iron oxide–stained sides. Ochre pile is ~35 cm high. (**B**) Stone marker cairn approximately 50 cm high in Monkey Dust. (**C**) Charcoal deposit between flowstone in close proximity to the ochre pile shown in (A). (**D**) Mine pit from Camilo Mina, the cave floor in the Grand Canyon Passage, is completely exploited, with pits reaching a constant depth to access the bedding plane ochre shown in (**E**) (see text S3 and fig. S2, B and C). (**F** to **H**) Ochre occurrence in Sagitario (La Mina). (F) Mine pit following a soil pipe within the limestone. Note the original fill line of the ochre, which has been removed and scraped clean. Soil pipe ochre is only found in La Mina. The pit is ~1 m deep and 3 to 4 m long. (G) Flowstone ochre from detrital sources is thin and discontinuous, requiring excessive effort to break the hard flowstone for little volume return. In contrast, soil-pipe ochre in La Mina has no flowstone covering and can be recovered easily (see text S3 and fig. S2, B and C). (H) Vug ochre that has been exposed with speleogenesis and cave formation. Vug is ~1 m above the cave floor. (**I**) Surficial ochre percolating through the overhead limestone and being incorporated into speleothem in the airdome at S19 (Fig. 1C). Photo credit: C. LeMaillot (CINDAQ) (A to E) and F. Devos (CINDAQ) (F to I).

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024

date between 8 and 7 ka (*24*). Paleoindian mining of caves has not previously been reported, however, either in the Yucatán or anywhere else in the Americas. The pristine site of La Mina has alerted us to mining activity in the submerged caves, and Monkey Dust and Camilo Mina have confirmed it. Now that we are alerted to underground ochre mining and its archaeological signatures, additional discoveries are certain to be made in the nearly 2000 km of known cave systems, which will clarify the process and chronology of Paleoindian ochre mining in Quintana Roo.

MATERIALS AND METHODS

Diving campaigns: Discovery of La Mina, Camilo Mina, and Monkey Dust and sample collection

Divers from CINDAQ (F.D., S.M., and C.L.M.) discovered the highly modified cave tunnels of La Mina within Sagitario in 2017 but were initially uncertain of their significance. A small section of Sagitario had been explored previously, but not mapped (2017). The sections now known as La Mina were found beyond a tight restriction where the ceiling height is <40 cm (Fig. 1D). E.G.R. visited the site in February 2018 and observed geoarchaeological evidence of human disturbance, mining activity, and charcoal deposits, the latter of which provided preliminary radiocarbon dates indicating a Paleoindian age for the activity (~11 to 12 ka; Table 1). Near the end of the tight restriction, the ordinarily highly decorated passages and smooth calcite floor abruptly gave way to an expanse of pits and rubble, with discrete rock piles and perched concentrations of charcoal. The divers named this new section of the system "La Mina" and reported it to the Instituto Nacional de Antropología e Historia (INAH). After documenting video and photographs of the mine features (movie S1 and fig. S5), and sampling the red colored sediments and nearby charcoal concentrations, E.G.R. contacted D.R. and J.C.C. who confirmed the significance of the site. E.G.R. documented reddish clay in vugs, soil pipes, and a thick stratum beneath the flowstone of the cave floor and obtained samples of this material for geochemical analysis by B.L.M. Analyses by B.L.M. revealed a high-quality red ochre (text S2 and fig. S1), which led to the site's designation as a mine and to further detailed mapping of the system (Figs. 1, C and D, and 2, A to D, and fig. S6), with additional sampling by E.G.R. Subsequently, preliminary surveys and sampling (charcoal and ochre) were conducted at Camilo Mina and Monkey Dust throughout 2019. All sampling was conducted under the auspices of the Subdirección de Arqueología Subacuática of INAH.

Cave survey and photo documentation

Photogrammetric models of cultural features in La Mina were produced using a Sony A7S camera and a Canon 16- to 35-mm lens in a Nauticam housing. Cave passages were illuminated during photography using 2600 lumen video lights. Because of the restrictive nature of the cave passages, a systematic grid could not be used for photo capture, so natural features and the main guideline were used to reference photographic transects. The largest photogrammetric model contains ~20,000 photographs taken over ten 3-hour dives, and the point cloud contains ~1.6 billion points. Models were rendered using Agisoft PhotoScan Pro and the computing facilities at the University of California, San Diego (Cultural Heritage Engineering Initiative).

Dry cave survey was conducted using an Electronic Leica Disto ×310 laser distance meter (±1% accuracy) to measure distance, azimuth, and inclinations. Underwater cave survey used a handheld compass (Suunto M-3 Global Compass), fiber tape measure, Shearwater digital water depth gauge (Shearwater Perdix; ±30 mbar), a Vexilar LPS-1 handheld digital sonar, and visual distance estimates (±4% accuracy). Overall cave geometry (bottom, ceiling, and sidewalls) were recorded referencing the main guideline, which was laid during initial exploration. Survey loops were corrected using cave survey software (Walls Project Editor-Version 2.0 Build 2016-11-18) and georeferenced using GPS measurements (Garmin Foretrex 601 GPS using Datum WGS84) from the Sagitario, Pu'bix, and Kilix Pach-Och entrances. Prominent cave geomorphic features (e.g., boulders, depressions, flowstone, and speleothems) and cultural features (mine pits, spoil, charcoal concentrations broken speleothems, and stone cairns) were mapped to ±10% accuracy.

Analytical procedures

Ochre, charcoal, and calcite rafts were sampled in various locations, which were marked on the main cave line and surveyed afterwards. Wherever possible, samples of charcoal were taken in the immediate proximity of cultural features, including cairns, mine pits, and spoil piles in the center of the Sagitario La Mina system (table S3), at a minimum of 200 m from the nearest cave entrances. During preliminary investigations (before obtaining a "Special Project" permit from Consejo de Arqueología), we preferentially sampled charcoal from among fragments rolled from the edges of features so as not to disturb feature integrity. The charcoal was collected into plastic vials, air-dried, and submitted for dating and identification. Selected fragments large enough for the purpose were split. Half of each sample was submitted for radiocarbon analysis at DirectAMS in Bothell, Washington. These samples received standard acid-base-acid pretreatment (*39*) before combustion to release CO_2, graphitization, and measurement on an National Electrostatics Corporation (NEC) Peletron 500-kV accelerator mass spectrometer (AMS). The other half was submitted to B.R. for taxonomic identification using scanning electron microscopy (SEM)–energy-dispersive x-ray spectrometry (EDS) (see text S4; Table 1). Neither DirectAMS staff nor B.R. was aware beforehand of the samples' context. Samples from Hoyo Negro were treated in a similar manner, although splits used for dating had in most cases been submitted years before. Calcite raft sheets were sampled underwater using a plastic card or forceps, selecting large sheet-like rafts that overlay the floors of mine pits. They were placed in a sample bag and then sorted using a binocular dissecting microscope (×60), avoiding calcite fragments (white) containing older limestone percolation (tan brown) for radiocarbon analysis. Samples were pretreated with a light acid wash (2% HCl) for several minutes and dried. They were then submitted to DirectAMS for calcite pretreatment and AMS measurement, as above. Previous research established a constant hardwater effect of −1267 years by analyzing paired seed and calcite raft ages from a core dating between 5 and 10 ka (*7*). This was treated as ΔR, which was applied before ages were calibrated (text S3 and table S2). All radiocarbon calibrations were computed using OxCal 4.3, based on IntCal 2013 (*40*).

Ochre analysis

Qualitative and geochemical analyses of all ochre samples were examined using a multimethod approach. Qualitative analysis was conducted by optical microscopy and scanning electron microscopy at University of Missouri Electron Microscopy Core. Chemical and mineralogical composition was characterized by neutron activation analysis

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024

(Archaeometry Laboratory, University of Missouri Research Reactor) and x-ray diffraction (McMaster University and University of Missouri) using previously reported procedures detailed further in text S2.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/27/eaba1219/DC1

REFERENCES AND NOTES

1. J. C. Chatters, D. J. Kennett, Y. Asmerom, B. M. Kemp, V. Polyak, A. N. Blank, P. A. Beddows, E. Reinhardt, J. Arroyo-Cabrales, D. A. Bolnick, R. S. Malhi, B. J. Culleton, P. L. Erreguerena, D. Rissolo, S. Morell-Hart, T. W. Stafford Jr., Late pleistocene human skeleton and mtDNA link paleoamericans and modern native americans. *Science* **344**, 750–754 (2014).
2. W. Stinnesbeck, J. Becker, F. Hering, E. Frey, A. G. González, J. Fohlmeister, S. Stinnesbeck, N. Frank, A. T. Mata, M. E. Benavente, J. A. Olguín, E. A. Núñez, P. Zell, M. Deininger, The earliest settlers of Mesoamerica date back to the late Pleistocene. *PLOS ONE* **12**, e0183345 (2017).
3. J. C. Chatters, D. Rissolo, J. Arroyo-Cabrales, T. W. Stafford, Jr., B. M. Kemp, A. Alvarez, A. Nava-Blank, F. Attolini, P. A. Beddows, E. Reinhardt, S. Kovacs, S. Collins, S. Morell-Hart, R. Chávez-Arce, S. Bird, P. Luna Erreguerena, in *The Archaeology of Underwater Caves*, P. B. Campbell, Ed. (Highfield Press, 2017), pp. 119–129.
4. A. H. G. González, C. R. Sandoval, A. T. Mata, M. B. Sanvicente, E. Acevez, The arrival of humans on the Yucatan Peninsula: Evidence from submerged caves in the state of Quintana Roo, Mexico. *Curr. Res. Pleistocene* **25**, 1–24 (2008).
5. W. Stinnesbeck, S. R. Rennie, J. A. Olguín, S. R. Stinnesbeck, S. Gonzalez, N. Frank, S. Warken, N. Schorndorf, T. Krengel, A. V. Morlet, A. G. González, New evidence for an early settlement of the Yucatán Peninsula, Mexico: The Chan Hol 3 woman and her meaning for the Peopling of the Americas. *PLOS ONE* **15**, e0227984 (2020).
6. S. R. Stinnesbeck, W. Stinnesbeck, A. T. Mata, J. A. Olguín, M. B. Sanvicente, P. Zell, E. Frey, S. Lindauer, C. R. Sandoval, A. V. Morlet, E. A. Nuñez, A. G. González, The muknal cave near Tulum, Mexico: An early-Holocene funeral site on the Yucatán peninsula. *Holocene* **28**, 1992–2005 (2018).
7. S. E. Kovacs, E. G. Reinhardt, J. C. Chatters, D. Rissolo, H. P. Schwarcz, S. V. Collins, S.-T. Kim, A. N. Blank, P. L. Erreguerena, Calcite raft geochemistry as a hydrological proxy for Holocene aquifer conditions in Hoyo Negro and Ich Balam (Sac Actun Cave System), Quintana Roo, Mexico. *Quat. Sci. Rev.* **175**, 97–111 (2017).
8. A. S. Brooks, J. E. Yellen, R. Potts, A. K. Behrensmeyer, A. L. Deino, D. E. Leslie, S. H. Ambrose, J. R. Ferguson, F. d'Errico, A. M. Zipkin, S. Whittaker, J. Post, E. G. Veatch, K. Foecke, J. B. Clark, Long-distance stone transport and pigment use in the earliest Middle Stone Age. *Science* **360**, 90–94 (2018).
9. C. W. Marean, M. Bar-Matthews, J. Bernatchez, E. Fisher, P. Goldberg, A. I. R. Herries, Z. Jacobs, A. Jerardino, P. Karkanas, T. Minichillo, P. J. Nilssen, E. Thompson, I. Watts, H. M. Williams, Early human use of marine resources and pigment in South Africa during the Middle Pleistocene. *Nature* **449**, 905–908 (2007).
10. L. Lahren, R. Bonnichsen, Bone foreshafts from a Clovis burial in southwestern Montana. *Science* **186**, 147–150 (1974).
11. B. A. Potter, J. D. Irish, J. D. Reuther, C. Gelvin-Reymiller, V. T. Holliday, A terminal Pleistocene child cremation and residential structure from eastern Beringia. *Science* **331**, 1058–1062 (2011).
12. A. K. Lemke, D. C. Wernecke, M. B. Collins, Early art in North America: Clovis and later paleoindian incised artifacts from the Gault site, Texas (41BL323). *Am. Antiq.* **80**, 113–133 (2015).
13. J. M. LaBelle, C. Newton, Red ochre, endscrapers, and the Folsom occupation of the Lindenmeier site, Colorado. *Curr. Res. Pleistocene* **27**, 112–115 (2010).
14. G. C. Frison, B. A. Bradley, *The Fenn Cache: Clovis Weapons & Tools* (One Horse Land & Cattle Limited Company, 1999).
15. G. C. Frison, G. M. Zeimens, S. R. Pelton, D. N. Walker, D. J. Stanford, M. Kornfeld, Further insights into Paleoindian use of the Powars II Red Ocher Quarry (48PL330), Wyoming. *Am. Antiq.* **83**, 485–504 (2018).
16. M. D. Stafford, G. C. Frison, D. Stanford, G. Zeimans, Digging for the color of life: Paleoindian red ochre mining at the Powars II site, Platte County, Wyoming, U.S.A. *Geoarchaeology* **18**, 71–90 (2003).
17. S. E. Zarzycka, T. A. Surovell, M. E. Mackie, S. R. Pelton, R. L. Kelly, P. Goldberg, J. Dewey, M. Kent, Long-distance transport of red ocher by Clovis foragers. *J. Archaeol. Sci. Rep.* **25**, 519–529 (2019).
18. A. M. Smallwood, T. A. Jennings, C. D. Pevny, Expressions of ritual in the Paleoindian record of the Eastern Woodlands: Exploring the uniqueness of the Dalton cemetery at Sloan, Arkansas. *J. Anthropol. Archaeol.* **49**, 184–198 (2018).
19. J. D. Speth, K. Newlander, A. A. White, A. K. Lemke, L. E. Anderson, Early Paleoindian big-game hunting in North America: Provisioning or politics? *Quat. Int.* **285**, 111–139 (2013).
20. S. Needham, When expediency broaches ritual intention: The flow of metal between systemic and buried domains. *J. R. Anthropol. Inst.* **7**, 275–298 (2001).
21. A. Krywy-Janzen, E. Reinhardt, C. McNeill-Jewer, A. Coutino, B. Waltham, M. Stastna, D. Rissolo, S. Meacham, P. van Hengstum, Water-level change recorded in Lake Pac Chen Quintana Roo, Mexico infers connection with the aquifer and response to Holocene sea-level rise and Classic Maya droughts. *J. Paleolimnol.* **62**, 373–388 (2019).
22. S. V. Collins, E. G. Reinhardt, D. Rissolo, J. C. Chatters, A. N. Blank, P. L. Erreguerena, Reconstructing water level in Hoyo Negro, Quintana Roo, Mexico, implications for early Paleoamerican and faunal access. *Quat. Sci. Rev.* **124**, 68–83 (2015).
23. J. Coke, E. C. Perry, A. Long, Sea-level curve. *Nature* **353**, 25 (1991).
24. F. Hering, W. Stinnesbeck, J. Folmeister, E. Frey, S. Stinnesbeck, J. Avilés, E. A. Núñez, A. González, A. T. Mata, M. E. Benavente, C. Rojas, A. V. Morlet, N. Frank, P. Zell, J. Becker, The Chan Hol cave near Tulum (Quintana Roo, Mexico): Evidence for long-lasting human presence during the early to middle Holocene. *J. Quat. Sci.* **33**, 444–454 (2018).
25. J. Velo, Ochre as medicine: A suggestion for the interpretation of the archaeological record. *Curr. Anthropol.* **25**, 674 (1984).
26. R. F. Rifkin, L. Dayet, A. Queffelec, B. Summers, M. Lategan, F. d'Errico, Evaluating the photoprotective effects of ochre on human skin by *in vivo* SPF assessment: Implications for human evolution, adaptation and dispersal. *PLOS ONE* **10**, e0136090 (2015).
27. J. Velo, The problem of ochre. *Mankind Q.* **26**, 229–237 (1986).
28. R. F. Rifkin, Assessing the efficacy of red ochre as a prehistoric hide tanning ingredient. *J. Afr. Archaeol.* **9**, 131–158 (2011).
29. E. N. Wilmsen, F. H. Robert Jr., Lindenmeier, 1934-1974: Concluding report on investigations. *Smithsonian Contrib. Anthropol.* (1978).
30. L. Wadley, T. Hodgskiss, M. Grant, Implications for complex cognition from the hafting of tools with compound adhesives in the Middle Stone Age, South Africa. *Proc. Natl. Acad. Sci. U.S.A.* **106**, 9590–9594 (2009).
31. L. Wadley, B. Williamson, M. Lombard, Ochre in hafting in Middle Stone Age southern Africa: A practical role. *Antiquity* **78**, 661–675 (2004).
32. R. F. Rifkin, Ethnographic and experimental perspectives on the efficacy of ochre as a mosquito repellent. *S. Afr. Archaeol. Bull.* **70**, 64–75 (2015).
33. A. M. Scott, J. E. Brady, Human remains in Lowland Maya caves: Problems of interpretation, in *Stone Houses and Earth Lords: Maya Religion in the Cave Context*, K. M. Prufer, J. E. Brady, Eds. (University Press of Colorado, 2005), pp. 263–284.
34. J. E. Brady, A. Scott, H. Neff, M. D. Glascock, Speleothem breakage, movement, removal, and caching: An aspect of ancient Maya cave modification. *Geoarchaeology* **12**, 725–750 (1997).
35. H. Moyes, Constructing the underworld: The built environment in Ancient Mesoamerican caves, in *Heart of Earth: Studies in Maya Ritual Cave Use*, J. E. Brady, Ed. (Association for Mexican Cave Studies, 2012), vol. 23, pp. 95–110.
36. J. E. Brady, W. Ashmore, Mountains, Caves, Water: Ideational landscapes of the Ancient Maya, in *Archaeologies of Landscape: Contemporary Perspectives*, W. Ashmore, A. B. knapp, Eds. (Blackwell, 1999), pp. 124–3145.
37. E. W. Andrews, *Balankanche: Throne of the Tiger Priest* (Middle American Research Institute, Tulane University, 1970).
38. R. E. Smith, *Cenote Exploration at Mayapan and Telchaquillo* (Carnegie Institution of Washington, Department of Archaeology, 1954).
39. R. E. Taylor, Dating techniques in archaeology and paleoanthropology. *Anal. Chem.* **59**, 317A–331A (1987).
40. P. J. Reimer, E. Bard, A. Bayliss, J. W. Beck, P. G. Blackwell, C. B. Ramsey, C. E. Buck, H. Cheng, R. L. Edwards, M. Friedrich, P. M. Grootes, T. P. Guilderson, H. Haflidason, I. Hajdas, C. Hatté, T. J. Heaton, D. L. Hoffmann, A. G. Hogg, K. A. Hughen, K. F. Kaiser, B. Kromer, S. W. Manning, M. Niu, R. W. Reimer, D. A. Richards, E. M. Scott, J. R. Southon, R. A. Staff, C. S. M. Turney, J. van der Plicht, IntCal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal BP. *Radiocarbon* **55**, 1869–1887 (2013).
41. Google Earth Imagery (Google Earth Pro V 7.3.2.5776 2019), pp. Eastern Yucatan coastline from Tulum to Playa del Carmen, Quintana Roo, MX. 17°20'10.29"N, 87°21'05.70"W, Eye alt 46.25 km. SIO, NOAA, U.S. Navy, NGA, GEBCO. TerraMetrics 2019, DigitalGlobe 2019 [September 2019]; https://www.google.com/earth/.
42. D. B. Deller, C. J. Ellis, J. R. Keron, Understanding cache variability: A deliberately burned Early Paleoindian tool assemblage from the Crowfield site, southwestern Ontario, Canada. *Am. Antiq.* **74**, 371–397 (2009).
43. D. C. Roper, A comparison of contexts of red ochre use in Paleoindian and Upper Paleolithic sites. *North Am. Archaeol.* **12**, 289–301 (1992).
44. P. J. Wilke, J. J. Flenniken, T. L. Ozbun, Clovis technology at the Anzick site, Montana. *J. Calif. Gt. Basin Anthropol.* **13**, 242–272 (1991).

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024

45. J. D. Kilby, *An Investigation of Clovis Caches: Content, Function, and Technological Organization* (The University of New Mexico, 2008).
46. D. C. Anderson, The Gordon Creek burial. *Southwestern Lore* **32**, 1–9 (1966).
47. D. A. Breternitz, A. C. Swedlund, D. C. Anderson, An early burial from Gordon Creek, Colorado. *Am. Antiq.* **36**, 170–182 (1971).
48. M. A. Jodry, D. W. Owsley, *A New Look at the Double Burial from Horn Shelter No. 2. Kennewick Man: The Scientific Investigation of an Ancient American Skeleton* (Texas A&M Univ. Press, 2014), pp. 549–604.
49. A. J. Redder, J. W. Fox, Excavation and positioning of the Horn Shelter's burial and grave goods. *Central Texas Archaeol.* **11**, 1–12 (1988).
50. A. E. Jenks, *Minnesota's Browns Valley Man and Associated Burial Artifacts* (American Anthropological Association, 1937).
51. G. C. Frison, Sources of steatite and methods of prehistoric procurement and use in Wyoming. *Plains Anthropol.* **27**, 273–286 (1982).
52. L. C. Bement, The Cooper site: A stratified Folsom bison kill in Oklahoma. *Plains Anthropol.* **42**, 85–100 (1997).
53. E. Lohse, K. Kvamme, S. Kohntopp, P. Santarone, An examination of the simon site, idaho. *Idaho Archaeol.* **36**, 15–23 (2013).
54. A. C. Goodyear, The chronological position of the Dalton horizon in the southeastern United States. *Am. Antiq.* **47**, 382–395 (1982).
55. D. Morse, *Sloan: A Paleoindian Dalton Cemetery in Arkansas* (University of Arkansas Press, 2017).
56. D. G. Anderson, A. M. Smallwood, D. S. Miller, Pleistocene human settlement in the southeastern United States: Current evidence and future directions. *PaleoAmerica* **1**, 7–51 (2015).
57. F. W. Robinson IV, The Thurman Station site: A probable late Paleoindian ceremonial artifact deposit in the Lake George region of New York. *Archaeol. East. N. Am.* **39**, 67–92 (2011).
58. J. M. Erlandson, T. C. Rick, T. J. Braje, M. Casperson, B. Culleton, B. Fulfrost, T. Garcia, D. A. Guthrie, N. Jew, D. J. Kennett, M. L. Moss, L. Reeder, C. Skinner, J. Watts, L. Willis, Paleoindian seafaring, maritime technologies, and coastal foraging on California's Channel Islands. *Science* **331**, 1181–1185 (2011).
59. K. B. Tankersley, K. O. Tankersley, N. R. Shaffer, M. D. Hess, J. S. Benz, F. R. Turner, M. D. Stafford, G. M. Zeimens, G. C. Frison, They have a rock that bleeds: Sunrise red ochre and its early paleoindian cccurrence at the Hell Gap site, Wyoming. *Plains Anthropol.* **40**, 185–194 (1995).
60. G. C. Frison, B. A. Bradley, *Folsom Tools and Technology at the Hanson Site, Wyoming* (University of New Mexico Press, 1980).
61. G. C. Frison, D. J. Stanford, *The Agate Basin Site: A Record of the Paleoindian Occupation of the Northwestern High Plains* (Academic Press, 1982).
62. S. Emery, D. Stanford, Preliminary report on archaeological investigations of the Cattle Guard site, Alamosa County, Colorado. *Southwestern Lore* **48**, 10–20 (1982).
63. A. T. Boldurian, Clovis type-site, Blackwater Draw, New Mexico: A History, 1929-2009. *North Am. Archaeol.* **29**, 65–89 (2008).
64. R. W. Yerkes, B. H. Koldehoff, New tools, new human niches: The significance of the Dalton adze and the origin of heavy-duty woodworking in the Middle Mississippi Valley of North America. *J. Anthropol. Archaeol.* **50**, 69–84 (2018).
65. J. H. Mayer, T. A. Surovell, N. M. Waguespack, M. Kornfeld, R. G. Reider, G. C. Frison, Paleoindian environmental change and landscape response in Barger Gulch, Middle Park, Colorado. *Geoarchaeology* **20**, 599–625 (2005).
66. M. G. Hill, D. W. May, D. J. Rapson, A. R. Boehm, E. Otárola-Castillo, Faunal exploitation by early Holocene hunter/gatherers on the Great Plains of North America: Evidence from the Clary Ranch sites. *Quat. Int.* **191**, 115–130 (2008).
67. T. Hodgskiss, L. Wadley, How people used ochre at Rose Cottage Cave, South Africa: Sixty thousand years of evidence from the Middle Stone Age. *PLOS ONE* **12**, e0176317 (2017).
68. F. d'Errico, R. G. Moreno, R. F. Rifkin, Technological, elemental and colorimetric analysis of an engraved ochre fragment from the Middle Stone Age levels of Klasies River Cave 1, South Africa. *J. Archaeol. Sci.* **39**, 942–952 (2012).
69. I. Watts, Ochre and Human Evolution. in *The International Encyclopedia of Anthropology*, H. Callan, Ed. (John Wiley & Sons, 2018), pp. 1–7.
70. I. Watts, The pigments from pinnacle point cave 13B, Western Cape, South Africa. *J. Hum. Evol.* **59**, 392–411 (2010).
71. A. M. Zipkin, S. H. Ambrose, J. M. Hanchar, P. M. Piccoli, A. S. Brooks, E. Y. Anthony, Elemental fingerprinting of Kenya Rift Valley ochre deposits for provenance studies of rock art and archaeological pigments. *Quat. Int.* **430**, 42–59 (2017).
72. A. M. Zipkin, J. M. Hanchar, A. S. Brooks, M. W. Grabowski, J. C. Thompson, E. Gomani-Chindebvu, Ochre fingerprints: Distinguishing among M alawain mineral pigment sources with H omogenized O chre C hip LA-ICPMS. *Archaeometry* **57**, 297–317 (2015).
73. A. M. Zipkin, thesis, The George Washington University, Washington, DC (2015).
74. P. S. C. Taçon, Ochre, clay, stone and art, in *Soils, Stones and Symbols: Cultural Perceptions of the Mineral World*, N. Boivin, M. A. Owoc, Eds. (UCL Press, 2004), pp. 31–42.
75. G. Mastrotheodoros, K. Beltsios, N. Zacharias, Assessment of the production of antiquity pigments through experimental treatment of ochres and other iron based precursors. *Mediter. Archaeol. Archaeom.* **10**, 37–59 (2010).
76. M. P. Pomiès, M. Menu, C. Vignaud, Red palaeolithic pigments: Natural hematite or heated goethite? *Archaeometry* **41**, 275–285 (1999).
77. D. C. Roper, Grinding stones in Plains Paleoindian sites: The case for pigment processing. *Curr. Res. Pleistocene* **6**, 36–37 (1989).
78. M. Elias, C. Chartier, G. Prévot, H. Garay, C. Vignaud, The colour of ochres explained by their composition. *Mat. Sci. Eng. B* **127**, 70–80 (2006).
79. L.-J. R. Marshall, J. R. Williams, M. J. Almond, S. D. M. Atkinson, S. R. Cook, W. Matthews, J. L. Mortimore, Analysis of ochres from Clearwell Caves: The role of particle size in determining colour. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **61**, 233–241 (2005).
80. D. I. Godfrey-Smith, S. Ilani, Past thermal history of goethite and hematite fragments from Qafzeh Cave deduced from thermal activation characteristics of the 110 C TL peak of enclosed quartz grains. *ArchéoSci. Rev. d'Archéom.* **28**, 185–190 (2004).
81. G. Rzepa, T. Bajda, A. Gaweł, K. Debiec, L. Drewniak, Mineral transformations and textural evolution during roasting of bog iron ores. *J. Therm. Anal. Calorim.* **123**, 615–630 (2016).
82. B. L. MacDonald, D. Stalla, X. He, F. Rahemtulla, D. Emerson, P. A. Dube, M. R. Maschmann, C. E. Klesner, T. A. White, Hunter-gatherers harvested and heated microbial biogenic iron oxides to produce rock art pigment. *Sci. Rep.* **9**, 1–13 (2019).
83. G. Cavallo, F. Fontana, S. Gialanella, F. Gonzato, M. P. Riccardi, R. Zorzin, M. Peresani, Heat treatment of mineral pigment during the upper palaeolithic in north-east italy. *Archaeometry* **60**, 1045–1061 (2018).
84. B. R. Gregory, E. G. Reinhardt, A. L. Macumber, N. A. Nasser, R. T. Patterson, S. E. Kovacs, J. M. Galloway, Sequential sample reservoirs for Itrax-XRF analysis of discrete samples. *J. Paleolimnol.* **57**, 287–293 (2017).
85. B. L. MacDonald, W. Fox, L. Dubreuil, J. Beddard, A. Pidruczny, Iron oxide geochemistry in the Great Lakes Region (North America): Implications for ochre provenance studies. *J. Archaeol. Sci. Rep.* **19**, 476–490 (2018).
86. R. S. Popelka-Filcoff, E. J. Miksa, J. D. Robertson, M. D. Glascock, H. D. Wallace, Elemental analysis and characterization of ochre sources from Southern Arizona. *J. Archaeol. Sci.* **35**, 752–762 (2008).
87. B. S. Eiselt, R. S. Popelka-Filcoff, J. A. Darling, M. D. Glascock, Hematite sources and archaeological ochres from Hohokam and O'odham sites in central Arizona: An experiment in type identification and characterization. *J. Archaeol. Sci.* **38**, 3019–3028 (2011).
88. M. D. Glascock, in *Chemical Characterization of Ceramic Pastes in Archaeology*, H. Neff, Ed. (Prehistory Press, 1992), pp. 11–26.
89. H. Neff, in *Modern Analytical Methods in Art and Archaeology*, E. Ciliberto, G. Spoto, Eds. (John Wiley & Sons Inc., 2000), vol. 155, pp. 81–134.
90. A. M. Pollard, C. Batt, B. Stern, S. M. M. Young, *Analytical Chemistry in Archaeology* (Cambridge Univ. Press, 2007).
91. V. A. Shatrov, G. V. Voitsekhovskii, Lanthanides and highly mobile elements in sedimentary and metasedimentary rocks as indicators of the tectonic activity in the platform basement: An example of the Voronezh Crystalline Massif. *Geochem. Int.* **51**, 221–230 (2013).
92. M. G. Babechuk, M. Widdowson, B. S. Kamber, Quantifying chemical weathering intensity and trace element release from two contrasting basalt profiles, Deccan Traps, India. *Chem. Geol.* **363**, 56–75 (2014).
93. S. E. Kovacs, E. G. Reinhardt, C. Werner, S.-T. Kim, F. Devos, C. L. Maillot, Seasonal trends in calcite-raft precipitation from cenotes Rainbow, Feno and Monkey Dust, Quintana Roo, Mexico: Implications for paleoenvironmental studies. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **497**, 157–167 (2018).
94. F. Bautista, G. Palacio-Aponte, P. Quintana, J. A. Zinck, Spatial distribution and development of soils in tropical karst areas from the Peninsula of Yucatan, Mexico. *Geomorphology* **135**, 308–321 (2011).
95. H. V. Cabadas, E. Solleiro, S. Sedov, T. Pi, J. R. Alcalá, The complex genesis of red soils in Peninsula de Yucatan, Mexico: Mineralogical, micromorphological and geochemical proxies. *Eurasian Soil Sci.* **43**, 1439–1457 (2010).
96. H. Cabadas-Báez, E. Solleiro-Rebolledo, S. Sedov, T. Pi-Puig, J. Gama-Castro, Pedosediments of karstic sinkholes in the eolianites of NE Yucatán: A record of Late Quaternary soil development, geomorphic processes and landscape stability. *Geomorphology* **122**, 323–337 (2010).
97. D. R. Muhs, J. R. Budahn, J. M. Prospero, G. Skipp, S. R. Herwitz, Soil genesis on the island of Bermuda in the Quaternary: The importance of African dust transport and deposition. *J. Geophys. Res. Earth* **117**, F03025 (2012).
98. P. J. Van Hengstum, E. G. Reinhardt, P. A. Beddows, H. P. Schwarcz, J. J. Gabriel, Foraminifera and testate amoebae (thecamoebians) in an anchialine cave: Surface distributions from Aktun Ha (Carwash) cave system, Mexico. *Limnol. Oceanogr.* **54**, 391–396 (2009).

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024

99. R. C. Baldwin, W. K. Murphey, P. R. Blankenhorn, Scanning electron microscope observation of rate carbonized hardwood bark and bark board. *Wood Sci.* **6**, 231–236 (1974).
100. F. C. Beall, P. R. Blankenhorn, G. R. Moore, Carbonized wood—Physical properties and use as an SEM preparation. *Wood Sci.* **6**, 212–219 (1974).
101. P. R. Blankenhorn, D. P. Barnes, D. E. Kline, W. K. Murphey, Porosity and pore size distribution in black cherry carbonized in an inert atmosphere. *Wood Sci.* **11**, 23–29 (1978).
102. B. E. Cutter, B. G. Cumbie, E. A. McGinnes Jr., SEM and shrinkage analysis of southern pine wood following pyrolysis. *Wood Sci. Technol.* **14**, 115–130 (1980).
103. T. J. Elder, W. K. Murphey, P. R. Blankenhorn, Thermally induced changes of intervessel pirs in black cherry (Prunus serotina Ehrh.). *Wood Fiber Sci.* **2**, 179–183 (1979).
104. E. A. McGinnes Jr., C. A. Harlow, F. C. Beall, *Use of Scanning Electron Microscopy and Image Processing in Wood Charcoal Studies* (IITRO/SEM, 1976).
105. E. A. McGinnes Jr., P. S. Szopa, J. E. Phelps, *Use of Scanning Electron Microscopy in Studies of Wood Charcoal Formation* (IITRI/SEM, 1974).
106. E. A. McGinnes Jr., S. A. Kandeel, P. S. Szopa, Some structural changes observed in the transformation of wood into charcoal. *Wood Fiber Sci.* **3**, 77–83 (1971).
107. G. Moore, P. Blankenhorn, F. Beall, D. Kline, Some physical properties of birch carbonized in a nitrogen atmosphere. *Wood Fiber Sci.* **6**, 193–199 (1974).
108. I. Théry-Parisot, S. Thiébault, J.-J. Delannoy, C. Ferrier, V. Feruglio, C. Fritz, B. Gely, P. Guibert, J. Monney, G. Tosello, J. Clottes, J.-M. Geneste, Illuminating the cave, drawing in black: Wood charcoal analysis at Chauvet-Pont d'Arc. *Antiquity* **92**, 320–333 (2018).
109. Committee on Nomenclature, International glossary of terms used in wood anatomy. *Tropical Woods* **107**, (1957).
110. I. Bulletin, List of microscopic features for hardwood identification. *IAWA Bull.* **10**, 226–317 (1989).
111. C. Metcalfe, L. Chalk, *Anatomy of Dicotyledons. Vol. 2* (Clarendon Press, 1950), vol. **6**, pp. 1–20.
112. E. A. Wheeler, Inside Wood–A web resource for hardwood anatomy. *IAWA J.* **32**, 199–211 (2011).
113. J. E. Brady, *In the Maw of the Earth Monster: Mesoamerican Ritual Cave Use* (University of Texas Press, 2005).
114. J. E. Brady, Settlement configuration and cosmology: The role of caves at Dos Pilas. *Am. Anthropol.* **99**, 602–618 (1997).
115. A. J. Stone, *Images from the Underworld: Naj Tunich and the Tradition of Maya Cave Painting* (University of Texas Press, 2010).
116. M. K. y. M. Strecker, in *Arte Rupestre de México Oriental y Centro América*, M. K. y. M. Strecker, Ed. (Indiana Beihefte Gebr. Mann Verlag, 1995), pp. 53–78.
117. D. Rissolo, in *Arte Rupestre de México Oriental y Centro América*, M. Künne, M. Strecker, Eds. (Indiana Beihefte Gebr. Mann Verlag, 2003), pp. 79–96.
118. D. Rissolo, E. Lo, M. R. Hess, D. E. Meyer, F. E. Amador, Digital preservation of ancient maya cave architecture: Recent field efforts in quintana roo, mexico. *Int. Arch. Photogramm. Remote Sens. Spatial Inf. Sci.* **42**, 613–616 (2017).
119. J. Thompson, in *The Hill-Caves of Yucatan: A Search for Evidence of Man's Antiquity in the Caverns of Central America*, H. C. Mercer, Ed. (University of Oklahoma Press, 1975).
120. J. E. Brady, D. Rissolo, A reappraisal of ancient Maya cave mining. *J. Anthropol. Res.* **62**, 471–490 (2006).
121. J. E. Brady, G. A. Ware, B. Luke, A. Cobb, J. Fogarty, B. Shade, Preclassic cave utilization near Cobanerita, San Benito, Peten. *Mexicon* **19**, 91–96 (1997).
122. D. E. Arnold, Maya Blue and palygorskite: A second possible pre-Columbian source. *Ancient Mesoamerica* **16**, 51–62 (2005).
123. D. A. Slater, *Into the Heart of the Turtle: Caves, Ritual, and Power in Ancient Central Yucatan, Mexico* (Brandeis University, 2014).
124. D. Rissolo, in *In the Maw of the Earth Monster: Mesoamerican Ritual Cave Use*, J. E. Brady, K. M. Prufer, Eds. (University of Texas Press, 2005), pp. 342–372.
125. D. E. Arnold, *Sak Lu'um in Maya Culture: Its Possible Relation to Maya Blue* (University of Illinois, Department of Anthropology, 1967).
126. D. E. Arnold, B. Bohor, Attapulgite and Maya Blue: An ancient mine comes to light. *Archaeology* **28**, 23–29 (1975).
127. W. J. Folan, Sacalum, Yucatán: A pre-Hispanic and contemporary source of attapulgite. *Am. Antiq.* **34**, 182–183 (1969).
128. P. A. Peterson, *Ancient Maya Ritual Cave Use in the Sibun Valley, Belize* (Boston University, 2006).
129. P. A. Peterson, P. A. McAnany, A. B. Cobb. De-fanging the earth monster: Speleothem transport to surface sites in the Sibun Valley, in *Stone Houses and Earth Lords: Maya Religion in the Cave Context*, K. M. Prufer, J. E. Brady, Eds. (University Press of Colorado, 2005), pp. 225–247.

Acknowledgments: We dedicate this published work to our coauthor, colleague, and friend, Pilar Luna Erreguerena, who passed away on 15 March 2020. A pioneer and a tireless champion for the study and conservation of underwater cultural heritage in Mexico, Pilar will be missed by all who knew her and will continue to inspire future generations of diving scientists throughout the Americas. This research was conducted as a Special Project of INAH Subdireccion Subacuatica directed by R. J. Sanchez. We thank landowners A. Romo, O. R. Crus, C. M. Ortega, and A. Ruiz for permission to conduct this research on their respective properties. We are grateful to additional members of the exploration and survey diving team: D. Dusek, O. Gobara, A. Perkins, and C. Russo. CINDAQ thanks Zero Gravity Dive Center, Halcyon Dive Systems, SUEX, DroneDeploy, The Mexico Cave Exploration Project, V. Petrovic (CHEI), F. Kuester, D. Drohobytsky (CHEI), and Global Underwater Explorers for their continuing support. We thank M. D. Glascock, C. E. Klesner, C. McNeill, V. Jarvis, and S. Kelley for assistance with ochre sample preparation and analysis. **Funding:** This study was supported by the Natural Sciences and Engineering Research Council (NSERC) Discovery Grant (E.G.R.: 2015-057250) and the Canada Foundation for Innovation John R. Evans Leaders Fund (CFI-JELF grant 105-04523). Ochre geochemical analysis was supported, in part, by NSF (USA) Archaeometry #1912776 (B.L.M.). CINDAQ wishes to acknowledge the generous support of R. Lourie, R. Shakarchi, B. Strauss, and the Friends of Mexican Development Foundation. DirectAMS subsidized radiocarbon dates. **Author contributions:** E.G.R., F.D., S.M., and C.L.M. led all diving expeditions and collected subsurface research materials. F.D., S.M., and D.R. conducted cave cartography, SfM, and 3D modeling. E.G.R. initiated and directed the study. J.C.C. coordinated AMS radiocarbon dating and charcoal analysis. B.L.M., D.S., and M.D.M. performed all analyses pertaining to ochre geochemistry. M.D.M. and E.L. assisted with geospatial analysis. B.R. conducted all analyses pertaining to wood species identification. B.L.M., J.C.C., and E.G.R. co-wrote the paper, with contributions from D.R. and B.R. P.L.E. provided administrative support. **Competing interests:** J.C.C. is a paid consultant to DirectAMS radiocarbon laboratory and serves as its Quality Manager. The other authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors. All unconsumed archaeological and geological specimens are archived at McMaster University, School of Geography and Earth Sciences (E.G.R.: speleothem, calcite raft, charcoal, and sediments), Applied Paleoscience (J.C.C.: charcoal), and MURR Archaeometry Laboratory (B.L.M.: ochre).

Submitted 6 November 2019
Accepted 22 May 2020
Published 3 July 2020
10.1126/sciadv.aba1219

Citation: B. L. MacDonald, J. C. Chatters, E. G. Reinhardt, F. Devos, S. Meacham, D. Rissolo, B. Rock, C. Le Maillot, D. Stalla, M. D. Marino, E. Lo, P. L. Erreguerena, Paleoindian ochre mines in the submerged caves of the Yucatán Peninsula, Quintana Roo, Mexico. *Sci. Adv.* **6**, eaba1219 (2020).

Downloaded from https://www.science.org at Universit de Montral on April 16, 2024