Chemical analysis to identify organic compounds in pre-Columbian monumental earthen architecture

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Abstract: In 2012 we started a program of chemical analysis on organic extracts of 14 samples of fills, adobes, floors and renders, dated AD 200–400, obtained during the excavations of monumental earthen buildings at the archaeological site of La Joya, Veracruz, Mexico, located on the humid tropical coastal plain of the Gulf of Mexico. The interest in identifying organic additives derives from the observation that the conservation conditions of buildings is better than expected, considering the mineral composition of construction materials in which smectite (montmorillonite), an expansive clay, dominates. This brought us to suspect the presence of certain compounds which served as consolidant and/or water-repellent. The organic compounds from the building samples are extracted in hexane and methanol, and analyzed by Thin Layer Chromatography [TLC], Fourier Transform Infrared Spectroscopy [FTIR], Nuclear Magnetic Resonance Spectroscopy [NMR] (^{1}H and ^{13}C) and Mass Spectrometry [MS] (Fast Atom Bombardment [FAB+]). The results of these analyses confirm the presence of the same organic compounds in all samples, especially more abundant in adobe samples. The compounds identified up to now are hydrocarbons, a triglyceride and a sugar. At the same time, the mucilage of plants used in the vernacular construction in humid tropical environments in Central America is analyzed using a similar process in order to compare it with the organic substances of the original materials. The importance of identifying additives in pre-Columbian earthen buildings resides not only in understanding what made a tradition of earth construction possible in humid tropical environments, which contributes to the history of technology, but also in the possible use of such an additive in the conservation of archaeological remains, as well as in modern construction.

Key words: organic additives, archaeology, Veracruz, México, Classic Period, adobe, Nuclear Magnetic Resonance Spectroscopy, Fourier Transform Infrared Spectroscopy

Introduction

The archaeological site of La Joya is located on the coastal plain of the Gulf of Mexico, close to the modern city and major merchant port of Veracruz. Though the site is occupied since the Olmec period, the monumental earthen architecture dates between 200 BC and AD 1000, spanning what is locally called the Late Preclassic and Classic period. Excavations in the severely damaged site since 2004 have revealed evidence of a sophisticated building tradition that used only raw earth, all the more surprising because of the adverse tropical conditions of heavy rainfall in the summer (>1500 mm/year) and strong winds and hurricanes in the winter. Since 2009 a coordinated effort uniting archaeologists, architects, engineers, chemists, and biologists, is under way to understand the building technique. Initially we analyzed 20 structural samples of structure fills, adobes, floors and facings for composition (sediment analysis, petrography, X-ray Fluorescence, X-ray Diffraction, FTIR, botanical analysis of chopped grass component), and mechanical properties (density, porosity and resistance to compression), the results of which are reported elsewhere (Daneels & Guerrero-Baca, 2011 and Liberotti & Daneels, 2012).

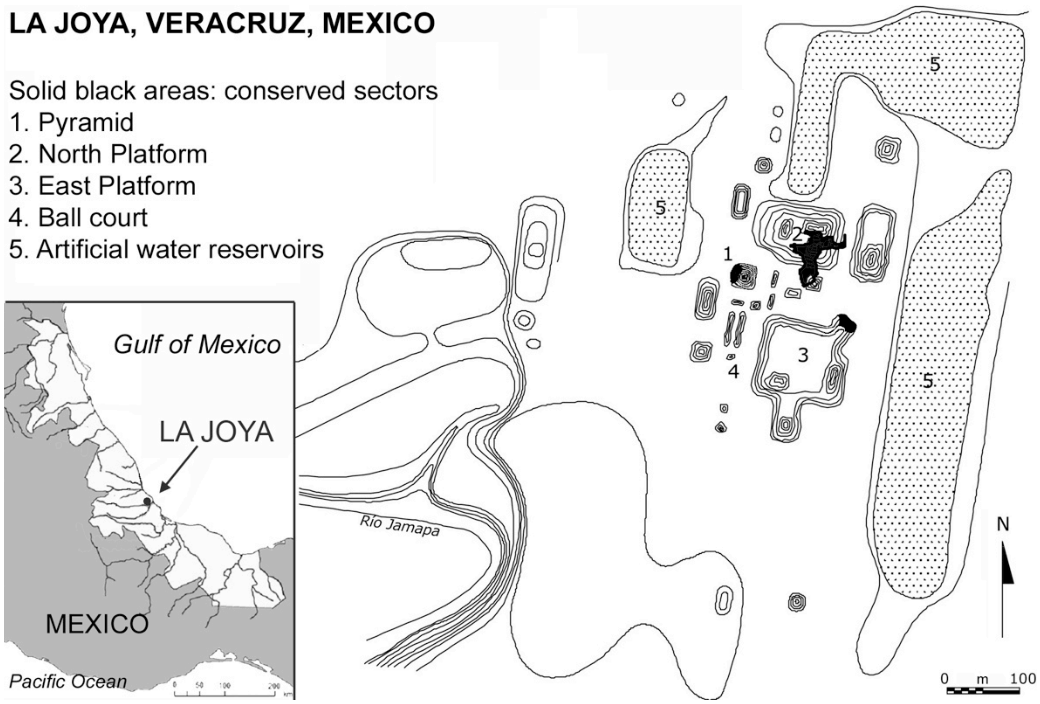


Figure 1: Layout of the La Joya site in the State of Veracruz (in white), and its location on the Gulf Coast of Mexico

The results showed materials to be of a medium to poor quality. This is especially due to the fact that the mineral composition analysis by X-ray diffraction revealed that smectite dominates in the composition of earthen construction materials. This is highly expansive clay, very difficult to manage with the strong seasonal variation in humidity conditions. This lead us to believe that the mineral mix was combined with a modifier that helped the earthen structure to resist the expansion-contraction cycles of smectite due to changes in environmental conditions such as precipitation, floods and hurricanes.

Organic additives such as fibers and polymers are often added to inorganic materials such as lime, earth, and sand to make mortar and adobe blocks. Today we can observe a large variety of natural organic additives used especially in vernacular architecture. These additives tend to be considered as "traditional materials" as well as "appropriate restoration materials" for archaeological and historical buildings, even though we do not know how long those materials have been used as additive. Interpretation of organic substances relies on the information based on local practice. Since the mucilage of a cactus called "nopal" (*Opuntia ficus-indica*) is used for vernacular construction in central Mexico (where semiarid conditions prevail)and is widely applied for restoration in Mexico, organic substances found in archaeological remains usually are supposed to be nopal mucilage. Although there are native and cultivated nopals in the region of La Joya, they are not as abundant as in the central highland of Mexico, due to the humid tropical climate. Also, the FTIR analysis of the initial sample series revealed the presence of an agglutinant that did not bear close resemblance to nopal mucilage (Daneels & Guerrero 2011). Therefore it was necessary to broaden the scope of the investigation. A promising lead comes from Central America,where traditional builders in humid tropical regions will use extracts of leaves and stems of the mallow shrub(*Sida rhombifolia*) or bark of the guacima tree (*Guazuma ulmifolia*) as additive for adobe, and apply it in archaeological restoration as additive for earth paste or as consolidant of earthen architecture surface (Ohi & Girón, 2000).

The formal research to identify the organic compounds in the pre-Columbian building materials started in 2011, testing a facing sample by Nuclear Magnetic Resonance Spectroscopy at The Institute of Chemistry of the National Autonomous University of Mexico. The ^{1}H NMR spectra of the methanolic extract from 105g of the sample in deuterated methanol (CD_3OD) recorded at 400 MHz showed signals of hydrocarbons, as well as signals between δ 3 and 3.8 which indicate the possible existence of a sugar, a signal indicative of a double bond at δ 5.34. This first result justified the design of a complete research protocol to identify the pre-Columbian substance that apparently made earthen architecture possible in humid tropical environments. In this paper, we present the preliminary results of this research.

Sample and Method

Encouraged by the 2011 results, we started a set of analysis based on a new series of 14 pre-Columbian construction samples from the La Joya site, consisting of 8 floor layers, 2 facings, 2 adobe and 2 fills, dated to AD 200 – 400, from two buildings: The North Platform, a palace, and the altar annexed to the main Pyramid (Table 1). These analyses, applied on extracts, are geared towards defining the possible modifiers added to the mineral mix, and were carried out by author Dr. Yuko Kita under the supervision of Dr. Alfonso Romo de Vivar at the Institute of Chemistry in the National Autonomous University of México.

Table 1: Sample list. Location: La Joya, Municipality of Medellín, Veracruz, Mexico (19˚04’00’‘N96˚09’00’’W; UTM zone 14 799799E 2110514N).

No.	Structure	Description	Date
1	North Platform	Base layer and lower floor layer	AD 200-400
2	North Platform	3 layers of the surface floor	AD 200-400
3	North Platform	2 superposed floors (a sandy layer and a loamy layer)	AD 200-400
4	North Platform	Adobe found loose in fill	AD 200-400
5	North Platform	Superior line of adobe at east perimeter wall	AD 200-400
6	North Platform	4 facings	AD 200-400
7	Pyramid SE	Sandy fill under the level of plaza	AD 200
8	Pyramid SE	Mixed fill under the floor	AD 200
9	Pyramid SE	2 layers of floor	AD 200-400
10	Pyramid SE	2 layers of floor	AD 200-400
11	Pyramid SE	2 layers of floor	AD 200-400
12	Pyramid SE	2 layers of floor	AD 200-400
13	Pyramid SE	3 layers of floor	AD 200-400
14	Pyramid SE	Clayey facing (exfoliated)	AD 200-400

The analyses were carried out according to the following procedure: a 300g portion of each ground earthen sample was weighed out, soaked in methanol (MeOH), stirred with a glass rod and left to settle for 24 hours to dissolve organic components. Then, the sample in methanol was heated up at ± 60°C for 30 minutes, stirred and filtered. This process was repeated thrice. The residue was concentrated by rotary evaporator. Each extract was then analyzed by Fourier Transform Infrared Spectroscopy [FTIR] and/or ^{1}H NMR.

Because the residues obtained from each sample are so scant, it was not possible to run ^{13}C NMR spectra, much less with hetero nuclear experiments. But, as all extracts were very similar, they were put together, obtaining a 101.2 mg combined residue sample, which was mixed with celite and then concentrated. To be able to have a better idea of the structures of the diverse components, the extract was separated into each component by column chromatography with hexane, ethyl-acetate and methanol. These extracted substances were analyzed by FTIR, ^{1}H NMR, with 2-dimensional homonuclear experiment: Correlation Spectroscopy [COSY], ^{13}C NMR, with 2-dimensional heteronuclear experiment: Heteronuclear Multiple-Quantum Correlation Spectroscopy [HMQC], and 3-dimensional heteronuclear experiment: Heteronuclear Multiple-Bond Correlation Spectroscopy [HMBC]. Some samples were analyzed also by Mass Spectrometry [MS] (Fast Atom Bombardment [FAB+]).

Results

The quantity of residue obtained through the extraction process varied from 0.7mg to 25.1mg; especially the adobe blocks, samples no. 4 and 5, contain large amount of organic component. The FTIR spectra reveal the presence of variable quantity of esters in a range between 1718 and 1740cm^{-1}. The ^{1}H NMR spectra recorded with deuterated chloroform ($CDCl_3$)provide a pattern similar to a fatty acid ester, and with deuterated methanol (CD_3OD)the spectra reveal the presence of a sugar whose characteristics correspond to methyl pentoses, such as rhamnose or fucose. Besides this we detected signals of aromatic compounds at δ 7.22 and 7.5 with coupling, and signals at δ 5.2 and 5.3 which seem to correspond respectively to a triglyceride and to a double bond.

The organic components show a complex but very similar composition. Because the quantities are very small to run ^{13}C NMR spectra, we decided to combine all extracts in order to be able to separate components by column chromatography. The spectra of ^{1}HNMR, ^{13}CNMR, and their correlations such as COSY, HMQC and HMBC of the separated components by chromatography do not only support the interpretation of the spectra obtained for the individual samples, confirming the presence of hydrocarbons, a triglyceride and a sugar, but also indicate two methyl esters, one of them probably butyl phthalate whose signals appear at δ 3.6 and 3.8 (Figure 2 - 6). The hydrocarbons and the aromatic ester do not look like impurities, since they are abundant in all samples and the impurities of solvents are few.

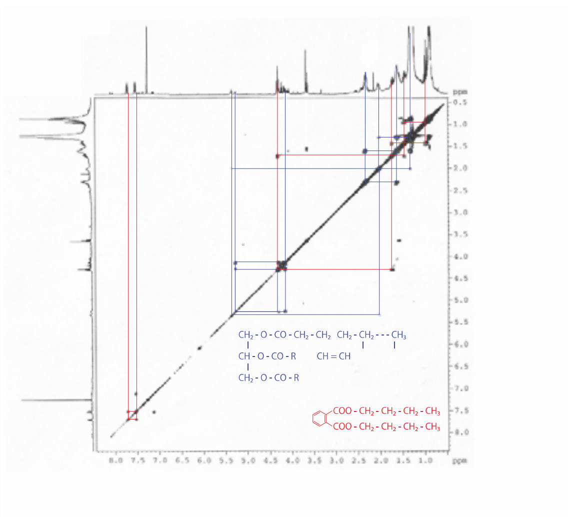
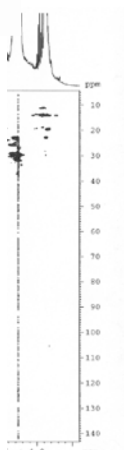
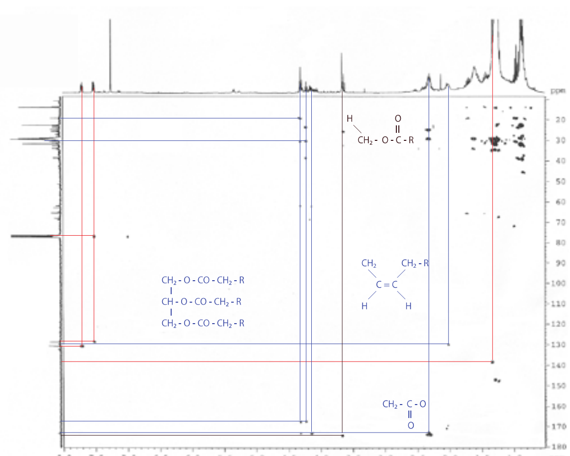


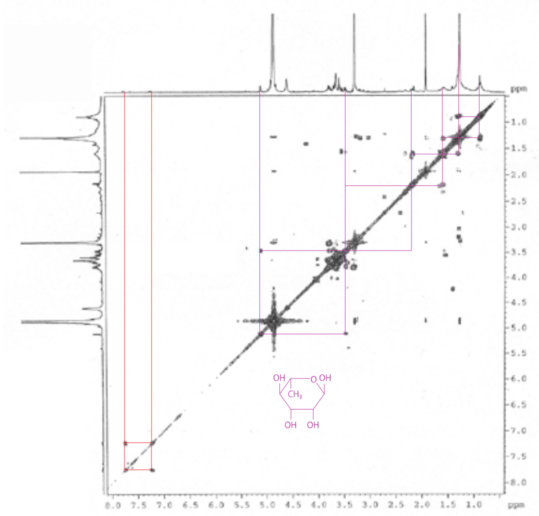
Figure 2 (left): The COSY spectrum which indicates the presence of hydrocarbons, a triglyceride and two methyl esters, one of them probably butyl phthalate.

Figure 3 (left below): The HSQC spectrum which indicates the presence of hydrocarbons, a triglyceride and two methyl esters, one of them probably butyl phthalate.

Figure 4 (right below): The HMBC spectrum which indicates the presence of hydrocarbons, a triglyceride and two methyl esters, one of them probably butyl phthalate.







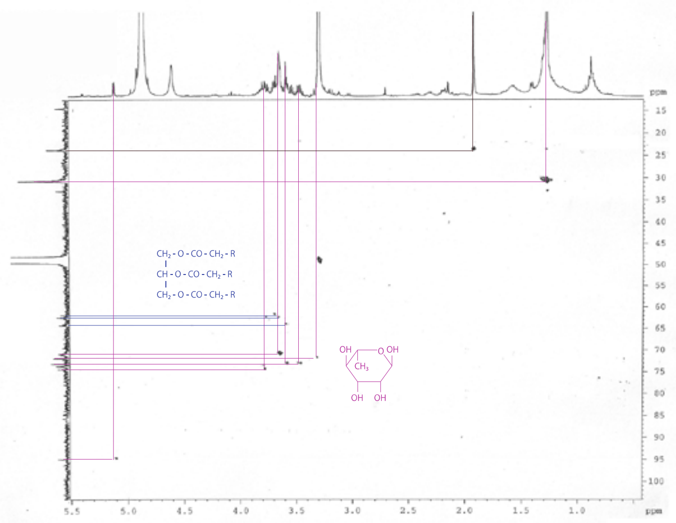


Figure 5 (left): The COSY spectrum which indicates the presence of a sugar.
Figure 6 (right): The HSQC spectrum which indicates the presence of a sugar and a small quantity of a triglyceride.

Discussion

Considering local practices in vernacular architecture in Mexico and other countries of Latin America, such as El Salvador and Peru, we expected the presence of some polysaccharide from plants, which brought us to think that the hydrocarbons could be impurities. However, hydrocarbons were observed in all samples extracting and rinsing with high quality of solvents, therefore they should come from the original samples. We must report that the local inhabitants of the La Joya site are currently exploiting the archaeological mounds to extract earth to make brick, and between the 1980's and 90's used a byproduct of petroleum processing as a fuel for the brick kilns. Therefore, some modern contamination could be possible, especially for the samples 7-14of the altar annexed to the main Pyramid, as they come from relatively shallow archaeological strata in an area close to where brick-kilns were in use in the 1990's. But, as the hydrocarbon signature shows up in all the samples, we are quite confident there is no modern contamination.

We do not have references on the pre-Columbian use of bitumen as a stabilizer of adobe blocks, but there is information on the use of bitumen to waterproof earthen structures and bind adobe blocks in ancient Mesopotamia (Barton, 1926; Taylor 1855),the Near East (Hollander, 2000), the Indus Valley and Egypt (Forbes, 1936). Besides, the use of water-in-bitumen emulsion is recommended as a good additive for adobe blocks for modern day construction in North America (O'Connor, 1973). The raw material was available and known by the ancient Gulf coast cultures since the Preclassic period (as early as 1600 B.C.), as there are natural seeps of bitumen along the coastal plains of Veracruz, and bitumen was traditionally used on ceramic and wooden objects, as well as building floors, as decoration and waterproofing (Belt, 1971;Daneels, 2006;Wendt&Cyphers, 2008).At the site of La Joya itself, there are instances of bitumen used as decorative paint on ceramic figurines and vessels dating to the same period as the architectural samples studied.

Regarding the sugar components found in the samples, these could stem from possible original organic additives. To identify them, we are using as an initial comparative base the organic compounds obtained from water extracts of leaves and stems of the mallow shrub (*Sida rhombifolia*) and bark of the guacima tree (*Guazuma ulmifolia*) which as we indicated above are used as additives for adobe blocks in humid tropical regions of Central America. We're currently applying the same analytical procedure to these extracts, and are also producing experimental adobe samples using local earth mixed with those organic extract to study their utility and polymerizing effects. Thus we will obtain results comparable to those obtained from the pre-Columbian samples.

Conclusions

It's been possible to identify hydrocarbons, a triglyceride, methyl pentoses and an aromatic ester in the organic extracts of the construction material of the pre-Columbian earthen architecture of La Joya, a Classic period site located in a humid tropical environment on the coastal plain of the Gulf of Mexico. At this moment we cannot identify the specific source of the original organic additives, but hydrocarbons might come from locally available bitumen, as its use is attested in even the earliest Gulf Coast cultures, albeit for different purposes. The other components may be from shrubs and trees abundantly available in the region. In both cases, we still have to develop a comparative corpus of local resources in order to identify the specific sources, a study that is currently under way.

The major contribution of our research up to now is to have proven that there is a consistent organic compound mix present in the building material of the monumental earthen architecture, as part of a systematic pre-Columbian building technique. This sustains our initial hypothesis that earthen construction based on an expansive clay building material would not have been viable in the adverse tropical environment without the use of an effective additive. The discovery of a hydrocarbon as a binder, though common knowledge in the Old World and still recommended today for adobe constructions, had up to now not been reported for Ancient Mexico. This opens up a completely new set of perspectives for the research on Pre-Columbian architecture.

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