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Aztec and Colonial Archeological Potteries: A Study on Fired Techniques[1]

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Mexican pottery, used during the Prehispanic period, showed different improvements in its manufacturing for some centuries before the arrival of Spaniards in Mexico. After this, new fired techniques were used to make ceramics during the Colonial period. Their composition, manufacturing, and fired process have not been fully understood. Photoacoustic spectroscopy (PAS), X-ray energy dispersive spectroscopy (XEDS), X-ray, transmission electron microscopy (TEM), and Mossbaüer spectroscopy studies of authentic archeological potteries of Aztec III (1450–1525), Aztec IV (1525–1550), and colonial Poblana (1780–1800) provide an understanding of different advances in their fired manufacturing. For the case of colonial Poblana pottery, some colors associated with metallic oxides, which were introduced in the Mexican colonial period, were found. The composition of the analyzed samples was mainly SiO_2, with Al, Ca, Na, Fe, S, Mg, Pb, K, Ti, and Cu impurities. Through the use of the techniques mentioned above, it was possible to determine the different processes of fired techniques associated with each type of pottery. These results were compared with archeological registers about the composition and technology in the pottery manufacturing processes.

KEY WORDS: archeological potteries; ceramic; Mossbaüer spectroscopy; photoacoustic spectroscopy; TEM; XEDS.

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1. INTRODUCTION

When archeological pieces were discovered in the excavations from the "Templo Mayor" (main Temple), the archeological site of downtown Mexico City, several Prehispanic and colonial potteries, often used as ceremonial and domestic artifacts, were found in different stratigraphic natural layers (see Fig. 1) [1–4]. The origin, composition, manufacturing, and fired process of these pieces have not been fully understood. In the present work we report a study of this ancient Mexican pottery from the Aztec culture (which was developed in Central Mexico from 1325 until 1521 AD) and Maiolica or Poblana ceramics (manufactured in Mexico during the 17th century). The first and second potteries analyzed, from "Templo Mayor" ruins, were Aztec potteries that, by their style and decorations, were attributed to the Aztec III (1450–1525) and Aztec IV (1525–1550) [1] periods, respectively. These potteries could have been fired with different processes that were not well known until recently. The third pottery analyzed was Poblana or Maiolica (1780–1800), also from "Templo Mayor" ruins but located in another stratigraphic natural layer, which shows the advances and innovations introduced by the Spaniards in new Prehispanic Colonial Mexico. After the conquest of Mexico, the native pottery satisfied the daily necessities of the new inhabitants. Later on, the importance of Iberian pottery increased, and simultaneously a new Hispanic ceramic was developed which showed a tangible fusion between these two traditional ceramics as a reflection of the new culture [2].

Fig. 1. Photograph of pottery obtained from "Templo Mayor" archeological site of Mexico City.

The potteries made by most of the ancient cultures were not characterized by advanced fired knowledge, and the combustion was imperfect, while the earthenware vessels became black due to the coal soot. For the case of the ancient Prehispanic potteries, these were fired at a room environment, i.e., under oxidizing atmospheric conditions without control of air, imperfect combustion, and oxidation; then, as a consequence of this, their color becomes dark [1]. When this kind of pottery is exposed to oxidation with high control of air circulation, the ceramics change to yellow, red, and brown colors. These colors are associated with temperatures between 400 and 800°C [1,2]. The colonial Poblana was fired in a closed furnace, with higher temperatures, between 400 and 1200°C and better control of air [1].

With regard to the decoration and finishing of these ceramics, the ancient Aztecs used a varnish partially vitrificated for the finishing with gumming of iron, Al, and Si which have similar color to Pb used in the Colonial ceramics [1]. In the Colonial ceramics, it was used for varnishing or glazing, which is a vitrificated, transparent, and colorless coating based in a mixture of Pb, Co, sand, and NaCl (called plumbed) that is applied to the ceramic pieces in order to give brilliance and impermeability after a second firing; in this case, if a metallic oxide is added, this pottery will be colored. This kind of enamel ceramic was named Maiolica Spanish or Puebla Talabera [2,4]. The production of Maiolica ceramics in New Spain was very important at that time, and was very appreciated in Europe [4]. The origin, composition, manufacturing, and fired conditions of these Aztec and Colonial potteries have not been fully understood.

2. EXPERIMENTAL

One problem in archeological research is to determine, in uncertain cases, about the origin and manufacturing of the potteries. The archeologists use different scientific disciplines such as botany, physics, biology, etc. to resolve these kinds of problems.

In the physics field two new spectroscopies, namely photoacoustic and Mossbaüer, have had significant development in recent years. Photoacoustic spectroscopy (PAS) is ideally suited for measuring optical absorption spectra of opaque materials such as powder and porous materials (such as ceramic materials). This technique depends on the thermal and optical properties of the sample. PAS involves the measurement of heat produced as an excited species relaxes through a nonradiative path [5,6]. The other technique, Mossbaüer spectroscopy, whose application to archeology is limited, becomes important due to the fact that the clays, used to manufacture the potteries, have around 10% of iron in their composition.

The study of iron with this technique is very useful and gives broad information about the chemical and crystal structure in the material [8].

In order to analyze the composition and structure of the ceramic used by Aztecs and Hispanics, different potteries have been analyzed by modern techniques such as photoacoustic spectroscopy (PAS) [5], X-ray energy dispersive spectroscopy (XEDS) [7], X-ray [6], transmission electron microscopy (TEM) [7], and Mossbaüer spectroscopy [8]. The samples were placed in sealed cells for their analysis using these techniques. For XEDS analysis an XEDS 2100/2110 EDS System Noran Instruments was used, for X-ray analysis we used a Voyager II diffractometer, and the Mossbaüer spectra were recorded at room temperature with a ^{57}Co in Rh source, using a constant acceleration spectrometer (from Wissel). Transmission electron microscopy was performed on the samples with a JEOL 2010 microscope with a point resolution of approximately 0.17 nm. From TEM images the grain size was directly measured.

Three samples were studied; two of them correspond to Aztec III and IV periods, and the third to the Poblana Colonial period [1–4]. Samples were obtained directly from the "Templo Mayor" archeological site of downtown Mexico City. They were cleaned with brush and water, then were ground, and finally sieved through a 250 μm mesh screen. Only a few grams of each sample were used in the present study.

3. RESULTS

The photoacoustic (PA) technique was employed to measure the optical absorption spectra of the samples. Fig. 2 shows the PA spectra for different samples; the solid, dashed, and dotted lines correspond to spectra for Aztec III, Aztec IV, and Poblana potteries, respectively. We observe mainly two absorption centers that contribute to the photoacoustic signal. The first one is located around 470 nm and the second at 770 nm. Furthermore, we can see in Fig. 2 that the photoacoustic spectrum of Aztec IV shows higher optical absorption than for Aztec III and Poblana ceramics. For all the samples the first absorption center, around 460 nm, could correspond to a ion of Fe 3^{+} [10], the other peak around 750 nm corresponds to some Fe oxides [10]. Ortega et al. [9] found that Aztec III ceramics contain less Fe and more oxygen than Aztec IV. They associated Na, Mg, Ca, and K with feldspars such as albite and anorthite and Mg and Ca with carbonates such as dolomite and calcite. For the peak at 770 nm, corresponding to Aztec IV pottery, it was found that the ceramic contains basically γ-F_2O_3 as we will see later in our Mossbaüer analysis. For the case of EDS analysis (for Aztec IV), we will observe further that the quantity of Fe is larger than for other elements, around 20% when compared

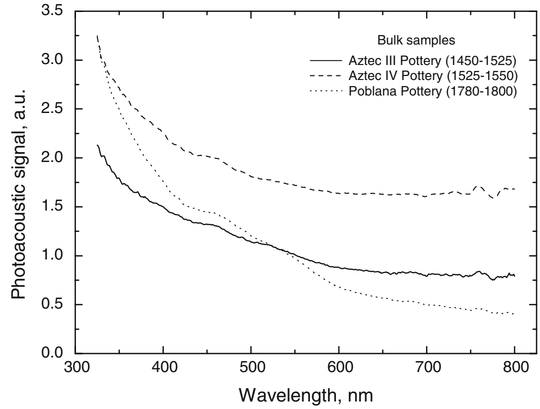

Fig. 2. Photoacoustic absorption spectra of bulk Aztec III (solid lines), IV (dashed lines), and Poblana (dotted lines) potteries.

with the other elements, such as S, K, and C, which correspond to minor fractions of feldspars and carbonates.

On the other hand, the elemental chemical composition of the bulk was determined by means of XEDS analysis, with a spot size of several micrometers, which revealed the elements previously found in the literature for these potteries [1–4]. For the Aztec III and IV potteries, the composition in the bulk was mainly SiO_2, Al, Ca, other secondary elements such as Fe, Ti, Ni, Mg, K, and Zn, and also other minor elements such as S and Pb in Poblana ceramics (see Fig. 3) The peak for oxygen was relatively high in the Aztec III sample (~65.5%) when compared with Aztec IV (~54.9%) and Poblana (~39.4%). The percentage of oxygen could explain the advances and innovations about the fired process in pottery manufacturing. These results show important differences in the composition between the Aztec and Poblana samples. For example, when comparing the EDS spectra of these potteries, several elements such as S, Pb, and other metallic oxides that were used in the decoration during the Colonial period [1,3], only appeared in the Poblana sample as we expected.

The X-ray analysis for the Aztec III sample showed that its composition consists of albite, calcium, di (Na, Ca)(Si, Al)40, disordered $Na(Si_3Al)O_8$, and anorthide sodian (Ca, Na)(Si, Al)40. For the case of Aztec IV pottery (see Fig. 4), a mixture of maghemite Fe_2O_3, barium hydroxide $Ba(OH)_2*3H_2O$, scorzalite (Fe, Mg)($Al_2(PO_4)$), and frondelite $MnFe_4(PO_4)3(OH)$ was found, which are classified in the plagioclase mineral

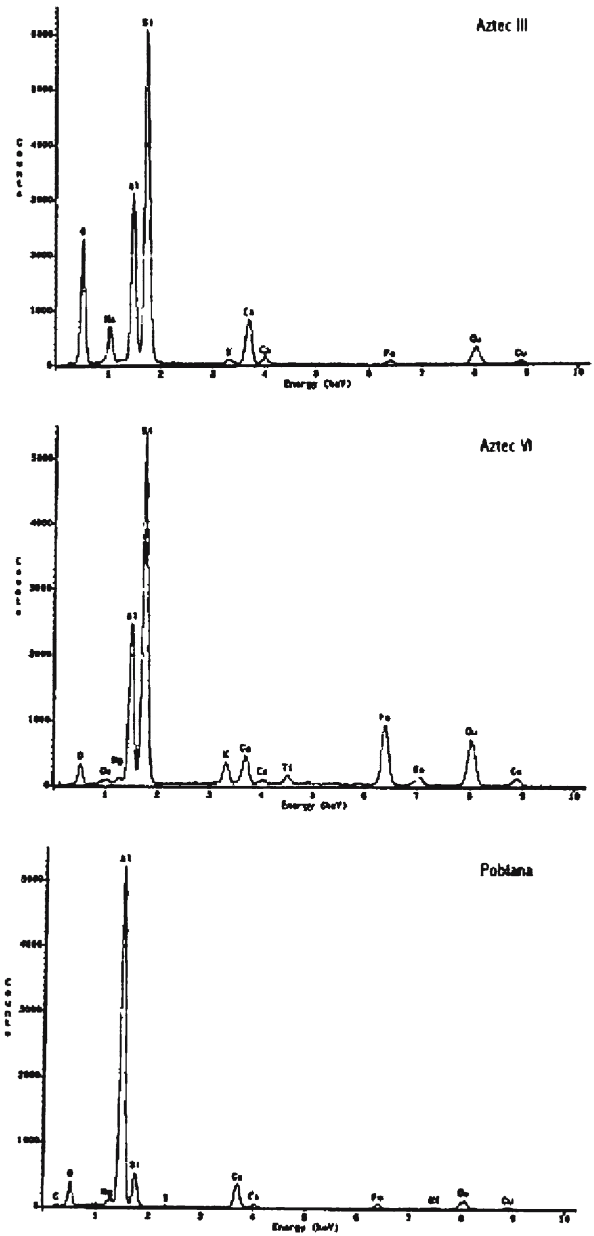

Fig. 3. EDS spectra of bulk Aztec III, Aztec IV, and Poblana potteries.

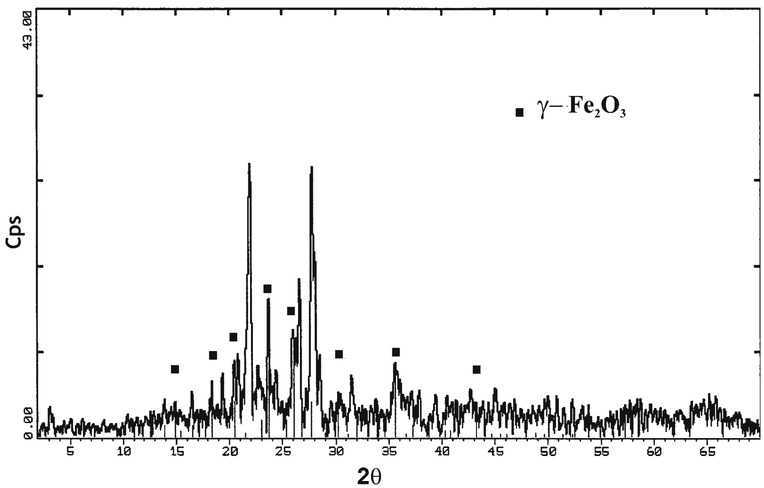

Fig. 4. X-ray powder pattern of bulk Aztec IV sample.

group [9]. These results revealed the same elements that were previously detected from EDS spectra. In order to make a complementary analysis of the metallic oxides mixed with iron found in these samples and determine their structure, we also used Mossbaüer analysis.

From X-ray and Mossbaüer studies, we determined the composition of our ceramics, which revealed that they contain silicates and γ-Fe_2O_3 (maghemite). Mossbaüer experiments were performed on surface and bulk samples. The bulk Mossbaüer spectra of Aztec III, Aztec IV, and Poblana potteries are shown in Fig. 5. These spectra reveal the presence of silicates and maghemite compounds which show one doublet, corresponding to Aztec III and IV potteries. The Aztec III sample shows more oxidation that the Aztec IV pottery. The sites AI, AII, BI, BII, CI, CII of iron in the bulk Mossbaüer spectra of our samples correspond to magnetite (I and II), and the possible presence of maghemite (I), which is confirmed by the X-ray diffractograms. The sites A, B, and C correspond to Aztec III, Aztec IV, and Poblana, respectively. We also observed that the spectra of Aztec III and Poblana potteries are similar.

The surface Mossbaüer spectra for Aztec III, Aztec IV, and Poblana samples are shown in Fig. 6. In this figure the labels A1, A2, B1, B2, C1, C2 of iron in the surface Mossbaüer spectra correspond to magnetite (1 and 2), and the possible presence of maghemite (1). The sites A, B, and C correspond to Aztec III, Aztec IV, and Poblana, respectively. In the surface spectra of Aztec III and Poblana we observed some differences; for example, for the case of Poblana pottery, there is a higher concentration of

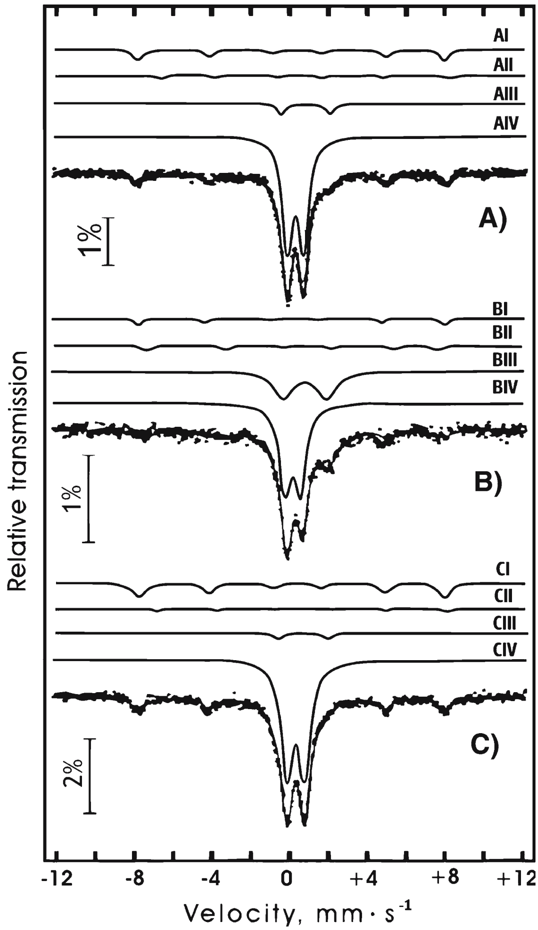

Fig. 5. Bulk Mossbaüer spectra of (A) Aztec III, (B) Aztec IV, and (C) Poblana samples.

maghemite (Fig. 6A, C; see peaks around the doublet). For the spectrum of Aztec IV ceramic (Fig. 6B), there is a higher concentration of natural iron, α-Fe (site B1); this could be due to a reduction of oxygen during its manufacturing. In the case of Aztec III and Poblana superficial samples, the behavior was very similar to the results found in the bulk spectra, which indicates that any pigment, with high iron content, was used in the surface.

In all spectra, bulk and surface, are found a pair of doublets which correspond to silicates with iron and other minerals (Na, Ca, and Al).

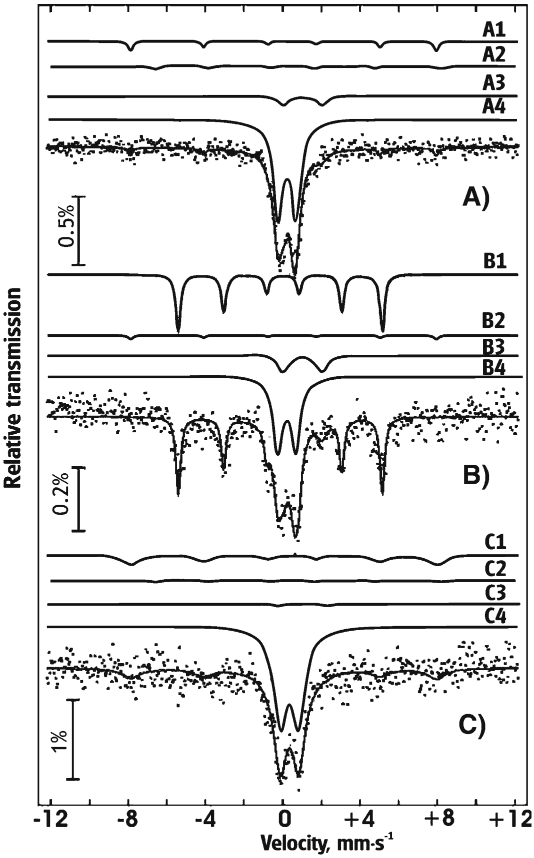

Fig. 6. Surface Mossbaüer spectra of (A)Aztec III, (B) Aztec IV, and (C) Poblana samples. In the spectrum of Aztec IV pottery a higher concentration of natural iron was identified (α-Fe); this could be due to a reduction of oxygen (high control of air circulation during its manufacturing process).

These doublets are labeled as AIII, AIV; BIII, BIV; CIII, CIV; A3, A4; B3, B4; and C3, C4 in Figs. 5 and 6. This result agrees with our EDS analysis as we have previously shown (Fig. 3). Our study of Aztec III, IV, and Poblana samples by TEM revealed a direct comparison between their bright field images and diffraction patterns as we show in Fig. 7. The Aztec III sample contained small crystallites less than 0.1 μm in size which result in ring diagrams, also indicating a random orientation distribution (Fig. 7A, B) [7]. For the Aztec IV sample, a fine grain of micrometer crystallite sizes has been observed, giving rise to ring diffraction patterns

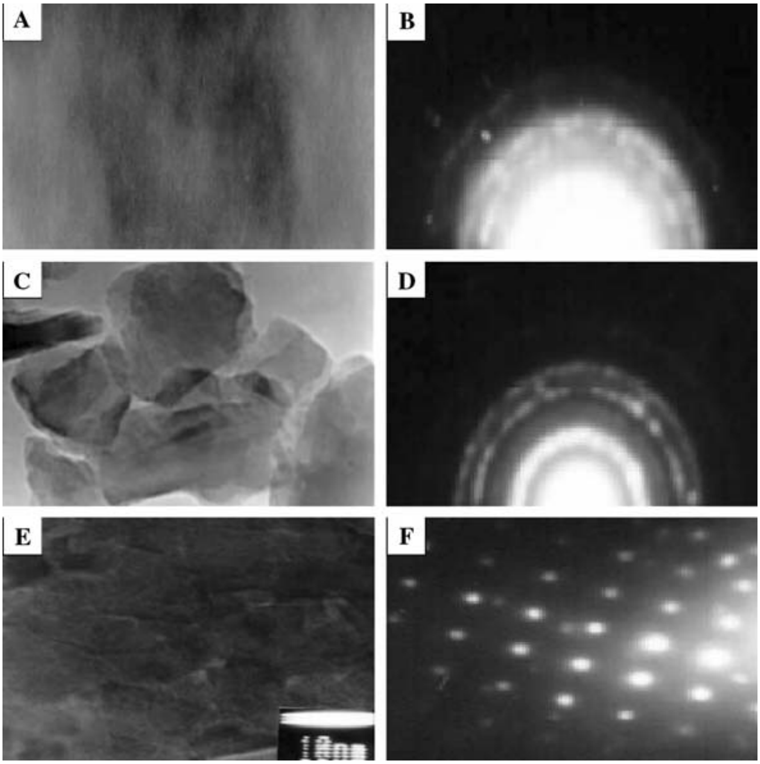

Fig. 7. TEM analysis: (A) Aztec III pottery with small metallic and oxide particles with nanometer dimensions and (B) its diffraction pattern; (C) Aztec IV pottery with nanometer size particles and crystalline structure and (D) its corresponding diffraction pattern; and (E) Poblana pottery with crystallite sizes $> 1 \mu$m and (F) its diffraction pattern.

(Fig. 7C, D). For the case of the Poblana sample, a coarse grain with crystallite sizes $>1\ \mu$m and single-crystal diffraction patterns are shown in Fig. 7E, F.

4. DISCUSSION AND CONCLUSIONS

The results of XEDS microanalysis show that Aztec III and Aztec IV ceramics have no Pb; this agrees with Cervantes's archeological registers [2] which mention that the Aztecs did not use Pb. This result tells us about the differences in the techniques of pottery manufacturing between the Aztec and Colonial periods. Another important result comes from XEDS analysis, which shows very different amounts of oxygen in Aztec III when compared with Aztec IV. This could be due to the fact that Aztec IV pottery was exposed to low oxidation with a high control of air circulation, and changes in color from brown to reddish orange were induced. This agrees with the findings of Jiménez Pérez and Bracamontes Cruz [3] who described a procedure to produce a ceramic with similar properties as those of the ancient potteries.

In this procedure the pottery was heated at $\sim$700°C for 40 min, and its color changed from brown to reddish orange when exposed to oxidation and controlled air circulation in the furnace [3]. Photoacoustic spectra show that Aztec IV pottery gives higher optical absorption in the range from 750 to 770 nm (dark reddish), which shows poor oxidation when compared with Aztec III and EDS spectra. Mossbaüer spectra suggest that Aztec III and Aztec IV potteries were manufactured by using different compositions of earth. Also, surface Mossbaüer spectra of the Aztec IV ceramic (Fig. 6B) show there is a higher concentration of γ-Fe (natural iron) than for the other samples; this could be due to the reduction of O_2 in the combustion, i.e., taking the relation: $3C + 2\ Fe_2O_3 \rightarrow 3CO_2 + 4Fe$, we can expect a high reduction of oxygen (see Fig. 6B) and the subsequent production of Fe.

According to Nogueira [1], there was an ancient furnace, called "Temazcalli", which was improved during the 25 years after the conquest of Mexico. This furnace was used to make potteries and was built using patches of mud. From our results we conclude that this furnace had good control of air circulation which produced the reduction of oxygen in the combustion as was described in the chemical reaction given above. However, the Poblana ceramic shows different advances when compared with the Prehispanic ceramic. EDS microanalysis of the Poblana ceramic indicated that this sample contained characteristic elements of plumbed for finishing which is similar to a glaze or varnish. Also, from this microanalysis we conclude that the metallic oxides (colors) were added at different temperatures in the furnace, which was operated at low or high temperatures and also with high control of air circulation. From the TEM results a larger size in the crystallites from the Poblana sample was observed, when compared with Aztec III and IV ceramics; this could be due to different oxygen pressures and temperatures of the fired ceramics that also influence the sinterization and grain sizes, i.e., the particles grow rapidly with the sinterization time, and the porosity of the conglomerates decreases [11], see Fig. 7. Similar results were observed on the *in situ* annealing sequences of Ir Si layers by TEM [11]. In addition, the Aztec III pottery was fired at a lower temperature than that of Aztec IV and Poblana. All these results are in agreement with the archeological registers concerning the manufacturing and firing of ancient Mexican pottery.

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