PROVENANCE OF THE LIMESTONE USED IN TEOTIHUACAN (MEXICO): A METHODOLOGICAL APPROACH*

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This work shows the preliminary results of an international project for the interdisciplinary study of the limestone used in the plasters of the ancient city of Teotihuacan. The limestone provenance was studied using a new approach based on the chemical analysis of the lime lumps that were selected because they represent the composition of the original limestone rock. The results show that the applied methodology was successful and that the limestone used to produce the lime employed to make the floor of the main courtyard at Teopancazco (Teotihuacan), comes from the region near Tula (Hidalgo).

KEYWORDS: LIMESTONE, LIME-PLASTER FLOOR, LUMP, PROVENANCE, OM, SEM-EDS, ICP-MS LASER ABLATION, TEOTIHUACAN, TEOPANCAZCO

INTRODUCTION

The main goal of this study was to characterize the limestone used to prepare the lime incorporated in the plasters of Teotihuacan, Central Mexico. For this reason, at the first stage of the research three outcrops from which the inhabitants of Teotihuacan could have taken the limestone were sampled and analysed. The results were compared with those obtained from the plaster samples of the floors of Teopancazco, a possible neighbourhood centre of Teotihuacan. This is the first stage of a long-term project to assess the use of the limestone outcrops during the construction of the ancient city of Teotihuacan (Figs 1 and 2).

Teotihuacan was one of the most important cities of the Mesoamerican Classic period and was characterized by, among other things, an extensive use of lime. For the first time in Central Mexico, lime was used to cover the external surface of the platforms and structures as well as all the internal and external floors, walls and ceilings of the apartment compounds in this urban settlement (Barba and Córdova 1999).

The amount of lime plaster used in the city is amazing: preliminary calculations (Barba 1995; Barba and Cordova 1999) have allowed an estimation of at least 12 million square metres of architectural surfaces in the whole city, covered with lime plaster. This is even more astonishing if we think that the raw material to produce it, limestone, is not present in the
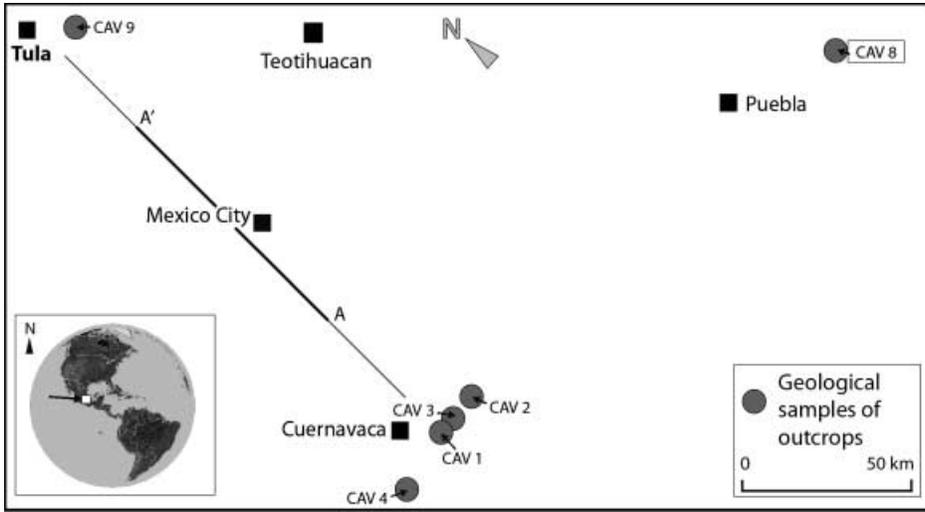
Figure 1   *Location of geological outcrops of limestone in relation to geological section.*
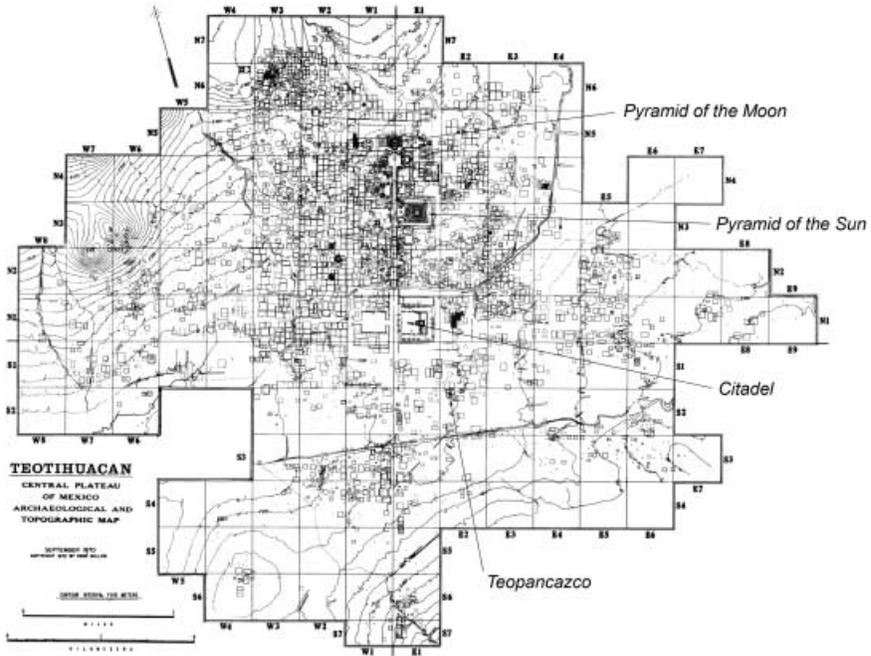
Figure 2   *Map of the Teotihuacan archaeological site (© 2008 René Millon).*

Geological Section of Mexico City Basin
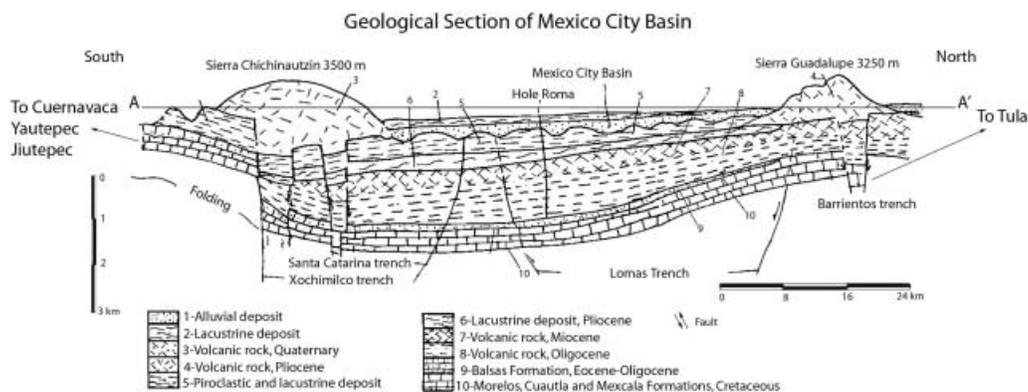
Figure 3 *Geological section of the Mexico City Basin (based on extensive excavation by Linda R. Manzanilla).*

Teotihuacan Valley, nor in the surrounding area, given that the Basin of Mexico has been covered by recent extrusive volcanic materials.

The limestone used to produce the plasters had to be brought to the city from a longer distance, presumably from one of the three closest outcrops in the surrounding regions. Almost all limestone formations are very deeply buried below more recent deposits under the Basin of Mexico and surrounding areas (Fig. 3). This means that few outcrops are readily available now and from ancient times. One is located to the north-west of Teotihuacan, in the area of Tula (in the current State of Hidalgo), another one is found to the east, in the Tepeaca region (in the State of Puebla), and the last one is located to the south, near Cuernavaca (State of Morelos) (Fig. 1). In spite of the distance, varying between 60 and 150 km between these three outcrops and Teotihuacan, this material was used extensively and the whole city was covered with lime plasters, many of which were painted or decorated.

The transformation process of the limestone into lime useful for mortars and plasters involves a series of steps. There is an initial need to quarry the raw material from one of these potential outcrops. The process then continues with the transformation of the limestone (calcium carbonate, $CaCO_3$) into quicklime (calcium oxide, CaO), by exposing the rocks to fire, usually inside kilns, reaching a temperature of at least 800°C for several hours. Once the stones have cooled, the extremely reactive quicklime needs to be slaked, by adding water; the result is the slaked lime (calcium hydroxide, $Ca(OH)_2$), which can be used to produce mortars or plasters by mixing it with various types of aggregate, and exposing it to air. Carbonation takes place, producing calcium carbonate ($CaCO_3$) again. Until now, no archaeological evidence of these production phases has been found, either in the excavations at the site of Teotihuacan, or in the surrounding areas.

Macroscopic and microscopic observations often reveal the presence of white nodules inside ancient mortars and plasters; these are known in the literature as 'lumps' (Bakolas *et al*. 1995). Their composition is predominantly carbonatic ($CaCO_3$). Their origin is to be sought in the properties of the slaked lime (calcium hydroxide), but also in the water/quicklime ratio. An insufficient seasoning of the calcium hydroxide can produce a lime with low plasticity; this, combined with a low water/lime ratio, makes the workability of the mixture of lime and aggregate difficult. In these circumstances, nodules of slaked lime can be formed, which produce calcium carbonate nodules (Bakolas *et al*. 1995) because of the carbonation process. The presence of lumps is very important for this work, because they retain the chemical composition of the raw

materials (geological limestone). In lime manufacture there are two important steps: the firing of the limestone and its transportation. It is possible that the firing of the limestone could have been performed close to the quarrying sites, or in an area where wood was more abundant, between the limestone sources and Teotihuacan. The knowledge derived from the production of lime in various parts of the world has shown that large amounts of fuel—usually wood— were necessary for the firing process (Barba 1995; Schreiner 2001).

Another fundamental step related to the production of lime plaster is its transportation. It is important to remember that in Ancient Mesoamerica there were no animals for transportation and no wheeled means of transport, so that all the limestone, or the quicklime, had to be transported in containers, and carried by man power. An interesting device, called *mecapal* had been developed to carry large weights using basket containers, with straps to the forehead of individuals.

There are few references concerning the use of lime plasters in Central Mexico in Preclassic times. Barba de Piña Chan (1980) mentioned that Tlapacoya had some rudimentary limed floors. Majewski (1976) reported lime in Chalcatzingo, Morelos. In Tlalancaleca, Puebla, thick lime plaster surfaces were found covering the walls of pyramid structures, their *tableros* and *alfardas* (García Cook 1972). Although lime was used earlier in the Maya area and in the Oaxaca Valleys, it was with Teotihuacan that lime began to acquire importance for later Prehispanic urban centres.

The combination of the technological skills needed for the production, transportation and use of the product, the distance from the ancient city to the quarrying sites, and the amount of material involved, make lime a very important material. This is why we think that understanding where the limestone used to come from is an important issue in the archaeology of Teotihuacan. It will notably improve understanding of the political and economical control that the city had to maintain over the mining areas and the people in general, considering that those involved in the production, transport and use of this material were surely numerous. Furthermore, the identification of the quarrying areas may help, in the future, to find the lime production areas which, as suggested above, were probably located between Teotihuacan and the limestone mines, where wood was more abundant.

Detailed studies of ancient artificial stone products have helped to solve important historical, archaeological and technological problems, on the provenance of the raw materials used for the manufacture, and on the conservation of these materials (Fralick *et al.* 2000; Franzini *et al.* 2000; Moropoulou *et al.* 2000; Damiani *et al.* 2003; Crisci *et al.* 2004; Meir *et al.* 2005; Miriello and Crisci 2006, 2007; Pavìa 2006).

Here, in order to study the provenance of the limestone used in Teotihuacan, analyses were carried out on the plasters of the central patio of Teopancazco, an important compound of the city. In particular, a new analytical approach was applied, comparing the results of the elemental analyses of 25 limestone samples from the three quarries to those of five samples from Teopancazco. Among the various analytical techniques used in this study to characterize the lumps, we have employed, for the first time, LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry). This methodology allowed us to execute rapid *in situ* analyses of very small lumps with microscopic spot sizes. The LA-ICP-MS method is particularly advantageous: it combines the capacity to analyse a large number of trace and rare earth elements with rapidity and analytical precision. This makes it very powerful for the character-ization and determination of the provenance of source material, especially when the major chemical composition does not appear to be particularly distinctive (Gratuze 1999; Barca *et al.* 2007).

As stated above, the limestone used to produce the plasters was most likely taken from one of the three above-mentioned outcrops, located in the areas of Tula, Puebla and Cuernavaca (Fig. 1).

Tula

Nine kilometres to the east of Tula, there is an archaeological site of the Classic period called Chingú, occupied during the Tlamimilolpa (AD 200–350) and Xolalpan (AD 350–550) phases of Teotihuacan. The architecture and materials found in the site are very similar to those found in Teotihuacan. Under Teotihuacan influence, Chingú has been considered as a first-level site for control and redistribution during the Classic in the Tula region (Díaz 1979, 156; 1980), while level-two sites such as El Tesoro and Acoculco may have worked as exploitation places for limestone. During the Postclassic period Atotonilco was the production place for lime, continuing into Colonial times (Mastache *et al.* 2002, 53). Melville (1990, 41) studied the same region for the first period after the Spanish Conquest, and stated that this limestone was used intensively to build colonial Mexico City.

Puebla

The second possibility is Puebla, near Tepeaca, a site that, some centuries later, is recorded to have paid tributes in the form of lime to the Aztecs (Barlow 1992). In this area there are sites with a strong Teotihuacan influence (García Cook 1972) and some archaeological traces of the production of lime, such as kilns, that have been found for different periods (Medina 2000). Although this area is more distant from Teotihuacan than Tula (150 km), trade between Teotihuacan and the region is known to have been very well established, since the thin orange pottery ('Anaranjado Delgado'), which was widely used in Teotihuacan, came from this area (Rattray 1998).

Cuernavaca

The third possibility is the mining area located to the south of Cuernavaca (in the State of Morelos). The region is still an important modern centre of lime production. Lime plasters from the Preclassic period (Majewski 1976) are present, and lime production activity areas have been found at Hacienda Calderón, Morelos (excavated by Enrique Nalda). Hirth's settlement study (1978) indicated that eastern Morelos was under Teotihuacan dominance, while western Morelos was probably not. For Yautepec, Smith and Montiel (2001) suggest that there was also a relationship between this region and Teotihuacan. In this particular case, the material could have been transported by boat from the southeastern corner of the Chalco-Xochimilco Lake in the Basin of Mexico, to the north, where Teotihuacan was sited.

THE ARCHAEOLOGICAL SITE

Teopancazco is a neighbourhood compound, excavated by the archaeological project 'Teotihuacan. Elite and Government' directed by Linda R. Manzanilla (1997–2005). This important compound was probably a *barrio* centre (Manzanilla 2003a, 2006; Padró and Manzanilla

2004). It is located to the south-east of the Ciudadela, in the E2–S2 square of Millon's Teotihuacan Mapping Project map (Millon 1973), just outside the modern archaeological site, within the contemporary settlement of San Sebastián Xolalpan (Fig. 2). It was discovered in 1884, when the owner of the land found some mural paintings and reported them to the authorities. Later, the Mexican archaeologist L. Batres excavated the southern part of the Teopancazco compound (Marquina 1922, 156). Some of these areas remained exposed after the excavation, especially those situated to the south of the courtyard. In 1997 new archaeological excavations were undertaken under the direction of Linda R. Manzanilla and discovered different construction phases, mainly from Tlamimilolpa to Metepec (AD 200–650), with some Coyotlatelco and Aztec reoccupations (Hueda *et al.* 2004).

As in many other compounds within Teotihuacan, Teopancazco is in fact formed of several rooms placed around a large central courtyard (Manzanilla 2003b, 2006). This courtyard is the most important ritual space of the compound, in which communal activities were performed around a central altar. The courtyard (approximately 15×15 m) originally had four stairways, and during the excavations two of them were found to have been destroyed (Fig. 4).

Figure 4   *Aerial photograph of the Teopancazco courtyard.*

Table 1 *Coordinates of the sampled limestone outcrops*

Outcrops	Latitude N	Longitude W
Cav 1	18° 52′ 6.4″	99° 10′ 27″
Cav 2	18° 52′ 43.8″	99° 3′ 13.4″
Cav 3	18° 51′ 59″	99° 7′ 12.1″
Cav 4	18° 48′ 17.1″	99° 17′ 53.1″
Cav 8	18° 59′ 44.5″	97° 57′ 6.1″
Cav 9	19° 59′ 36.4″	99° 15′ 41.7″

SAMPLING

For this study, several samples from each of the three possible limestone outcrops were taken to characterize the geological outcrops, trying to embrace the whole variety of current limestone within them. In all the cases the limestone is still exploited for the production of modern lime and cement. In all the quarries the samples were recovered based on macroscopic variability of the rocks. We observed some differences in the limestone outcrops, which may be explained by differences in the time and conditions of deposition of the sedimentary layers. All the sampling points were recorded with a GPS. The latitude and longitude coordinates of the sampled outcrops are shown in Table 1.

In the area of Cuernavaca (Fig. 1), six samples (samples Jiu 1, Jiu 2, Jiu 3, Jiu 4, Jiu 5, Jiu 6; Outcrop Cav 1) were recovered in the modern quarry of Jiutepec (Colonia Campanario). In the same region, three samples were recovered from the outcrops of Yautepec, in the land of the commercial firm of CALIDRA, which still produces lime (Cerro Tenayo el Chico S/N Col. Buenavista, Yautepec, Morelos) (samples Yau 1, Yau 2, Yau 3, Outcrop Cav 2). The Jiu and Yau samples were taken from the Cuautla Formation, a sequence of limestone and clastic limestone that outcrops to the west of the city of Cuautla in Morelos (Fries 1960); these rocks show several colours, such as cream, grey and dark grey.

Two samples were between Yautepec to Xochicalco, a famous Epiclassic (AD 650–850) archaeological site, located in the same region (samples Car 1 and Car 2, Outcrop Cav 3). These samples were collected from the Morelos Formation, a group of limestones and dolomites with grey and dark grey coloration, outcropping in the sedimentary basin of Morelos-Guerrero (Fries 1960). In the same formation, in order to compare the data, one sample was taken from the outcrops in the tunnels under of the site of Xochicalco (Outcrop Cav 4, sample Xochi). The ancient city was, in fact, built on top of a limestone mountain.

In the area of Puebla, seven samples were recovered near Tepeaca, in Santiago Acatlán where some open kilns for lime production have been recorded by the archaeologist Miguel Medina. Samples SA4A, SA4B, SA4C, SA4D, SA4E, SA4F, SA4G were recovered in the outcrops present in the area (Outcrop Cav 8). These outcrops belong to the Cipiapa Formation (López Rubio 1956; Viniegra 1965) which includes limestones and dolomites with grey and cream colorations.

Near Tula, six samples were recovered from the Cantera Xaxnal, of the commercial firm PROCAL, Ejido Progreso, Tula (samples Tula 1, Tula 2, Tula 3, Tula 4, Tula 5, Tula 6, Outcrop Cav 9). All the samples were collected in the higher part of the quarry, except for Tula 4, which was collected instead from the lower part. This is important, because this quarry was opened and mined only in modern times, and therefore was not available to the Teotihuacans.
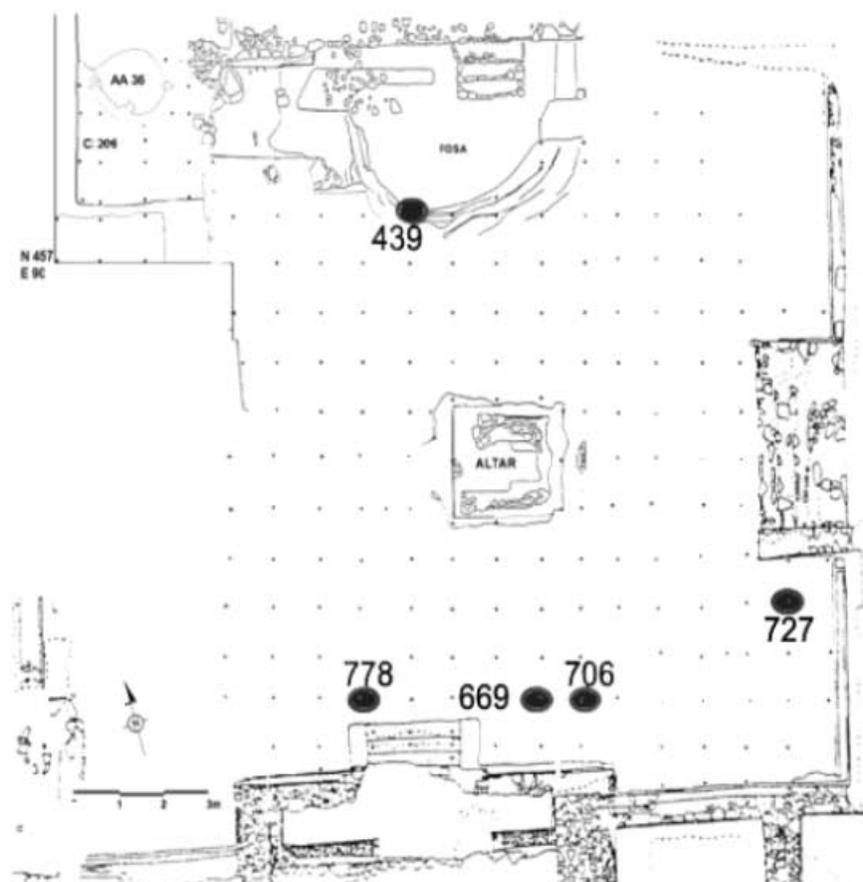
Figure 5 *Sampling points of lime plaster floor in Teopancazco courtyard.*

The Tula outcrop belongs to the Cuautla geological formation, the same formation as the Jiutepec and Yautepec samples, taken in Morelos.

In addition, five samples from the central courtyard of Teopancazco were analysed (Fig. 4). They were taken from different areas of the plastered floor of the courtyard dated to the Xolalpan phase (*c*. AD 350–550, see Cowgill 1996; Manzanilla 2003b), of the Teotihuacan Classic period. Among the *c*. 800 powder samples recovered in the whole Teopancazco compound to study the activity areas through the analysis of organic residues (Pecci 2000, 2005; Pecci *et al*. in press), the five samples (439, 669, 706, 727, 778) were chosen because they were the only ones available in block form in the whole courtyard (Fig. 5).

ANALYTICAL TECHNIQUES

The geological samples were analysed by X-ray fluorescence (XRF), to determine the major chemical composition (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5), using a Philips PW 1480 spectrometer, following the method for correcting matrix effects proposed

by Franzini *et al*. (1972, 1975). Chemical elements were analysed with scandium/molybde-num tubes. The lime plasters sampled from the Teopancazco courtyard were carefully studied in thin sections under polarized light Zeiss microscopy. These samples were also analysed to determine major chemical composition by scanning electron microscopy – energy dispersive spectroscopy (SEM–EDS) microanalysis using FEI Quanta 200 equipped with an EDAX Si (Li detector).

Subsequently, trace element analysis for both geological and archaeological samples was performed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). This is a technique used for analyses of trace and rare earth elements (Sc, V, Co, Ni, Cr, Zn, Rb, Sr, Y, Zr, Nb, La, Ce, Pr, Pb, U) in solid samples. It can determine a great number of elements in the periodic table with a high degree of accuracy and precision. The method complements the electron microprobe analysis, typically measuring trace elements at a lower concentration range (10 ppb to 100 ppm) with very low detection limits, in a short time. The analyses were carried out at the Department of Earth Sciences, Università della Calabria (Italy) using an Elan DRCe (Perkin Elmer/SCIEX), connected to a New Wave UP213 solid-state Nd-YAG laser probe (213 nm). Measurements were made on a section of 80–100 μm thickness for the lumps and on the polished plane surface for the limestones. The samples were ablated by laser beam in a cell and the ablated material was then flushed in a continuous flow of an argon and helium mixture to the ICP, where it was atomized and ionized for quanti-fication in a mass spectrometer (Gunther and Heinrich 1999). In the present study, ablation was performed with spots varying between 50 and 80 μm, with a constant laser repetition rate of 10 Hz and power of ~20 J/cm^2. For each analysis, background levels for all elements were established by acquiring data for about 60 s (acquisition of gas blanks) before starting the 60 s of ablation. Data were transmitted to a PC and processed by the GLITTER program. Since carbonate standards are not easily available, the calibration was performed using glass reference material, 50 ppm NIST 612 (Pearce *et al*. 1997), in conjunction with internal standardization applying CaO concentrations (Fryer *et al*. 1995) from SEM–EDS analyses. On the other hand, the recent study by Wyndham *et al*. (2004) demonstrated that the use of a matrix-matching external standard is not essential, and that accurate and reproducible results can be obtained from different matrices using the NIST suite of glass standards (610, 612, 614); especially by using UV laser (Fallon *et al*. 2002; Lazareth *et al*. 2003; Sinclair 2005). In order to evaluate possible errors, within each analytical sequence, determinations were also made on BCR 2G glass reference material and element concentrations were compared with reference values from the literature (Gao *et al*. 2002). Accuracy, as the relative difference from reference values, was always better than 10%, and most elements plotted in the range ±5%.

This method allowed us to carry out spot analyses exclusively on the lumps of the archaeo-logical plasters to obtain trace element concentrations. Lumps are usually very difficult to analyse with other methodologies, due to the low concentration of impurities: from 10 ppb to 10 ppm. To compare lumps and raw materials and to overcome the difficulty of calibrating the instrument with a glass standard for carbonate analyses, we analysed small fragments of all the geological samples of the limestone, with the same method and the same analytical conditions (diameter of crater ablation, frequency, energy, power of laser beam). In particular, on each lump, a variable number of spot analyses (from 2 to 10) were executed depending on its dimension. To minimize heterogeneity effects for each lump, we calculated the mean value of all the analytical data. On each limestone sample, six spot analyses were carried out, and the mean value was calculated as representative of the chemical composition. The use of lumps is relevant because they provide direct information from the original composition of the limestone.

RESULTS AND DISCUSSION

The petrographic study of geological samples

All geological samples were characterized petrographically and subdivided into five groups in relation to their outcropping site. Car 1 and Car 2 are two very similar biocalcarenites (Fig. 6 (a)). They are constituted by several foraminifera skeletons with an average size of 1 mm and by peloids with dimensions varying from about 0.3 to 0.5 mm. Among the grains locally there is a micritic matrix (packstone by Dunham's 1962 classification).

In the Jiutepec, Morelos group Jiu 4, Jiu 5, Jiu 6 samples are biocalcarenites (Fig. 6 (b)) constituted by peloids and bioclasts of foraminifera and bivalve fragments; in some parts there are also larger grains of cyanobacterial skeletons. Often the clasts show micritized rims or growth of rim with oncoid structure. The three samples can be differentiated only on the basis of the ratio of bioclasts and peloids (grainstone by Dunham's 1962 classification). The Jiu 3 sample is a calcirudite (Fig. 6 (c)). The fossiliferous content is similar to the previous samples
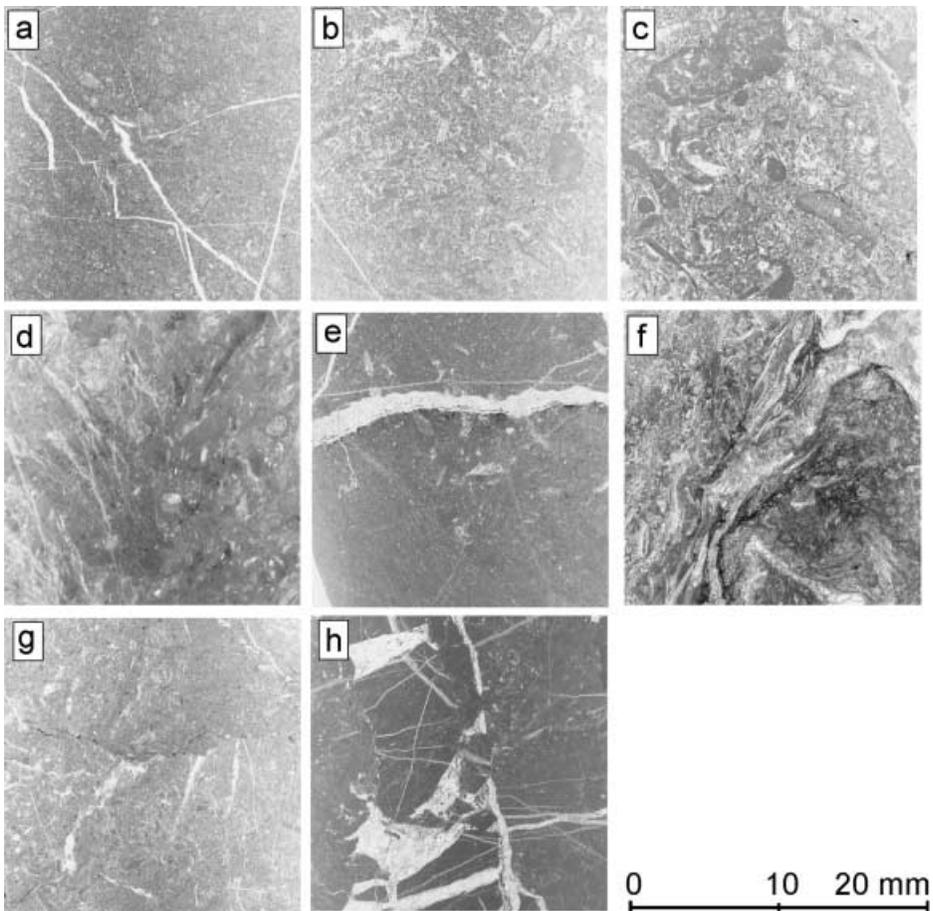

Figure 6 *Geological samples. Images acquired through flatbed scanner under transmitted natural light: (a) Car 1; (b) Jiu 4; (c) Jiu 3; (d) SA4D; (e) Tula 5; (f) Tula 3; (g) Yau 1; (h) Yau 2.*

but it is coarser because the grains range in size from 2 to 3 mm. In the Jiu 2 sample the bio-clasts are also of millimetre size but they are dispersed in a micritic matrix of peloids; in some parts there are bioturbations and the grains are often micritized (wackestone of Dunham's 1962 classification). The Jiu 1 sample is partially recrystallized.

Within the limestone samples of the Santiago Acatlán group, we can group the samples SA4A, SA4B and SA4C which are very similar, with light-grey colour mudstone and small quantities of recrystallized bioclasts. The SA4C sample shows peloidal calcarenite areas. The samples SA4D, SA4E, SA4G (Fig. 6 (d)) can be classified as wackestone (Dunham 1962). In these samples the quantity of bioclasts (constituted essentially by valves of ostracods) increases differently. The SA4F sample is partially recrystallized.

Within the Tula group, samples Tula 1, Tula 2, Tula 5 and Tula 6 are calcilutites (Fig. 6 (e)) (mudstone by Dunham's 1962 classification), characterized by the presence of peloidal structures. The bioclast content is always less than 10%. In Tula 1 there are small fragments of ostracods and samples Tula 5 and Tula 6 contain recrystallized gastropods. Often the samples show calcite veins. Tula 3 and Tula 4 are calcarenites (Fig. 6 (f)), constituted by bivalve fragments of brachiopods and/or ostracods with micritic mud among the grains (packestone by Dunham). The difference between the two samples lies in the smaller dimension of the bioclasts and the presence of carbonatic cement between the grains in Tula 4.

The only sample collected in the Xochicalco area (Xochi) is a peloid calcarenite with local bioturbations. The Yau 1 and Yau 3 samples coming from Yautepec (Morelos) (Fig. 6 (g)) are peloidal calcilutites with bioclasts of bivalve fragments, echinoderms and recrystallized radiolarians. The Yau 2 is a compact mudstone (Fig. 6 (h)) with very small quantities of bioclasts and is frequently cut by calcite veins.

The petrographic study of the archaeological samples

The Teotihuacan floors were usually composed of three layers (Margain 1966, 162): a layer of compacted volcanic tuff (15–20 cm), on top of the fillings; a layer of the so called '*firme*' of the floor, made of an *hormigón* of crushed *tezontle*—volcanic scoriaceous material—mixed with mud (6–10 cm); and a thin and polished layer of lime plaster, which was very strong, resistant and waterproof (Marquina 1922, 118).

The analysis of the five samples from the Teopancazco courtyard verify that the floors were formed of a thin lime layer (1–4 mm thickness) which was a small part of the preparation of the floor (Fig. 7), composed of beaten earth and crushed volcanic scoriaceous material. We must emphasize that this work is focused only on the study of the lime plaster layer of the floor samples. The macroscopic aspect of the lime plasters is sandy (Fig. 8 (a)). Macropores (IUPAC 1972), between 0.3 and 0.8 mm, can be rarely observed in the binder. On the other hand, the binder seems homogeneous and it is difficult to discern the aggregate with the naked eye. The cohesion of the samples is good.

In thin section all the archaeological samples show very similar microscopic petrographic properties. Lime plasters are formed of a binder of lime and of an aggregate of volcanoclastic origin. The latter is formed primarily of rhyolitic shards (Fig. 8 (b)), with rare fragments of basaltic andesites (Fig. 8 (c)), plagioclase and amphibole in traces. Only in sample 439 was the presence of an earthen material fragment (Fig. 8 (d)) observed, which can be probably interpreted as recycled construction material. The distribution of the aggregate and the aggregate/binder ratio (about 3/2) are similar in all samples. The granulometric size of the volcanoclastic fragments varies between 45 and 1678 μm; their average size is about 227 μm. The colour of
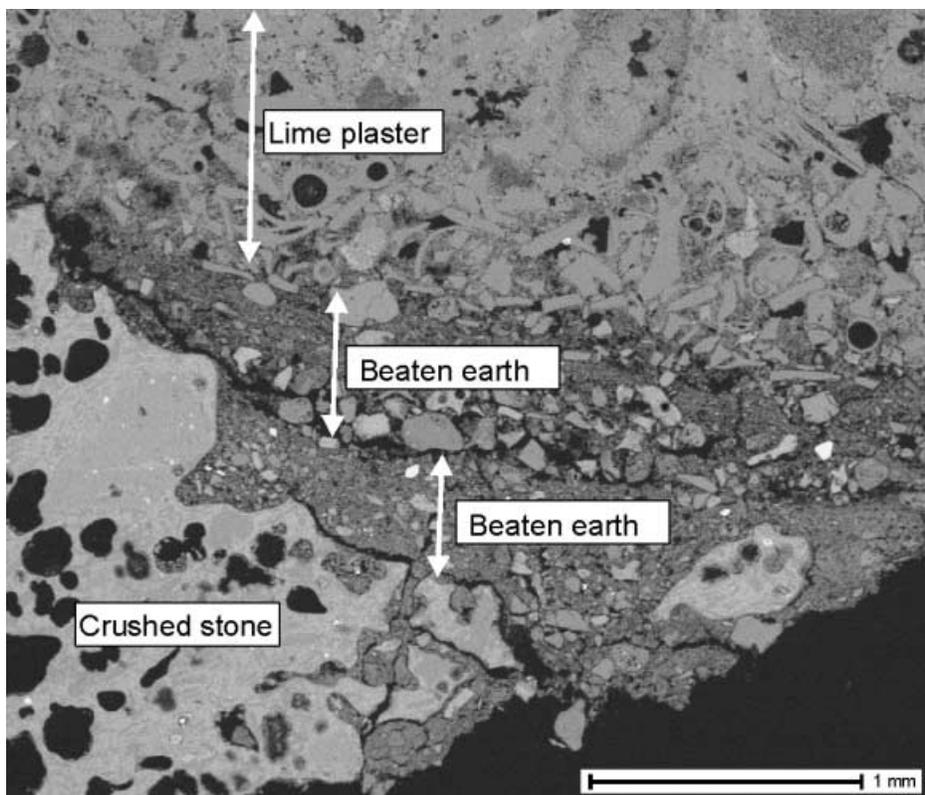
Figure 7   *SEM image of the sample 669.*

the binder is greyish-brown and it has a microcrystalline aspect. Lumps, between 50 μm and 1 mm, can be frequently discerned in the binder of all the samples (Figs 8 (e) and 8 (f)).

Geochemical study

The major element composition of the geological samples was determined by XRF. The major element composition of the lumps was determined by SEM-EDS. Trace element composition was determined by LA-ICP-MS, including La and Ce, among the rare earth elements (REE). Tables 2, 3, 4 and 5 list representative analytical results for each geological sample and the results of the analyses carried out on the lime plasters.

The data obtained on the lime plasters and on the limestone samples were compared using binary diagrams to distinguish between the sources and to attribute the provenance of the raw material. The elements were chosen according to the capacity to discriminate among the various groups. The major element analysis shows important differences between the samples recovered in the Tula area, and the other samples. Among all the elements, Ca and Si are the most discriminating (Fig. 9). The Tula samples show, in fact, low concentrations of CaO (from 72% to 92%) and high concentrations of SiO_2 compared to the other limestone samples, which, on the contrary, show very high values of CaO (97–98%) and very low values of SiO_2. All the
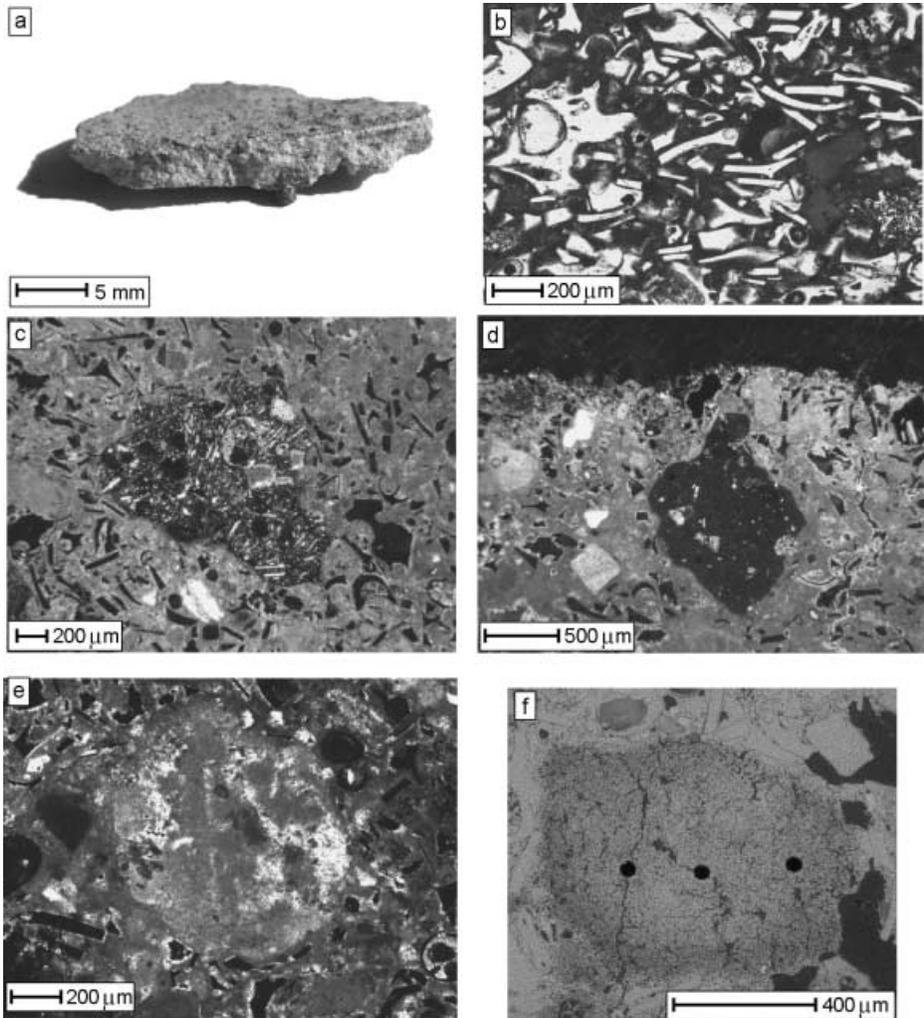
Figure 8 *(a) Macroscopic aspect of a lime plaster floor, sample 706. (b)–(e) Microphotographs of: (b) volcanic shards in the sample 669, plane polarized; (c) a basaltic andesite fragment in sample 706, crossed polars; (d) an earthen material fragment in sample 439, crossed polars; (e) a lump in sample 706, crossed polars. (f) SEM image of a lump in the sample 669; circular holes produced by ICS–MS laser ablation can be seen inside the lump.*

samples from Tula show within-group compositional homogeneity and are different from the other limestones sampled. The two samples Car 1 and Car 2 have a similar composition to the Tula samples, but small variations among major and trace element concentrations and between ratios of elements discriminate these two samples from the Tula ones. The samples from the Puebla area (SA samples) and from the Cuernavaca area (Yau and Jiu samples) can be clearly differentiated from the Tula samples (Fig. 10). All of them are very similar, especially in Figure 10 (a) to Figure 10 (c). The La/Ce ratio (Fig. 10 (d)) distinguishes between them.

The archaeological samples in the CaO versus SiO_2 diagram overlap the Tula samples (Fig. 9). Nevertheless, considering that we are dealing with limestone samples, and that Ca is

Table 2   *Major chemical composition of samples from the central courtyard of Teopancazco*

Sample	Lump no.	SiO₂	TiO₂	Al₂O₃	Fe₂O₃	MnO	MgO	CaO	Na₂O	K₂O	P₂O₅
439	2	7.42	n.d.	1.16	0.52	n.d.	5.42	83.78	0.50	1.20	n.d.
	3	8.67	n.d.	1.11	0.62	n.d.	3.09	85.19	0.21	1.10	n.d.
	10	8.14	n.d.	1.21	0.61	n.d.	3.73	84.40	0.55	1.35	n.d.
669	1	3.84	n.d.	0.80	0.50	n.d.	3.11	90.60	0.42	0.72	n.d.
	2	6.53	n.d.	1.34	0.36	n.d.	2.44	88.04	0.38	0.91	n.d.
	3	9.11	n.d.	1.27	0.54	n.d.	2.13	85.58	0.34	1.02	n.d.
	4	11.54	n.d.	1.21	0.19	n.d.	1.51	83.95	0.4	1.19	n.d.
706	1	7.76	n.d.	0.85	0.11	0.01	5.06	84.5	0.15	0.73	0.81
	2	6.73	0.02	0.72	0.19	n.d.	4.60	84.10	0.10	0.59	0.92
	3	8.09	n.d.	0.49	0.26	n.d.	7.75	82.10	0.14	0.44	0.75
727	2	3.60	n.d.	0.51	n.d.	n.d.	2.34	92.20	0.14	0.41	0.79
	3	4.39	n.d.	0.32	n.d.	n.d.	3.71	89.90	0.08	0.36	1.24
	4	4.05	n.d.	0.52	0.19	n.d.	3.20	90.90	0.11	0.31	0.64
778	7	4.57	n.d.	0.83	0.51	n.d.	5.19	87.65	0.4	0.85	n.d.

n.d., Not detected.
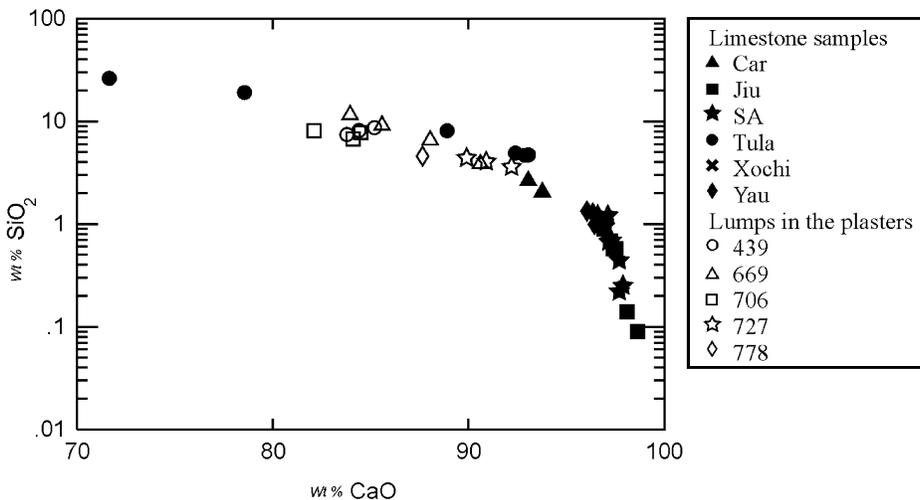
Figure 9   *CaO versus SiO₂ diagram of limestone geological samples and lumps of plasters. All the lumps analysed, marked with open symbols, are plotted in the diagram in the same area as the Tula limestone (anhydrous analyses).*

the principal component of limestone, the major elements analysis is not sufficient to assign the provenance. Therefore trace element analysis was carried out. Ni, Co, Sr, Zr, Y, Nb, Pb, U trace elements of the limestone samples discriminated the Tula samples from the others. Among the REEs, only La and Ce show relevant concentrations, while the other REEs show very low concentrations, generally close to the detection limits, and for this reason it was impossible to analyse them. Among all the trace elements, the ratios Y/Nb and La/Ce were selected as a discrimination index, in order to separate the limestone samples. They show that

Table 3   *Trace element analysis of samples from the central courtyard of Teopancazco*

| Sample	Lump no.	No. spot analyses	Sc	V	Cr	Co	Ni	Zn	Rb	Sr	Y	Zr	Nb	La	Ce	Pr	Pb	U
439	2	4	0.69	10.45	4.83	1.63	6.22	49	3.22	881	1.91	10.45	0.47	1.27	2.48	0.24	2.09	1.51
	3	2	0.87	12.7	7.4	1.37	5.88	42	1.47	903	1.11	8.46	0.44	0.96	1.89	0.16	2.13	1.41
	10	2	0.59	16.2	5.1	2.34	9.6	43	8.64	679	2.44	12.92	1.11	3.43	6.19	0.413	3.91	1.65
669	1	10	0.27	2.0	3.7	0.53	2.19	5.12	0.08	411	0.12	4.37	0.07	0.05	0.12	0.02	0.44	1.79
	2	3	0.24	3.27	6.30	0.88	4.10	8.61	0.27	563	0.36	5.44	0.15	0.15	0.27	0.03	1.01	2.04
	3	2	0.20	3.3	3.8	0.85	3.40	9	0.12	524	0.28	4.12	0.14	0.11	0.24	0.01	1.12	1.86
	4	3	0.24	4.2	4.1	0.76	2.61	10	0.55	474	0.41	4.20	0.12	0.34	0.55	0.04	1.14	1.82
706	1	3	0.38	7.9	8.4	0.75	7.01	223	2.78	680	0.37	1.86	0.05	0.24	0.49	0.07	1.82	3.57
	2	4	0.76	20.3	5.5	1.86	6.12	51	1.62	843	0.55	4.79	0.39	0.57	1.31	0.11	5.44	2.79
	3	3	0.47	16.7	7.5	1.16	4.95	68	1.57	558	0.72	3.30	0.16	0.60	1.09	0.14	1.45	4.08
727	2	4	0.32	4.1	6.1	0.36	3.50	19	0.72	667	0.49	2.06	0.06	0.22	0.28	0.06	1.18	2.06
	3	3	0.24	6.1	3.9	2.47	4.51	23	0.68	704	0.49	2.87	0.10	0.19	0.40	0.03	1.45	1.99
	4	2	0.18	10.0	8.9	0.72	5.94	28	1.81	1031	0.49	3.50	0.14	0.37	0.92	0.11	1.67	2.38
778	7	2	0.57	8.3	5.3	0.55	5.20	26	1.39	947	0.62	4.97	0.22	0.50	0.93	0.05	0.72	1.80
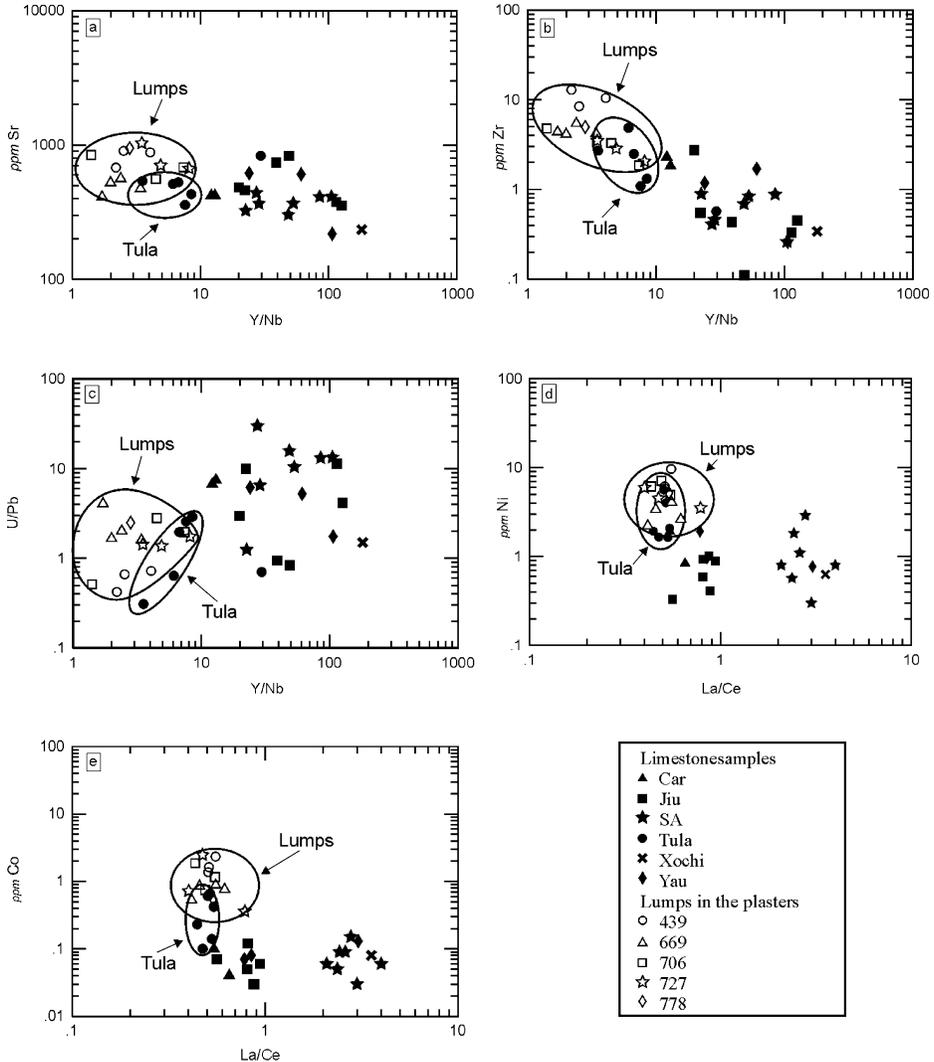
Figure 10   *Diagrams plot the analytical results for studied archaeological and geological samples.*
Ellipses enclose the compositional group of Tula limestone and lumps, pointing out the superimposition of the
two areas. (a) Y/Nb versus Sr; (b) Y/Nb versus Zr; (c) Y/Nb versus U/Pb; (d) La/Ce versus Ni; (e) La/Ce versus Co.

Tula samples are different from the others. The two samples collected on the road from
Yautepec to Xochicalco (Car 1 and Car 2) show geochemical compositions similar to the Tula
samples. Nevertheless the U/Pb ratio (Fig. 10 (c)) separates them.

Although the geological studies state that Tula, Yautepec and Jiutepec formations are the
same, these outcrops have been clearly differentiated according to trace element composition.
Some differences in limestone characteristics can be explained as a consequence of marine
sedimentation conditions. Cuautla formation outcrops in Tula region have predominant reef
facies, while in Yautepec and Jiutepec most of the facies come from coastal environments

Table 4 *Major chemical composition of geological samples*

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
Car 1	2.63	0.06	0.45	0.35	0.03	3.17	93.05	0.03	0.24	n.d.
Car 2	2.04	0.06	0.42	0.33	0.03	3.06	93.77	0.02	0.27	n.d.
Jiu 1	0.09	0.02	0.04	0.04	0.04	1.13	98.64	n.d.	n.d.	n.d.
Jiu 2	0.57	0.04	0.19	0.07	0.02	1.7	97.41	n.d.	0.01	n.d.
Jiu 3	0.14	0.03	0.07	0.06	0.01	1.55	98.1	0.04	n.d.	n.d.
Jiu 4	0.89	0.05	0.14	0.15	0.01	1.82	96.93	n.d.	0.02	n.d.
Jiu 5	0.57	0.03	0.11	0.05	0.02	1.69	97.51	0.01	0.01	0.01
Jiu 6	0.68	0.03	0.13	0.04	0.01	1.84	97.26	0.01	0.01	n.d.
SA4A	0.69	0.04	0.12	0.09	0.02	1.69	97.3	0.02	0.01	0.03
SA4B	0.67	0.04	0.08	0.06	0.02	1.94	97.17	n.d.	n.d.	0.02
SA4C	0.22	0.05	0.06	0.04	0.02	1.86	97.7	0.01	n.d.	0.05
SA4D	0.25	0.02	0.07	0.04	0.03	1.69	97.89	n.d.	n.d.	0.03
SA4E	0.44	0.02	0.06	0.03	0.02	1.69	97.7	0.01	n.d.	0.03
SA4F	1.22	0.04	0.08	0.04	0.02	1.96	96.6	0.01	n.d.	0.03
SA4G	1.21	0.03	0.08	0.07	0.02	1.42	97.12	0.01	n.d.	0.03
Tula 1	26.3	0.05	0.47	0.28	0.04	1.1	71.65	n.d.	0.11	n.d.
Tula 2	19.1	0.08	0.69	0.18	0.02	1.17	78.56	0.01	0.19	n.d.
Tula 3	4.9	0.05	0.45	0.35	0.03	1.68	92.39	0.03	0.1	n.d.
Tula 4	4.71	0.04	0.32	0.17	0.03	1.59	93.06	0.03	0.05	n.d.
Tula 5	4.67	0.05	0.41	0.29	0.03	1.55	92.87	0.02	0.11	n.d.
Tula 6	8.08	0.07	0.63	0.45	0.02	1.67	88.9	n.d.	0.17	n.d.
Xochi	1.13	0.02	0.07	0.05	0.03	1.63	97.07	n.d.	n.d.	0.01
Yau 1	0.99	0.04	0.31	0.19	0.02	1.94	96.43	0.01	0.06	0.01
Yau 2	1.33	0.06	0.31	0.16	0.02	1.98	96.05	0.02	0.07	n.d.
Yau 3	1.27	0.05	0.28	0.1	0.02	1.86	96.35	0.03	0.06	n.d.

n.d., Not detected.

(Comisión Nacional del Agua 2002). In addition, the Cuautla formation is associated with a gradual change from carbonate to siliciclastic sedimentation (González-Partida *et al*. 2004).

The results of trace element analysis show that the lumps of the archaeological samples partially overlap the Tula ones in all the diagrams (Fig. 10 (a) to Fig. 10 (e)). Within the Tula samples group, only Tula 4 shows small compositional differences from the others. This sample was recovered in a very deep part of the quarry that could only be exposed using modern machines. This can explain the geochemical difference, and confirms that in archaeological times this part of the quarry was not in use.

CONCLUSIONS

The geochemical results, for both the major elements and the trace elements, show that Tula is the only possible source area of the limestone used in the Teopancazco courtyard plasters, built during Xolalpan phase (AD 350–550). The major elements analysis and the trace elements analysis strongly discriminate Tula samples from the other limestone samples. As stated above, even the Carretera samples (Car 1 and Car 2), which were the most similar ones, were discriminated by the U/Pb ratio. In particular, not all the typologies of the Tula limestone were used in Teopancazco. The Tula 4 sample doesn't fit, probably because it was taken from the

Table 5   *Trace element composition of geological samples*

Sample	Sc	V	Cr	Co	Ni	Zn	Rb	Sr	Y	Zr	Nb	La	Ce	Pr	Pb	U
Car1	0.36	5.09	3.26	0.10	1.93	4.07	0.52	420	0.78	1.83	0.06	0.68	1.25	0.18	0.21	1.57
Car2	0.37	5.02	1.83	0.04	0.84	6.17	0.87	421	0.73	2.29	0.06	0.79	1.21	0.18	0.31	2.08
Jiu1	0.24	1.72	3.78	0.07	0.33	1.52	0.06	830	0.49	0.11	0.01	0.09	0.16	0.01	0.06	0.05
Jiu2	0.24	7.28	2.62	0.06	0.89	2.47	0.52	355	1.26	0.45	0.01	0.80	0.85	0.13	0.32	1.33
Jiu3	0.44	2.28	3.37	0.12	0.93	1.82	0.49	740	0.78	0.43	0.02	0.31	0.38	0.06	0.56	0.53
Jiu4	0.84	6.54	11.60	0.05	0.59	1.82	0.16	461	0.89	0.55	0.04	0.55	0.68	0.07	0.25	2.48
Jiu5	0.22	7.08	4.61	0.03	0.41	2.14	0.08	376	1.14	0.33	0.01	0.61	0.69	0.08	0.10	1.14
Jiu6	0.23	7.63	6.69	0.03	1.01	7.27	0.55	484	1.39	2.74	0.07	0.82	0.94	0.13	0.48	1.42
SA4A	0.63	4.79	4.04	0.15	2.90	28.53	0.66	325	1.58	0.89	0.07	1.56	0.56	0.20	0.96	1.20
SA4B	0.70	5.56	5.72	0.09	1.10	12.58	0.20	367	1.43	0.46	0.05	1.46	0.56	0.19	0.35	2.28
SA4C	0.43	4.34	3.04	0.06	0.60	6.23	0.07	440	0.82	0.41	0.03	0.48	0.12	0.04	0.05	1.50
SA4D	0.31	4.66	2.56	0.09	1.82	10.56	0.07	411	0.85	0.88	0.01	0.51	0.21	0.05	0.23	3.03
SA4E	0.29	6.06	3.20	0.03	0.30	7.51	0.03	413	1.05	0.26	0.01	0.81	0.27	0.10	0.15	2.00
SA4F	0.35	5.40	5.69	0.05	0.57	6.42	0.43	368	1.06	0.84	0.02	0.83	0.35	0.10	0.11	1.15
SA4G	0.27	3.62	2.40	0.06	0.80	7.01	0.11	303	0.97	0.69	0.02	0.73	0.35	0.10	0.08	1.26
Tula1	0.71	8.71	3.76	0.42	2.09	7.37	3.30	359	0.76	1.09	0.10	0.70	1.29	0.16	0.28	0.72
Tula2	0.34	8.90	5.49	0.23	1.93	4.96	2.99	528	0.74	2.49	0.11	0.98	2.20	0.27	0.29	0.57
Tula3	0.57	17.82	6.78	0.61	5.63	15.96	4.92	512	1.16	4.86	0.19	1.37	2.71	0.31	1.38	0.88
Tula4	0.34	7.75	10.89	0.10	1.66	9.08	0.68	833	0.59	0.57	0.02	0.68	1.43	0.17	1.01	0.71
Tula5	0.64	22.40	5.94	0.66	4.02	4.28	4.40	541	0.92	2.71	0.26	1.01	1.95	0.23	2.52	0.78
Tula6	0.59	12.13	3.56	0.14	1.64	5.23	1.53	431	0.85	1.32	0.10	0.78	1.47	0.18	0.54	1.57
Xochi	0.35	0.98	3.87	0.08	0.63	1.57	0.04	234	1.81	0.34	0.01	0.64	0.18	0.05	0.14	0.21
Yau1	0.51	21.59	5.56	0.07	1.92	5.12	0.69	606	2.44	1.70	0.04	1.40	1.79	0.28	0.50	2.62
Yau2	0.33	10.66	5.64	0.08	0.96	4.13	1.46	616	1.68	1.18	0.07	1.25	1.47	0.24	0.23	1.42
Yau3	0.13	0.85	1.73	0.13	0.77	1.57	0.01	218	2.13	0.26	0.02	0.76	0.25	0.07	0.12	0.21

deepest part of the quarry, which was not exposed in archaeological times. Figure 6 shows macrophotos of the samples of the limestone taken from Tula.

As stated in the introduction, the fact that Tula is recognized as the only possible source area of the limestone used to produce the Teopancazco courtyard plasters, is an important issue for the technological history and archaeology of the city of Teotihuacan. In fact, for the first time, it is possible to prove, with a scientific basis, the hypothesis made in the past by the archaeologists (Crespo and Mastache 1981) that some of the lime used in Teotihuacan came from the region of Tula. Teotihuacan should therefore have had an important role in the control of this area. This find also supports the hypothesis that the Chingú site could have had a key role in the exploitation of the quarries. Furthermore, we now know that lime (in the form of pure limestone and/or already transformed into lime) had to be transported on foot for about 60 km, from the Tula area to Teotihuacan. This implies the control and use of a great amount of human energy and a complex social organization that was possible only in such an important state as Teotihuacan.

The data presented above show that LA-ICP-MS analysis, applied to the lumps, is a very good method for identifying the provenance of the limestone used in plastered materials. Once the methodology is established, the next steps of this project will be to analyse different lime plasters from Teotihuacan, in order to verify whether the limestone exploited always came from the same region, or if the sources changed in different parts of the city or through time.

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