Palaeoenvironmental reconstruction of Holocene calcareous tufas distributed over a manganese deposit in Mexico

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Abstract

The Holocene calcareous tufa deposits are located in the north-central sector of the state of Hidalgo, Mexico. These deposits outcrop on the Upper Jurassic Chipoco Formation in the Molango Manganese District. Calcareous tufa deposits correspond to carbonate formations of inactive tufas disconnected from the current hydrological network. To better understand the textural, geochemical, and biological characteristics and environmental conditions during their formation, a detailed study involving field analysis, X-ray diffraction analysis, X-ray fluorescence analysis, and morphometric analysis with light microscopy, and scanning electron microscopy was carried out. Similarly, ^{14}C analysis was undertaken to determine the age of the deposit. On this basis, two biofacies were defined, one with stem structures and the other with Phyto clasts, bryophytes (*Plagiomnium cuspidatum*), and copepods, limited both at the base and the top by lenticular-shaped erosive surfaces and sigmoidal clinoforms. These bio facies formed in lacustrine and paludal environments, and barrier waterfalls. From a geomorphological point of view, the accumulations of these calcareous tufas originated on slopes and/or at the foot of karstic springs, where the accumulation of material originated from the height of the spring with respect to the bottom of the valley, giving rise to a set of stepped tuffaceous plains with a wedge-shaped profile, colonized by important masses of bryophyte mounds, copepods, and vascular plants. This suggests a swampy environment where sedimentation took place in shallow water accumulations, where there is clear evidence of exposure and pedogenetic modification, indicating wet and dry episodes that translate into seasonal fluctuations in the water table. Six mineral phases were observed including silicates, carbonates and arsenates. The ^{14}C analysis indicates that the plant found in the charcoal sample within the calcareous tufa deposit is of Holocene age.

Keywords: calcareous tufas, manganese district, palaeoenvironmental, reconstruction, Mexico

1. INTRODUCTION

Calcareous tufa is a sedimentary rock composed of calcium carbonate deposited as calcite, aragonite or dolomite. These deposits are formed mainly by the precipitation of calcium carbonate, associated with karst outcrops on the continent (CARCAVILLA et al., 2019). These deposits are generated in aquatic conditions related to carbonate aquifers that adopt different morphologies and contain remains of micro and macrophytes that have been covered with carbonate, being located around upwellings or are associated with fluvial systems rich in calcareous materials (CARCAVILLA et al., 2019; ARENAS et al., 2010; PENTECOST, 2005; FORD & PEDLEY, 1996). The calcareous tufa deposits are associated with different environments: along the coast; in areas of saline or alkaline lakes; springs; barriers; margins of fluvial courses; marshes; and fluvial-lacustrine environments, where the dynamics of karstic aquifers control the distribution of such deposits (ARENAS-ABAD, 2017). According to PENTECOST & VILES (1994) and ARENAS-ABAD (2017), several factors are required for calcareous tufa deposits to form: warm climate; physicochemical processes favourable for carbonate precipitation; organic structural elements; tectonics; and characteristics of the substrate (lithological composition). Carbonate precipitation is influenced by the physical and chemical properties of the water, the amount of CO_2 degassing, and the development of vegetation (cyanobacteria, mosses, vascular plants), causing different morphologies, such as springs, rivers, and lake barriers, waterfalls, and stromatolites. Regarding the physicochemical conditions of the water (JONES & RENAUT, 2010; PENTECOST et al., 2003; PENTECOST, 2005; ARENAS-ABAD et al., 2010), mention that the waters that form calcareous tufa deposits usually have temperatures below 20°C, while the pH is generally greater than 7 and very frequently around 8 to 8.5, favouring the development of vegetation of the community due to high humidity, and carbonate saturation. Concerning the precipitation of calcareous tufas, the pressure of CO_2 plays a very important role, with the most common range of pCO_2 being between $4x10^{-4}$ and $8x10^{-4}$ atmospheres (KANO et al., 2003; MINISSALE, 2004; DILSIZ, 2006; AUQUÉ et al., 2009, 2013; ARENAS et al., 2014). For the accumulation of calcareous tufa deposits to occur, the geo-environmental factor plays a very important role when it interacts with the morpho-structural conditions of the area and the hydrological conditions (VILES et al., 2007). All these elements in one way or another regulate the types of precipitate and their rate of growth. Based on this, calcite precipitation is physically controlled by the degassing rate of dissolved CO_2 and water temperature, determining factors that unbalance the ionic solution, while the soil tends to exclusively influence scale nucleation which occurs at upwelling points or along with the turbulent flow, in rapids, jumps, and waterfalls of the fluvial course. The carbonate impregnation of cyanobacterial covers, mosses, and vascular plants occurs both in calm waters and waterfalls with thin water runoffs (CARCAVILLA et al., 2009). The Molango manganese district reveals the existence of a series of geomorphological and palaeoenvironmental elements that had gone unnoticed in the descriptions and studies carried out to date and where a series of calcareous tufa deposits can be observed. One of the problems represented by the study of calcareous tufa deposits is the difficulty of recognizing them since their morphologies are highly modified by erosion and diagenesis, so their recognition requires the characterization of the biofacies. Another problem is the small number and volume of the outcrops, which are being ignored due to their lack of perceived relevance. Taking into account the above, the objectives of this study were: 1) to characterize the geomorphological and geological context on which the calcareous tufa deposits developed; 2) to characterize these deposits from the petrological, mineralogical, and geochemical points of view; and 3) to establish the most probable time range for the development of calcareous tufa deposits using ^{14}C dating, to highlight geomorphological, palaeo-ecological and palaeoenvironmental reconstructions.

2. TECTONIC AND REGIONAL GEOLOGIC SETTING

The study area (Fig. 1) is part of the Sierra Madre Oriental physiographic province, formed by the uplift and deformation of Jurassic siliciclastic and marine rocks (EGUILUZ et al., 2000). These deposits represent basin material related to the opening of the Gulf of Mexico (CARRILLO & SUTER, 1982). During this geological time, the Tethys Sea flooded areas where evaporitic-carbonate banks and platforms were developed (EGUILUZ et al., 2000). In the manganese district of Molango, carbonate rocks from the Lower, Middle, and Upper Jurassic can be observed, which correspond to the Huayacocotla sector (CARRILLO & SUTER, 1982). This sector is located at the southeast end of the Sierra Madre Oriental, corresponding to an anticlinorium, represented by low-angle reverse faults and thrusts (CARRILLO & SUTER, 1982). The Lower Jurassic is characterized by the Huayacocotla Formation, represented by three members: the lower member (conglomerate, sandstones, siltstones, and mudstone with fusulinids and crinoids); intermediate member (conglomerate, sandstones, siltstones, and mudstone with ammonites); and upper member (sandstones,

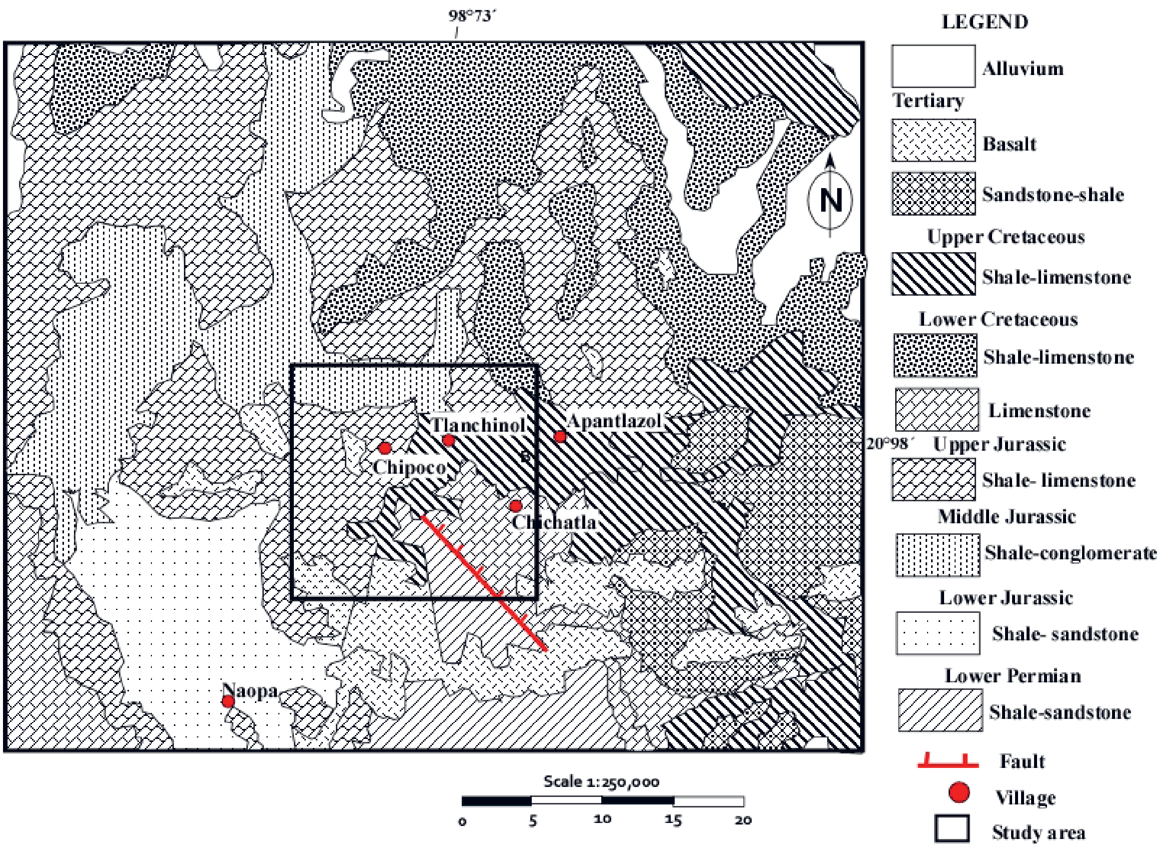


Figure 1. Geological map of the study area.

siltstones, mudstone, and conglomerate with continental fossil plants). The Middle Jurassic is comprised of two units: red layers of the Cahuasas Formation and the Tepexic Formation, characterized by sandy limestone, marl, and mudstone with trigonous and oysters. The Upper Jurassic comprises the Santiago, Chipoco, and Pimienta formations. The Santiago Formation consists of black and calcareous siltstone, resting concordantly on the Tepexic Formation. The Chipoco Formation corresponds to a set of sedimentary rocks that represent the transition zone between the Cuenca and Platform deposits (HERMOSO DE LA TORRE & MARTINEZ-PEREZ, 1972), made up of four lithological units: Unit 1, composed of manganese limestone with calcareous mudstone intercalations; Unit 2, characterized by calcareous sandstone interbedded with sandy calcareous shale; Unit 3, formed of limonite and calcareous mudstone with intercalations of clayey limestone; and Unit 4 comprising a limestone sequence rhythmically interbedded with black mudstone, dark gray grain-stones and mudstones, alternating with calcareous mudstone (OCHOA-CAMARILLO 1996; OCHOA-CAMARILLO et al., 1998). According to HERMOSO DE LA TORRE & MARTÍNEZ-PÉREZ (1972), the Chipoco Formation rests concordantly on the mudstone of the calcareous-clay member of the Tamán Formation (Santiago Formation) which, in turn, lies below the Pimienta Formation. At the beginning of the Palaeogene, the entire Mesozoic sequence was uplifted and folded derived from the Laramide orogeny (CARRILLO-MARTÍNEZ & SUTER, 1982). During the Eocene and early Oligocene (54-30 Ma), a normal fault system prevailed, forming steep Graben and Horst fault blocks and volcanic activity (OCHOA-CAMARILLO, 1996). The Oligocene-Miocene (30-3 Ma) records the presence of an active intracontinental volcanic arc (Trans-Mexican Volcanic Belt). Active volcanism together with the Laramide orogeny caused changes in the topography and the formation of basins and lakes, allowing great diversification of freshwater fish (OCHOA-CAMARILLO et al., 1998). During the Quaternary, glaciation effects from climate change, causing vegetation changes can be observed. At the end of the Pliocene (2-4 Ma), the mafic volcanism that obstructed the drainage of the basins manifested itself and generated palaeo-lakes (LÓPEZ RAMOS, 1972), (Fig. 1).

3. STUDY AREA

The study area is located within the Manganese District of Molango in the north-central sector of the state of Hidalgo, and belongs to the municipality of Tehuacan de Guerrero, within the geographic coordinates 20°98' N and 98° 73' W. The Molango Manganese District represents the most important manganese deposit in North and Central America and one of the ten largest deposits in the world, covering an area of 960 km^2 (Figure 2), (HERMOSO DE LA TORRE & MARTINEZ-PEREZ, 1972). The calcareous tufa deposits extend 50 m over the Chipoco Formation, reaching 5 to 10 m in thickness. Macroscopically, it presents as an ochre color, with an irregular wavy base, spongy texture, and massive or stratified structure with decametric strata. One of the characteristics of these deposits is their occurrence in the form of layers on a gently sloped palaeo-topography (< 10°).

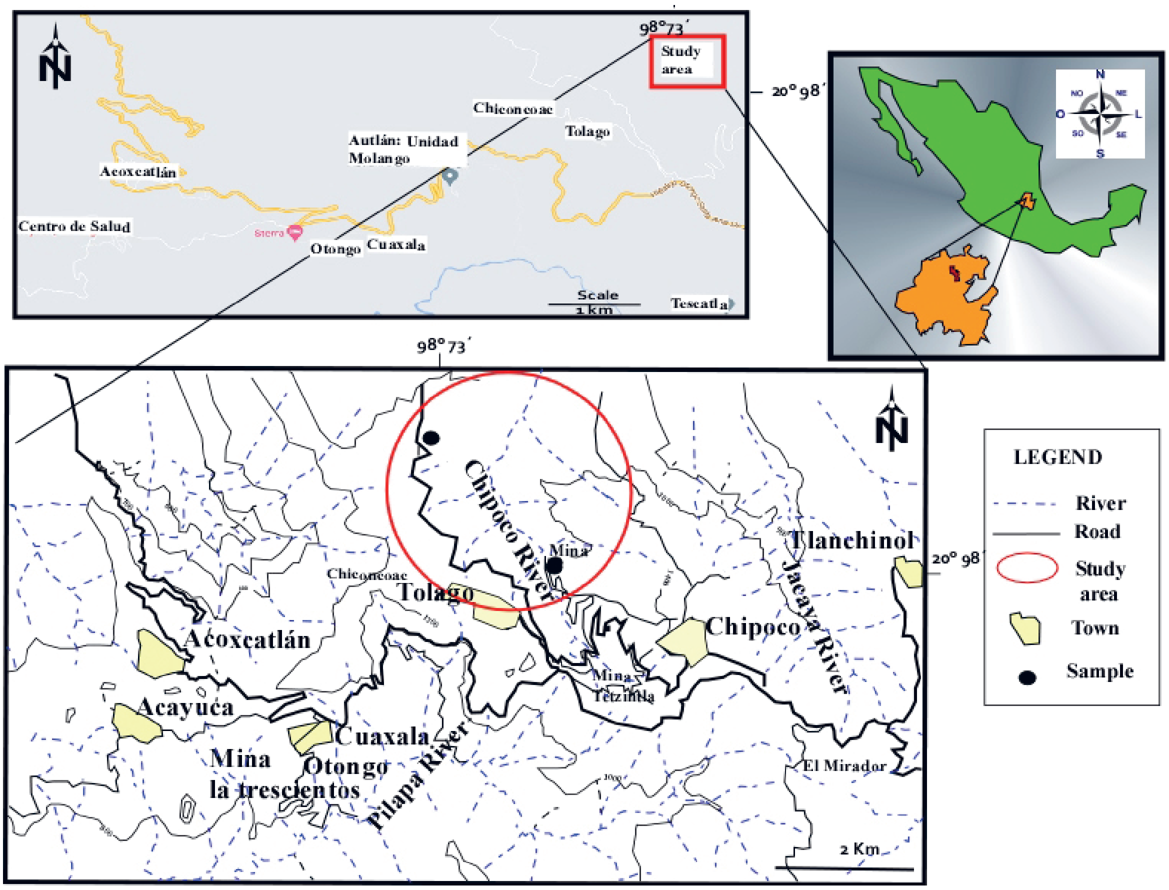


Figure 2. Location of the study area.

4. MATERIALS AND METHODS

4.1. Characterization of the geomorphological and geological context

Field reconnaissance was carried out allowing for the selection of outcrops in which a geological section was raised, creation of a stratigraphic profile, and sampling of calcareous tufas with remains of vascular plants, bryophytes, and pieces of coal. Samples were taken from both the base and the top of the outcrop. To classify the type of habitat where the calcareous tufa deposits were formed in the Molango manganese district, the classification proposed by CARCAVILLA et al. (2019) was taken into account. The classifications of BUCCINO et al. (1978), PEDLEY (1990), and VIOLANTE et al. (1994) allowed classifying the biofacies of calcareous tufas concerning their biological components.

4.2. Analytical methods

4.2.1. Petrographic analysis

Four samples were obtained from the calcareous tufa deposits that outcrop in the manganese district of Molango Hidalgo. These samples were analyzed using various techniques such as petrographic analysis whereby samples were cut into thin sections with a circular rock cutter and mounted on glass slides with epoxy resins. The samples were ground and polished with carbide shot to a thickness of 0.3 mm. The sections were then covered with glass slides so that the texture and minerals in the stone could be characterized by optical microscopic analysis. The identification and characterization of minerals were carried out employing the Olympus BX41 petrographic microscope, using cross-polarized light.

4.2.2. Geochemical analysis

For determination of their chemical composition, the samples were analyzed using a Rigaku NEX CG X-ray fluorescence (XRF) spectrometer, using energy dispersive mode (EDXRF). The spectrometer has an X-ray tube with a Pd anode and maximum power of 50 W (maximum voltage of 50 kV and current of 2 mA), and operates in a He atmosphere. Calibration was performed with the MCA Standard (Rigaku patent).

4.2.3. Mineralogical analysis

To determine the mineral phases, the four samples were analyzed using the ULTIMA IV X-ray Rigaku diffractometer with CuKα radiation. XRD patterns were compared with the Powder diffraction File (PDF) data from International Center for Diffraction Data (ICDD) to determine the phases present.

4.2.4. Scanning Electron Microscope (SEM-EDS) analysis

The morphological properties of the four samples were investigated by SEM observations without any sample coating. A JEOL Scanning Electron Microscope (SEM-EDS), model JSM-6010 PLUS/LA, was used, operated at 15 kV in a low vacuum, while an energy dispersive spectrometer (EDS), attached to the SEM, was used for semiquantitative chemical analysis. All the analyses were carried out in the LICAMM laboratory of the University of Guanajuato.

4.3. Radiocarbon analysis

One sample was dated using the radiocarbon method. A fragment of charcoal found within the calcareous tufa deposits was sent to the Beta Analytic laboratory in Miami Florida. Vegetable remains (plant) and organic sediments were found inside. The content recovered from the plant remains was 2.6 mg, while the content of the organic sediments was 408.8 mg. The plant was pretreated with acid/alkali/acid for the removal of carbonates and soluble humic acids, while the organic sediment was pretreated with acid only to eliminate carbonate (Fig. 3). The plants were dated as they are short-lived and,

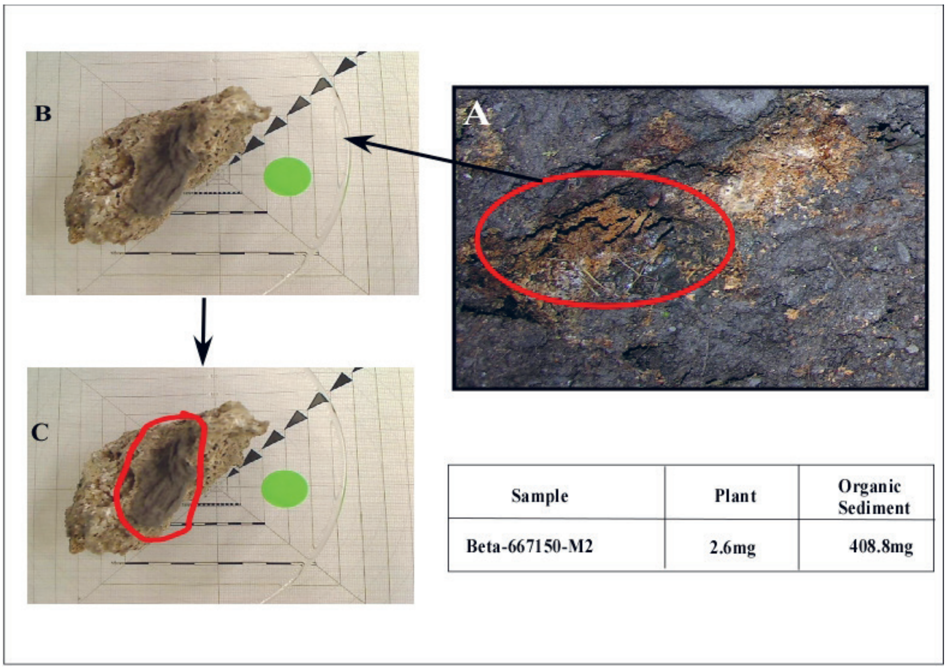


Figure 3. Charcoal analyzed for 14C dating. A) Facies of calcareous tufa deposits. B, C) sample of charcoal found in calcareous tufa deposits; D) Sample of charcoal pretreatment, E) Plant pre-treatment with acid/alkali/acid.

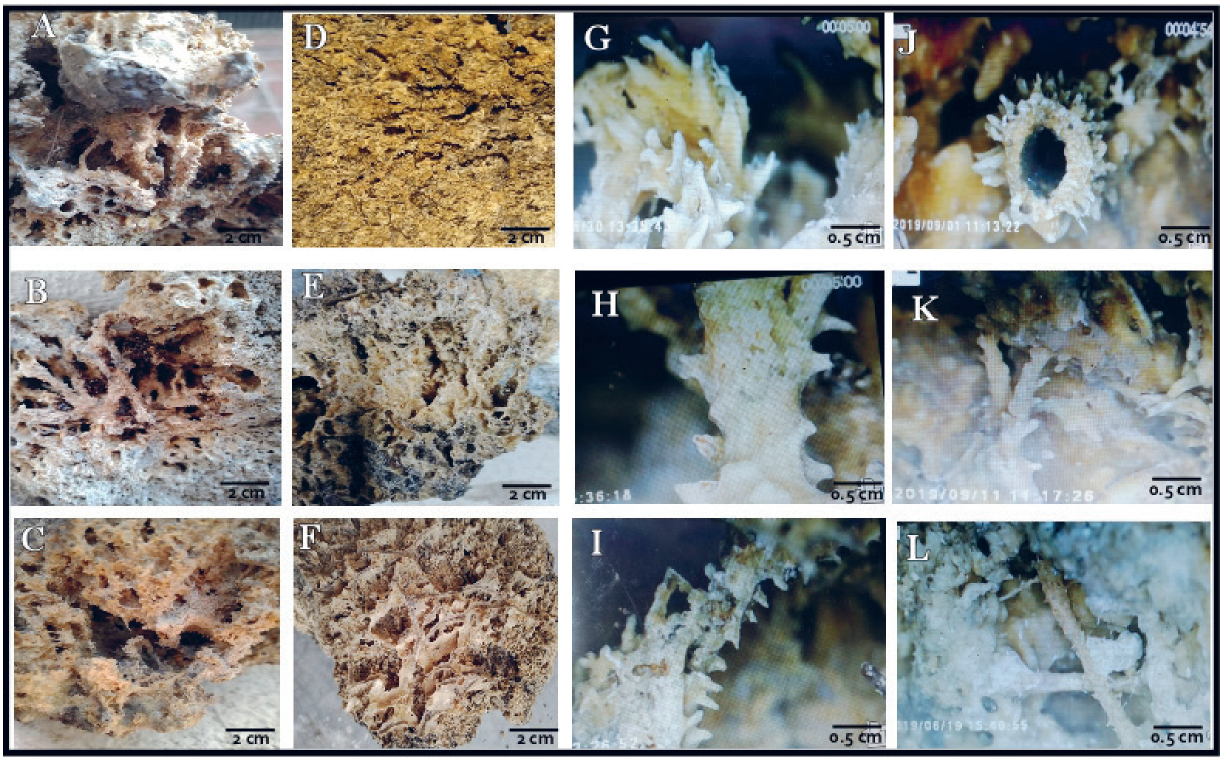


Figure 4. Biofacies in the calcareous tufa deposits: A, B, C) the lithoid type is presented as a stony variety, in the form of porous and tubular masses; D, E, F) the dendritic type is characterized by a structure of compact columns with stems branching upwards bryophyte; G, H, I) bryophyte replaced by calcium carbonate; J, K, L) vascular plants replaced by calcium carbonate.

therefore, represent a unique event in time. The organic sediment was not dated as it could represent an open system, where carbon could enter or leave the depositional environment. The date of the plant material represents the carbon within the plant cells, while the date of the sediment represents an average of the multiple organic components it contains. Based on this, only the plant material was dated.

5. RESULTS

5.1. Geomorphological, and geological characterization of calcareous tufa deposits

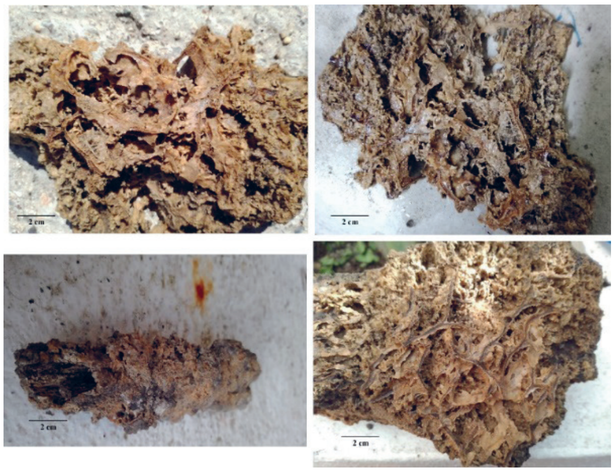
5.1.1. Geomorphological and calcareous tufa appearance

The topographic characteristics of the Molango manganese district have led to tributaries cutting into carbonate deposits, favouring the development of important tufaceous formations during the Holocene. Along the section between the towns of Otongo and Chipoco, there are terraced morphologies on the banks of the Chipoco River, with little longitudinal development and reduced thickness showing a longitudinal geometry of the calcareous tufa deposits. The calcareous tufa formations discussed in this article are white to yellow in colour, have cavities, and are porous with a large number of trunks observed. RUSSELL (1883, 1889) was one of the first to describe carbonaceous tufa types based on structural variation and depositional age. Taking into account their classification, the Molango calcareous tufa deposits correspond to the lithoid and dendritic types. The lithoid type is presented as a stony variety, in the form of porous and tubular masses, while the dendritic type is characterized by a structure of compact columns with stems branching upwards. These two types can occur in layers of different thicknesses to form a calcareous tufa tower. The origin was possibly in a paludine environment, where the calcareous tufa developed on poorly drained soils, in slopes colonized by hydrophyte macrophytes and bryophyte mounds. Waters enriched in calcium carbonate leaked, depositing a vegetal cover on the surface (Figure 4 (A-L)). Small ephemeral pools may develop in the valley bottoms and may persist for a sufficient time to allow carbonate fouling of associated macrophytes and aquatic vegetation. Micro-detrital tufa (lime mud) can also accumulate locally within the pools partly from rainfall on the site and partly from material washed in from the surrounding swamp slopes (Figure 4 (A-L)). The thicker bioclastic material can enter the system by this route and leaf fall can also lead to the deposition of humus-rich layers (gyttja) within shallow and stagnant bodies of water.

5.1.2. Classification of biofacies in the calcareous tufa deposits

In the calcareous tufa of Molango, the biological components developed in the spring system sub-environment and a Barrera-cascade sub-environment, where an abundance of fragments of vascular plant communities, replaced by calcite, are observed. Taking into account the biofacies classification (BUCCINO et al., 1978; PEDLEY, 1990; VIOLANTE et al., 1994), two types of biofacies can be observed in the calcareous tufa deposits in the Molango district (Table 1): Biofacies I (phytoclastic tufa) and Biofacies II (Mosse Tufa). Biofacies I (phytoclastic tufa) represents allochthonous deposits that correspond to a macrodetritic tufa. These facies are formed by fragments of stems and leaves from 5 mm to 7 cm long and

Table 1. Main features of the depositional environments and the associated sedimentary facies.

Facies	Geometry of deposits	Texture and Structure Characteristics	Environment	Photography
Facies I: Phytoclastic Tufa	Tabular, lenticular, and domic; centimeters to decimeters of thickness, and meters to decameters of extension	Boundstones of plants that grow upwards or pendants. Plant stems are recrystallized by calcite.	Calcite precipitation around the part submerged hydrophilic plants. Marshy areas on the banks of rivers and lakes, river floodplains, and areas between river channels. Vertical and staggered cascades.	
Facies II. Moss Tufa	Lenticular, plano-convex, and domic; centimeters to meters thickness and decimeters to decameters of lateral spread	Boundstones of mosses. A succession of centimetric layers and sheets made of mosses whose caulidia and phyllidia are arranged perpendicular or oblique to the deposit surface. These items are covered by calcite and have their interior empty or filled with calcite cement.	Calcite precipitation around caulidia and phyllidia of mosses, forming mats. Waterfalls, waterfall barriers, and small jumps, spray zones; illuminated areas of caves.	

with diameters of 0.5 to 1 cm (Fig. 5). They are coated with calcite, locally derived within the sedimentation zone. These fragments of vegetable stems are exposed in the upper part of the calcareous deposit. The calcitic envelopes' thickness is variable and usually laminated, with evidence of microbes. Sometimes the fragments are arranged parallel to the flow.

5.2. Petrological, mineralogical, and geochemical characterization of calcareous tufa deposits

5.2.1. Petrological analysis

Twenty-five thin sections were made of the rock samples collected in the field. The main mineral observed is calcite,

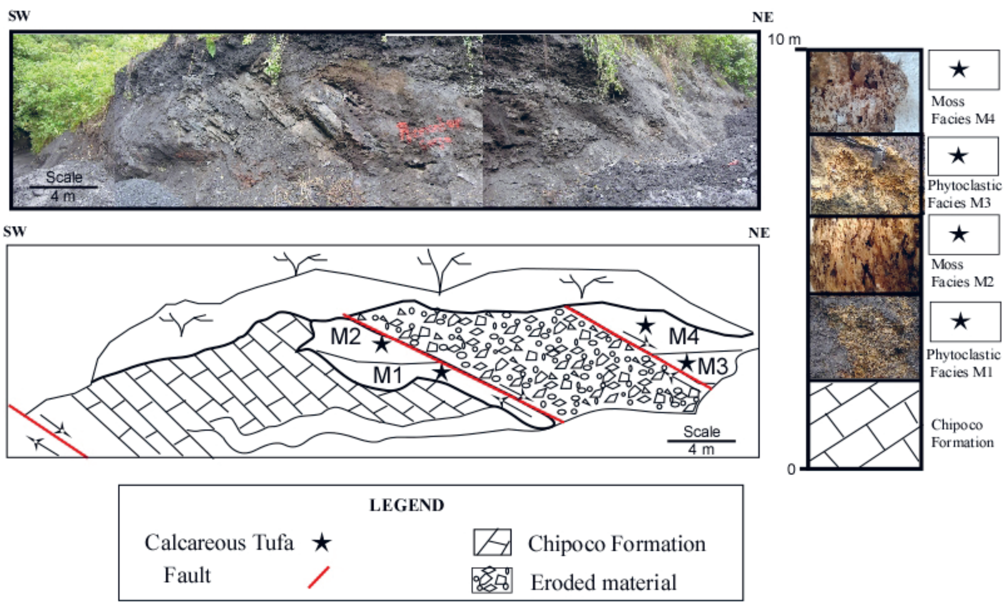


Figure 5. Classification of the calcareous tufa facies according to the biological components.

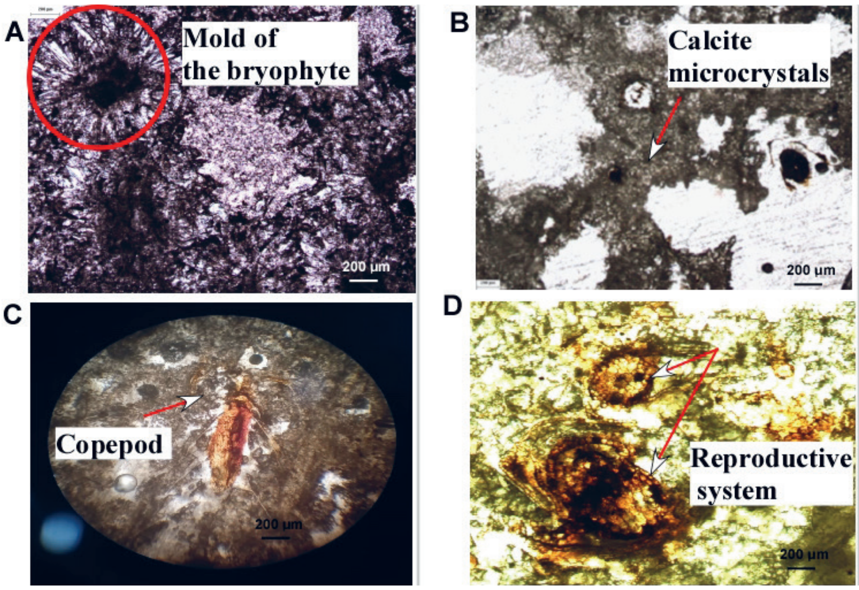


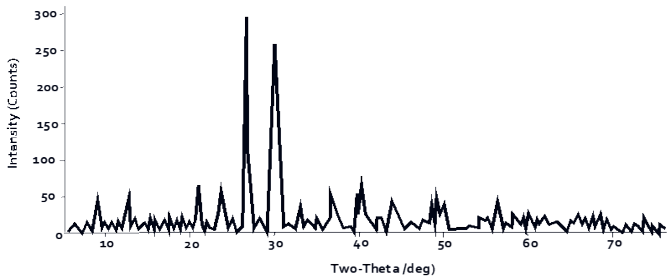
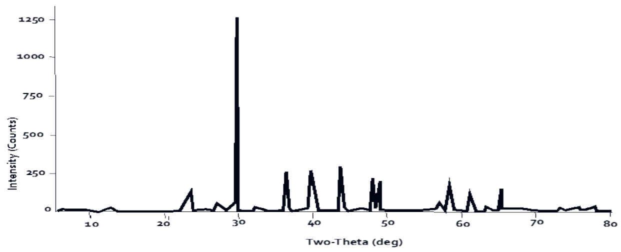
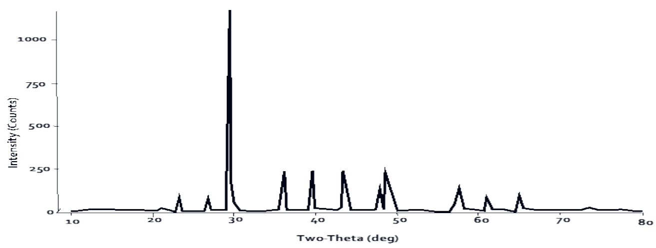
Figure 6. Photographs of the thin layers of calcareous tufa deposits. A) The external mould of the bryophyte can be observed, replaced by calcite; B) Calcite microcrystals; C) Copepod; D) Reproductive system.

and manganese oxides are minor constituents. Textural analysis of the analyzed samples showed that the deposits are composed of calcite coatings on biological substrates (mosses and vascular plants). The mosses are replaced by calcite where spherical structures are observed showing a concentric or radiant internal pattern. Vascular plants, especially the tubes, are filled with mosaics of equigranular calcite. Microbial structures are generally associated with copepods, bryophytes, vascular plants, trunk fragments, and possible reproductive systems (Fig. 6).

5.2.2. Mineral phases – X-ray Diffraction (XRD)

Table 2 shows the different mineralogical phases found in the calcareous tufa deposits studied. The dominant mineral phases are silicates (quartz (SiO_2), and moganite (SiO_2)), carbonates

Table 2. X-ray Diffraction (XRD). Mineralogical phases of carbonate tufa deposit.

SAMPLE	XRD	XRD DIFFRACTOGRAM
M1	Quartz- SiO_2 Moganite- SiO_2 Calcite, magnesian (Ca, Mg) CO_3 Pyrosmalite -(Mn) (Mn^{+2} Fe)$_8$(Si_6O_{15}) (OH, Cl)$_{10}$ Muscovite - (K, Na) (Al, Mg, Fe)$_2$(Si_3.1$Al_{0.9}$) $O_{10}(OH)_2$ Hidalgoite - $PbAl_3(AsO_4)$ (SO_4) $(OH)_6$ Pennantite-1MIIb - Mn_5^{+2} Al (Si_3Al) $O_{10}(OH)_8$ Wallkilldellite, (Ca, Mn)$_4$ Mn_6^{+2} $As_4O_{16}(OH)_8$ x $18H_2O$	
M2	Calcite $CaCO_3$ Calcite, magnesian (Ca, Mg) CO_3	
M3 and M4	Calcite - $CaCO_3$ Quartz - SiO_2 Moganite - SiO_2	

(calcite ($CaCO_3$), and magnesian calcite ((Ca, Mg) CO_3)). Moganite is a mineral that is a type? of chalcedony. The formation of chalcedony is linked to the existing pH in the medium, so the presence of chalcedony is justified in alkaline pH. Chalcedony in carbonate tufa deposits is found as a replacement material for calcite and/or dolomite and cementing pores. The presence of silica (SiO_2) may be due to local geological and environmental conditions. Silica could be incorporated through the interaction of silica-rich rocks and water; it may also come from decomposing organic material such as diatoms or other organisms that contain silica in their structures. Other identified mineral phases are arsenates (wallkilldellite, hidalgoite), the chlorite group minerals (pennantite), and other phyllosilicates (muscovite, pyrosmalite-(Mn)). These mineral phases are associated with the Molango manganese deposit, which is considered to be a large-scale marine sedimentary deposit typical of the Kimmeridgian - Tithonian in Mexico. The calcareous tufa deposits were formed on the Chipoco Formation, where manganese enrichment occurs, hence the presence of mineral phases related to the manganese deposit.

5.2.3. Geochemistry – X-ray Fluorescence (XRF)

The main mineralogical phases are carbonates, represented by calcite. Chemical analyses indicate that calcite ($CaCO_3$) contains quantities of magnesium (Mg), iron (Fe) and manganese (Mn). Other elements that appear are chlorine (Cl), sulfur (S), phosphorous (P), aluminum (Al), silicon (Si), potassium (K), vanadium (V), cobalt (Co) nickel (Ni), copper (Cu), zinc (Zn), tin (Sn), titanium (Ti), strontium (Sr), barium (Ba), arsenic (As) and lead (Pb) (Table 3).

5.2.4. Microbial structures – Scanning Electron Microscopy (SEM-EDS) analysis

The morphological aspects of the microbial samples are shown in Figure 7. In all samples, the SEM examination revealed Ca-rich particles, and magnesium (Mg), aluminum (Al), silicon (Si), and sulfur (S). Wollastonite occurs in all the samples analyzed, it is calcium inosilicate ($CaSiO_3$) that can contain small amounts of iron, magnesium, and manganese substituting for calcium (Ca). Regarding the biological structures, it is observed that these are covered by calcite formed around the bryophytes, where it is common to distinguish palisades of calcite tubes perpendicular to the substrate. It is important to mention the absence of lithic sediments in the samples. The presence of pyrite microcrystals, circular spheres (microbial), and phytoclasts is common. As for the metals, it can be observed that most of the samples studied contain iron, copper, zinc, manganese, molybdenum, and sulfur.

5.3. Radiocarbon dating

The results of the radiocarbon dating indicate that by pre-treating the charcoal, no carbon was recovered. Instead, plant fragments were recovered, which were pre-treated with acid/alkali to remove carbonate and soluble humic acids. The plant fragments were dated by the ^{14}C method, obtaining the conventional radiocarbon age of 360 ±30 BP. Two-time intervals are shown in Figure 8, where there is the first interval of 490-421 Cal BP, and a second interval of 410-316 Cal BP. These data place the deposit of calcareous tufa in the Holocene.

Table 3. Chemical compositions of the carbonate tufa deposit obtained with X-ray fluorescence (major elements in wt%, and minor elements in ppm; ND – not determined).

	SAMPLE M1	SAMPLE M2	SAMPLE M3	SAMPLE M4
Major elements (wt%)				
MgO	1.92	0.43	0.32	0.75
K_2O	1.38	0.76	0.53	0.37
CaO	30.90	57.50	74.80	79.40
Al_2O_3	9.29	2.05	1.32	2.53
SiO_2	26.10	4.61	2.82	5.42
P_2O_5	0.16	0.01	0.00	0.04
SO_3	4.30	0.84	0.99	2.41
TiO_2	0.42	0.06	0.05	0.01
MnO	16.90	15.0	6.19	8.0
Fe_2O_3	8.60	18.7	12.90	1.08
Na_2O	ND	ND	ND	ND
Minor elements (ppm)				
V	65	ND	5.36	ND
Cr	ND	ND	ND	ND
Co	216	17.6	ND	30.2
Ni	60.2	21.7	ND	116
Cu	28.2	9.64	5.54	32.6
Zn	55	32.3	3.17	100
As	42.9	2.07	ND	2.89
Sr	402	172	139	415
Sn	29.9	11.5	12.6	19.6
Sb	ND	ND	ND	ND
Ba	194	ND	ND	ND
Hg	ND	ND	ND	ND
Pb	13.3	5.58	2.66	12.6
Cl	152	25.6	27.8	ND

5.4. Palaeoenvironmental reconstruction

The calcareous tufa deposits found in the upper part of the Chipoco Formation in the Molango manganese district correspond to deposits of a spring system sub-environment and a Barrera waterfall sub-environment. The sub-environment of a spring system relates to places where groundwater emerges to the surface through fractures or discontinuities, with a horizontal or gently sloping topography, favouring the accumulation of these deposits in conical mounds, frequent in underwater springs (lacustrine and paludine) (CAPEZZUOLI et al., 2014; DELLA PORTA, 2015), while the Barrera waterfall sub-environment originates from the accumulation of phytoclasts or calcification linked to plants and microorganisms. The development of a barrier generates a topographic drop immediately downstream, giving rise to a waterfall. The morphology of this sub-environment is a mound composed of clinoforms. The succession of barrier-cascade pairs generates stepped sections (CHAFETZ et al., 1994; ORDOÑEZ et al., 2005; ARENAS-ABAD et al., 2010; GRADZIŃSKI et al., 2013). The calcareous tufa deposits studied were formed by physicochemical or biological precipitation or by a combination of these two processes. Organic factors such as vascular plants' presence have influenced these deposits' geomorphological characteristics. The petrological, morphological, and geochemical characteristics observed in the Molango calcareous

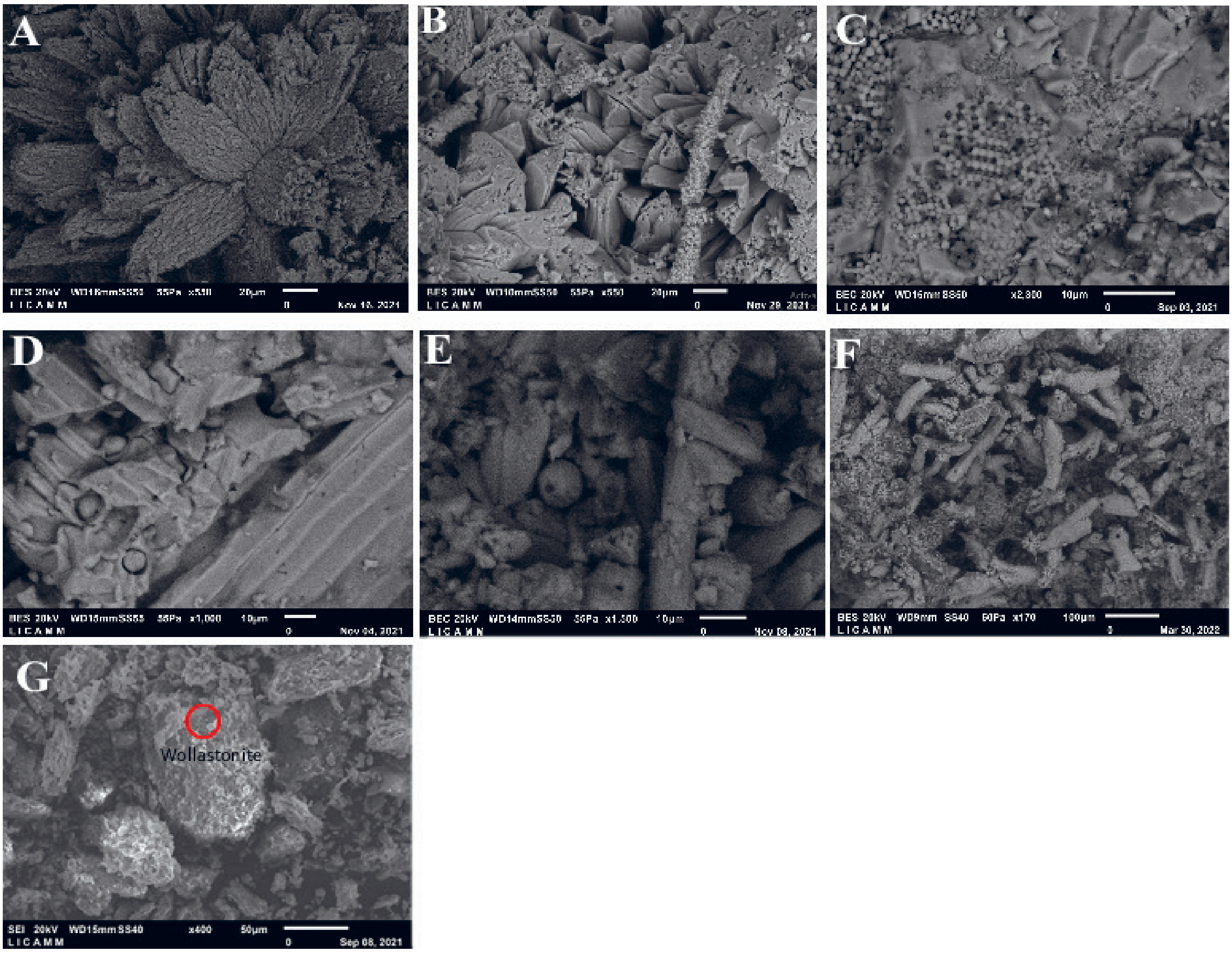


Figure 7. Images obtained with the scanning electron microscope in the samples of the calcareous tufa deposits. A, B) Mould of bryophyte stem. C) Packing of pentagonal-dodecahedral pyrite microcrystals. D) Microbes formed by connected circular spheres. E) Detail of circular sphere (microbial). F) Phytoclast. G) Wollastonite.

tufa deposits suggest that they were formed in a marshy environment, located in a disk system in low-lying areas near or associated with lagoons or springs that provided them with water, allowing the colonization of macrophytes, hydrophytes, mounds of bryophytes with little presence of lichens. They represent shallow and stagnant bodies of water, relating to a marshy environment (Fig. 9). The palustrine carbonates were formed by periods of saturated water and subaerial exposure,

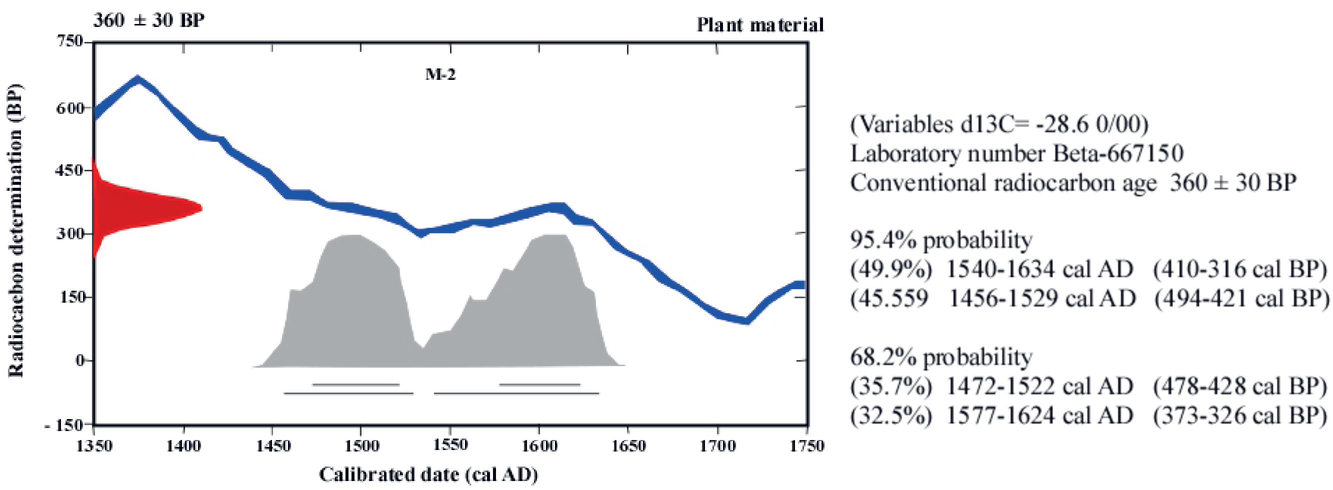


Figure 8. Results of 14C dating.

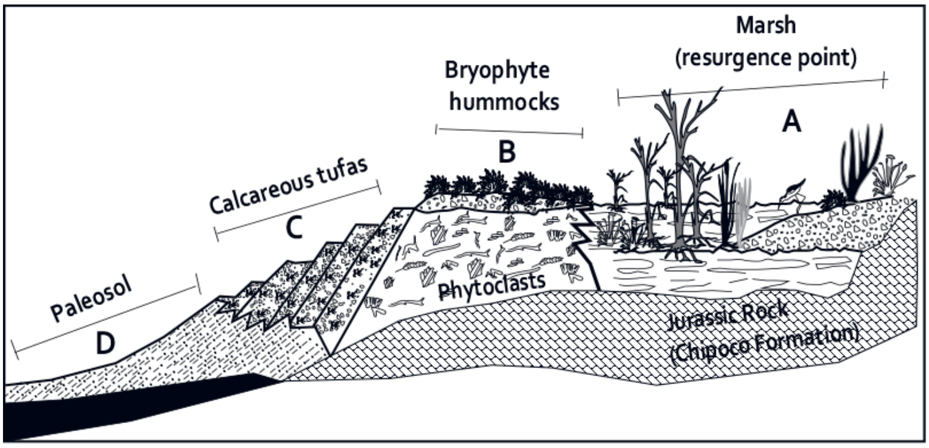


Figure 9. Palaeoenvironmental reconstruction. Diagram illustrating the associations of calcareous tufa lithofacies in a paludal environment. A) Paludal environment resurgence point; B) Bryophyte hummocks and phytoclasts; C) Cascade constituted by calcareous tufas; D) Palaeosols. Modelled from calcareous tufa deposits of Molango, Hidalgo, Mexico (modified from PEDLEY, 1990).

indicating fluctuations due to seasonal or long-term climatic changes. These deposits provide evidence of pedogenic carbonate precipitation, a process that suggests calcite saturation in the vadose zone fluids. ALONSO-ZARZA (2003) suggests that marsh deposits are formed mainly during periods of very low subsidence, with limited accommodation space for basins with more fill, giving way to facies deposition in more shallow systems. Furthermore, PLATT & WRIGHT (1992) suggest that marsh deposits are common in relatively stable basins, usually formed during periods of tectonic quiescence where clastic supply from alluvial-fluvial systems is reduced. It is then suggested that the sedimentation took place in shallow water accumulations, where there is a clear evidence of exposure and pedogenic modification, indicating wet and dry episodes that translate into seasonal fluctuations of the water table. According to GOLUBIC (1969), calcareous tufa deposits are subject to subaerial exposures where such deposits are susceptible to local changes within drainage patterns and short-term fluctuations in the water table that can lead to stream incision, thus the development of these deposits is cyclic and the deposition ends at the end of a natural cycle by incision and erosion of the deposits. This subaerial exposure occurred in the calcareous tufa deposits studied where the development of vadose calcite cement and the mobilization of Fe and Mn are observed, the latter precipitated at the air/water interface.

6. DISCUSSION

In the Molango district, the origin of the carbonates that make up the tufa deposits is linked to the nature of karstic aquifers. The water flows generated by the calcareous tufas come from karstic massifs and are associated with meteoric waters with temperatures usually close to 10ºC with slightly basic pH values (7.5 -8.4), and calcium concentrations between about 30 mg L-1 and 60 mg L-1 (MERZ PREIß & RIDING, 1999; PENTECOST & ZHAOHUI, 2002; PENTECOST, 2005). According to SLACK (1967), the origin of calcareous waterfalls is primarily in the precipitation of calcium carbonate due to the degassing of the dissolved CO_2 and the temperature of the water. In biochemical precipitation, plants are an essential component, and the loss of CO_2 could be linked to the extraction of CO_2 from the water through the photosynthesis of macrophytes, bryophytes (mosses), filamentous algae, diatoms, charophyte algae, cyanobacteria, bacteria, vascular plants, and prokaryotes. Especially, the organic substrate plays a key role in the nucleation of calcite incrustations and the primary porosity is provided by the calcareous tufa material (PENTECOST, 2005). An important characteristic of calcareous tufa deposits is that their study allows us to understand the regional evolution of the geographical areas in which they are located, providing information on their karstic evolution, their tectonic behaviour, and the gradation or incision processes of their watercourses. In the Molango district, the calcareous tufa deposits are considered the only morphological witnesses that are found interacting with the karstic morphology, being able to link the origin of the carbonated tufas with the dissolution processes developed on the exo-karstic morphologies modeled in a more or less closed environment. Taking into account the PEDLEY (1990) classification, the deposits of calcareous tufa Molango correspond to phytoherms, where the tufa constructions are porous, derived from primary factors linked to the insertion of multiple plant elements (hydrophytes and semiaquatic macrophytes) colonized by microfilms cemented by calcitic carpets with a low content of magnesium. These deposits are composed of multiple plant devices generally cemented after their sedimentation. Under magnification, the calcified stem casts are 2 cm long, 2-3 mm in diameter, and are covered with micrite (Fig. 4). The Biofacies I was formed on gentle slopes, in lacustrine and swampy environments, favouring hydrophilic soil development plants, for which stem and phytoclast abound. Biofacies II (bryophyte hummocks tufa) alternates with Biofacies I. Bryophytes are non-vascular plants, do not have roots or vascular tissue, and absorb water and nutrients from the air over their entire surface. Most of them just reach a few centimetres in height, they grow in places where other plants could not, such as on the surface of rocks, walls, pavements, etc. Bryophytes grow in humid and shady environments but can be found in diverse and even extreme habitats, from deserts to arctic areas. In the facies described, the dominant species corresponds to *Plagiomnium cuspidatum*. These bryophytes grew on carbonate rocks, which formed mounds developed in a palustrine environment. The aforementioned facies is made up of a succession of centimetre layers and sheets of hummocky bryophytes that are arranged perpendicular or oblique to the surface of the deposit, and formed in small stepped cascades (Fig. 5). *Plagiomnium cuspidatum,* also known as toothed or "baby-tooth", is a species of thyme-moss that originated in North America, but can now also be found throughout Middle America, Africa, Northern and Southern Asia (excluding China), and Europe. Copepods have been observed within this species. The facies arrangement in all the environments indicates the initial incision of the fluvial network, subsequent development of ponded/shallow lacustrine areas, and formation of cascades on steps in the palaeo-relief (CARCAVILLA et al., 2019). The sampling points studied indicate that the present facies are associated with marsh carbonates formed by periods of saturated water and subaerial exposure, indicating fluctuations due to seasonal or long-term climate changes. These deposits provide evidence of pedogenic carbonate precipitation, a process that suggests calcite saturation in the vadose zone fluids. Considering the model proposed by PLATT & WRIGHT (1992) for marshy environments, the deposits studied were deposited in a moderate climate, characterized by the presence of vascular plants, bryophytes, and rhizolites. The work of ALONSO-ZARZA (2003) suggests that marshy deposits are formed mainly during periods of very low subsidence, with limited accommodation space for basins with more fill, giving way to a facies deposition in shallower systems. Furthermore, PLATT & WRIGHT (1992) suggest that salt marsh deposits are common in relatively stable basins, typically formed during periods of tectonic inactivity where the supply of clastic material from alluvial-fluvial systems is reduced. It is then suggested that sedimentation took place in shallow water accumulations, where there is clear evidence of exposure and pedogenic modification, indicating wet and dry episodes that translate into seasonal fluctuations in the water table. Calcareous tufa deposits formed under these conditions are very common in tropical forests where the presence of plant matter is common. The plant structures found in the calcareous tufa deposits were dated using ^{14}C, and a Holocene age was obtained. The Holocene has been catalogued as one of the Quaternary epochs in which the formation of calcareous tufa deposits occurred throughout all the karstic regions of the planet. This was due to the increase in atmospheric CO_2 during said period (GRIFFITHS & PEDLEY, 1995). In Hidalgo, during the Holocene, mafic volcanism obstructed the drainage of basins, generating karst palaeo-lagoons where a great diversity of copepods, calanoids and cyclopoids as well as structures of stems and vascular plants were replaced by calcium carbonate. This formed a part of the biofacies of the calcareous tufa deposits (LÓPEZ RAMOS, 1972; FERNÁNDEZ-BADILLO et al., 2016). Regarding the mineral phases and chemical composition, the calcareous tufa deposits are mainly composed of calcium carbonate, varying its composition in some samples such as M1, where the presence of other minerals is observed (silicates and arsenates) as a result of its proximity to the Molango manganese deposit, which exerted specific conditions for formation of the calcareous tufa deposits, influencing the texture, colour and characteristics of these deposits.

7. CONCLUSION

The calcareous tufas of Molango have their origin in springs located on the slopes of gently sloping valleys and at the foot of karstic springs related to a marshy environment. Considering the model types proposed by PEDLEY (1990), the calcareous tufa deposits studied originated in a palaeoenvironment in their distal part, where cascading formations dominated by mounds of bryophytes, vascular plants, and phytoclasts, and associated with local channels, can be observed. These have an almost horizontal shape with a gentle slope, constituting a series of terraces that present properties of the paludal environment. Its longitudinal development is in the form of a cascade of small to moderate growth with concave profiles, where bryophytes, lichens and vascular plants tend to adapt to a centimetre jump in terraces developed parallel to the watercourse, providing progradation structures downstream. The sedimentation of the calcareous tufa in Molango took place in shallow water accumulations, where there is clear evidence of exposure and pedogenic modification, indicating wet and dry episodes that translate into seasonal fluctuations in the water table. Precipitation due to the physico-chemical degassing is the main factor for the deposition of calcareous tufa deposits. These carbonatic accumulations, rich in vegetal remains and not exclusive of karstic substrates, are precipitated in springs, where they formed deposits consisting of calcite with a low magnesium content, and are generally not stratified. In addition, they are formed by bodies of irregular distribution, scarce lateral continuity, are poorly to strongly lithified, and of different petrographic facies. Their genesis and development are determined by tectonics and/or trends towards the aggravation or incision of river networks during the Holocene.

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