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Mercury intrusion porosimetry (MIP) study of archaeological pottery from Hualfin Valley, Catamarca, Argentina

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ABSTRACT

Mercury intrusion porosimetry (MIP) on archaeological potteries classified as Belen fine and ordinary types from Catamarca, Argentina, was analysed. The MIP technique allowed identifying high percentage of uniform pore size in fine pottery, and inhomogeneous pore size in ordinary pottery. Fragments of neck and body sections of the same ordinary vessel were also studied. The porosity of the body section was smaller than the one of the neck, and the cumulative pore volume curve analysis of the body sectors (of the same vessel) evidenced that some pore sizes were sealed partially with respect to the one of the neck. Such behaviour may provide evidence of physical or chemical transformations from their manufactured process, during their use, and post-depositional effects.

1. Introduction

Ancient pottery involves culture, civilization, customs, religion, art, technology, and aboriginal inhabitants, of the region where the vessels were found. The different civilizations of the human history can be known by means of ceramic objects which may help to provide answers to the past.

In the early days, the vessels were prepared with mud dried in the sun but history shows that replacing the sun-dried process by the firing one transformed soft vessels into hard and durable ones. "Vessels are used, broken, discarded, reused, or buried and subjected to alterations natural and cultural agents" (Rye, 1994) and this involves important changes in the original properties of the vessels. Mineralogical, textural, structural and other archaeological analyses allow obtaining most evidences about manufacture techniques and their uses.

The so-called "ordinary" pottery in archaeological sense is referred to vessels usually used for domestic function (cooking or heating, storage of food or liquid) with or without the presence of soot deposits and/or organic adhesions. In general, they have coarse inclusions and rustic appearance without decorations. The "fine" pottery is referred to vessels showing compact paste, no inclusions visible to the eye, thin walls, and a fine finish (polished with uniform lustre) with or without decoration and exhibits no evidence of domestic use. Similar classification, as low- or high-fired vessels, respectively, has been referred in Rice (1987).

Porosity is relevant in ceramic microstructural properties and involves mechanical resistance (strength, hardness); electrical and thermal conductivity; chemical erosion; permeability; adsorption; and refractoriness properties (Kingery, 1985; Rice, 1987; Rye, 1994; Shepard, 1985). Textural properties of the solids involve, among others, pore volume, specific surface area, pore surface and pore size. The vessels can be evaluated by several methods such as mercury intrusion porosimeter (MIP), water adsorption and nitrogen adsorption. MIP is widely used for characterizing pore volume and size in porous materials which are very important in adsorbents, catalysts, ceramics, and biomedical and other materials.

Mercury porosimetry determines larger pores that are not within the detection range of nitrogen adsorption (Gregg and Sing, 1991). The water adsorption method determines pore volume but not pore size. It is very important to take into account that if the pottery was not treated at high temperatures and if in it pristine clay mineral phase remains, the water adsorption method is not suitable because the clay mineral can interact with water and the measurement of porosity will be erroneous.

The IUPAC (International Union Pure Applied Chemistry) defines the pore size as micro, meso and macropores according to the diameter size: <20 Å; between 20–500 Å and >500 Å, respectively (IUPAC, 1985).

There is scarce information about the use of mercury intrusion porosimetry for analyzing ancient potteries (Morariu et al., 1977; Sanders, 1973; Velraj et al., 2009; Wolf, 2002). Sanders (1973) and

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Wolf (2002) analysed pore size distribution in 0.1–70 μm and 0.03–360 μm ranges of ancient potteries, respectively, by using the mercury intrusion method. Morariu et al. (1977) studied the pore structure of the ancient pottery in the pore size range 110–150,000 Å (0.0110–15 μm) by using similar equipment. The different ranges analysed by these authors may be due to the model of mercury intrusion equipment used.

There is no information in literature about comparative porosimetry analysis of sherds which come from different sections of the same vessel, neither from where exactly the sherd sections come from.

The aim of this work was to obtain a comparative porosimetry study by using not only sherds of different vessels but also sherds that represent different sectors of the same vessel. For this study, Belen fine and ordinary potteries from Catamarca, Argentina, were analysed by using mercury intrusion porosimetry (MIP) in a wide range of pore size (0.0074–15 μm).

2. Materials and methods

The archaeological pottery samples of this work were found in excavations at the Belen culture site "Campo de Carrizal" (27° 19′ south latitude and 67° 02′ west longitude). The site is located a few kilometres from the modern village of Azampay, in the Hualfin Valley (Catamarca province, Argentina), at an elevation of 2000 m above sea level. The potteries belonged to the 15th century AD (Capparelli et al., 2003; González, 1977; Wynveldt, 2009; Zagorodny and Balesta, 2010).

Two types of sherds were analysed of *fine* (Caz14.2, Caz14.3 and Caz14.7) and *ordinary* (CazV1, CazV2 and CazV3) potteries. The Caz14.2 and Caz14.3 correspond to jar type pottery and Caz14.7 to bowl type. Fine ceramic of the Belen culture is recognized because the vessels were painted in black on red colour. Fragments from different parts of domestic ceramic containers (neck and body) above mentioned as *ordinary* potteries were also analysed and identified as shown in Table 1. Mineralogical compositions by X-ray diffraction and optical microscopies of thin section (petrography) results of potteries analysed in this work have been already published by Wynveldt (2009) and Zagorodny et al. (2010).

2.1. Description of ordinary potteries

The CazV1 vessel showed firing defects possibly due to the manufacturing process because ochre to grey range colour in breaking off sections was observed. However, there was no evidence of burning. Given the thickness of the neck and wall, it can be inferred that it was a large vessel. The internal surface of the sherd that is analysed was smoother than the external one which presented narrow parallel linear facets.

The CazV2 presents coarse and porous aspects. The surface is roughening with important burned contents in both the internal and external surfaces of the neck. In the body sector, an important amount of soot only in the external surface was observed, whereas in the internal surface star-shaped cracks were seen. Then, the vessel may have had a utilitarian role in cooking.

The CazV3 vessel presents an aspect of compacted paste with fine inclusions. The vessel is grey and its "fresh fracture" is dark grey. The fragments of this vessel did not show evidence of burning. The internal and external surfaces of the neck showed a smooth with striated combing texture, whereas the body fragment presented roughened parallel facets on the surface; perhaps, it was treated with the paddle technique by using corncobs (abundant in this place) on the surface. This type of surface in this vessel might indicate that the jar could have been used for transporting water or substances.

Table 1
Porosity of sherds from different sections of ordinary potteries.

Sample	Section	Porosity %
CazV1	CazV1P1: neck	34.4
	CazV1P2: body	31.7
CazV2	CazV2P3: neck	41.4
	CazV2P4: body	37.9
CazV3	CazV3P5: neck	42.7
	CazV3P6: body	41.3

2.2. Equipment

Mercury intrusion tests were performed by using a Porosimeter 2000 Carlo Erba and pressures ranging from 1 to 2000 kg/cm^2. The intrusion volumes were measured at stepwise increasing pressures equilibrating at each pressure step.

The volume of mercury V (mm^3/g) intruded at a given pressure P (kg/cm^2) gave the pore volume that can be accessed. The intrusion pressure was translated into equivalent pore radius rp (Å) following the Washburn (1921) equation: $rp = -0.2\ \gamma \cos\alpha / P$; where γ is the mercury surface tension (485 dynes/cm^1), and α is the mercury/solid contact angle (taken as 141.3° for all studied minerals). In these conditions, the equipment determines pore radii from 37 to 75,000 Å (0.0037–7.5 μm) or pore diameter 74 to 150,000 Å (0.0074–15 μm).

3. Results and discussion

3.1. Porosimetry analyses of fine and ordinary potteries

The cumulative pore volume of the fine and ordinary samples showed different types of curves (Fig. 1), with narrower contribution for fine ceramic (Caz14.3, Caz14.7, Caz14.2), and broader for ordinary ones (CazV1P2, CazV2P4, CazV3P6) centred at different pore sizes (also in Fig. 2). The fine sherds presented higher total pore volumes than the ordinary ones (range 230–350 mm^3/g and 150–230 mm^3/g, respectively) (Fig. 1). Similar total pore volume (0.170 mm^3/g) was found by Morariu et al. (1977) on Dacian and Bronze Age potteries. Nevertheless, the analysed pore size was higher (0.0110–15 μm) than our values (0.0074–15 μm).

The higher slope at low pore size (Fig. 1) may be indicative of the fact that the sherds have pore radius smaller than 37 Å (below MIP detection limit).

The fine potteries presented higher pore size than the ordinary ones (Fig. 2). The contribution of the dominant pore radius size to pore volume for fine pottery was located between 3000 and 6000 Å (0.3–0.6 μm), Fig. 2A, with around 70% of the volume contribution, as shown in Fig. 1. This range of the pore size was similar to those of Roman pottery found by Sanders (1973); however, the total volume cannot be

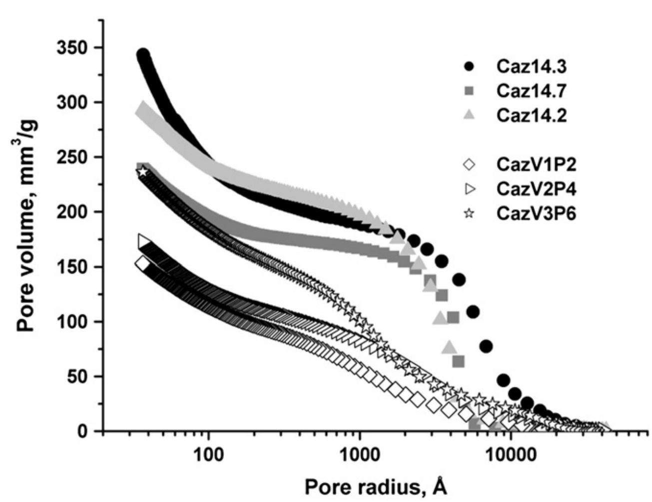

Fig. 1. Cumulative pore volume curves of *fine* (Caz14.3, Caz14.7, Caz14.2) and *ordinary* (CazV1P2, CazV2P4, CazV3P6) potteries.

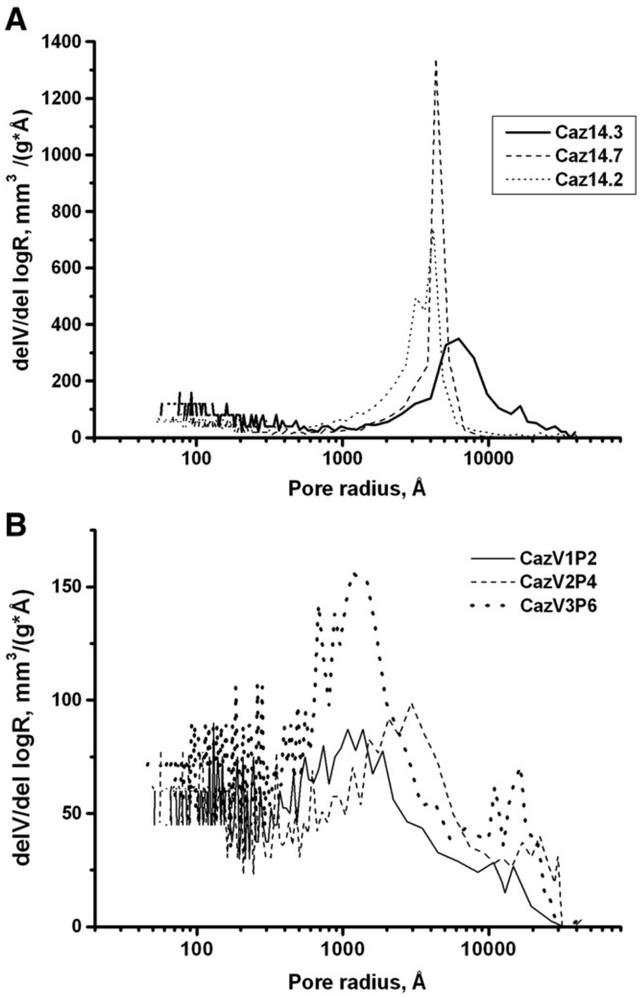

Fig. 2. Pore size distribution. A) *fine* and B) *ordinary* potteries.

compared because the mentioned author analysed pore sizes higher (0.1 μm) than this paper (0.0074 μm).

Two broad peaks corresponding to preferential size radii contribution, at around 1000–2000 Å (0.1–0.2 μm) and 10,000–20,000 Å (1–2 μm) for the ordinary pottery (Fig. 2B) were present, with 33 and 16% contribution to total volume, respectively, as it can be appreciated in Fig. 1. Then, the MIP technique allowed, in this work, identifying high percentage of uniform pore size in fine potteries, and inhomogeneous pore size in ordinary potteries. However, the total volume of both types of potteries can be different, or similar as shown in Fig. 1 for Caz14.7 (fine) and CazV3P6 (ordinary) samples. Fine potteries from other places from Hualfin Valley (Zagorodny et al., 2010) also showed similar behaviour with respect to narrower distributions of pore size.

The distinctive behaviour between fine and ordinary potteries which present narrow and broad pore size distribution curves, respectively, may be attributed to diverse factors: paste composition (Zagorodny et al., 2010), size and morphology of mineral inclusion, surface treatments, firing, and domestic or non domestic use of vessels.

3.2. Porosimetry analyses of samples from different sectors of ordinary vessels

For this analysis, it was established that the original vessel had the same pore size distribution throughout the piece. Based on this hypothesis, different sectors (neck and body) of the three vessels under study, characterized as ordinary ceramic containers were analysed. The samples were named as shown in Table 1: CazV1 (P1: neck, P2: body), CazV2 (P3: neck, P4: body), CazV3 (P5: neck, P6: body). Comparative mercury intrusion analyses between body and neck sectors of the vessels are shown in Fig. 3.

The cumulative pore volume of the neck fragment for the CazV1 vessel (CazV1P1: neck) (Fig. 3A) showed a higher value (around 14%) than the body fragment, CazV1P2: body, in all analysed range of the

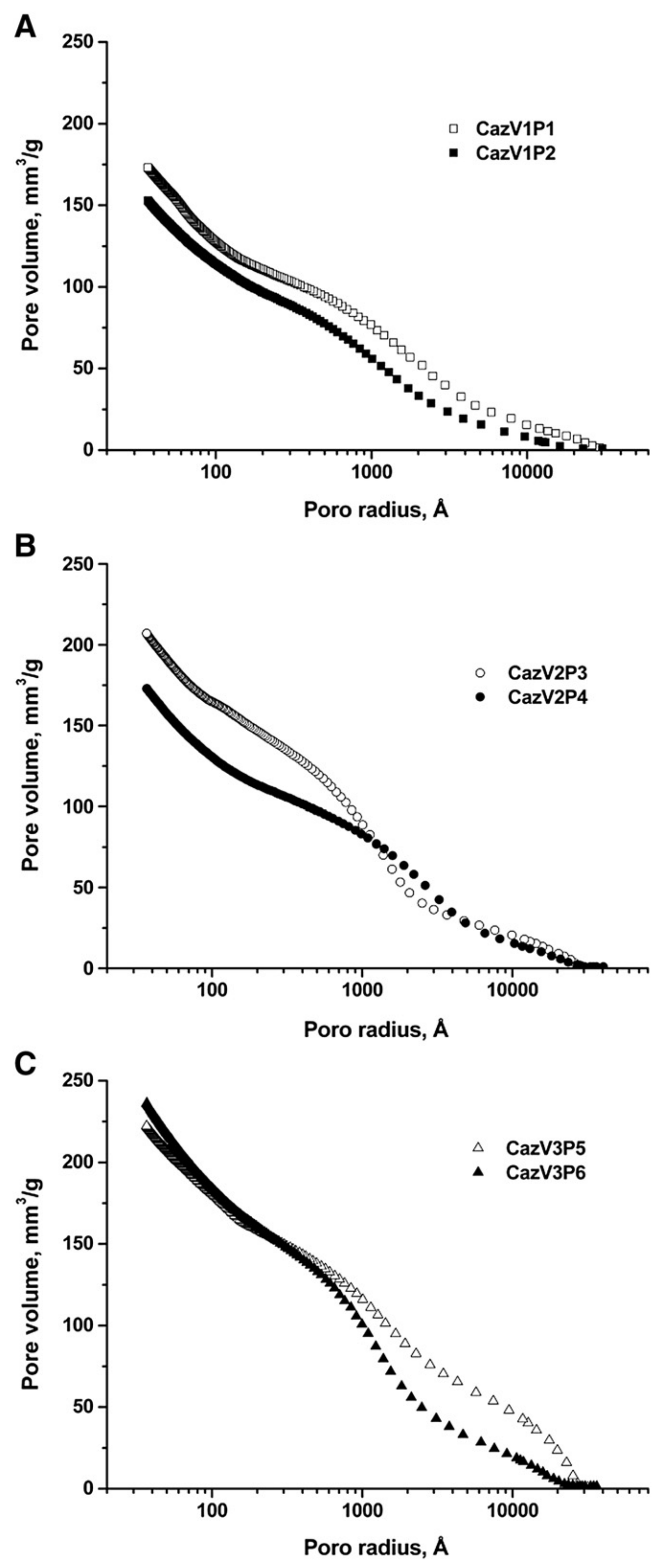

Fig. 3. Cumulative pore volume of neck and body fragments from *ordinary* potteries: A) CazV1, B) CazV2 and C) CazV3.

pore size. Such vessel has not shown soot deposits. Perhaps, it was used for water storage and the contained minerals in water may have partially sealed the pores of the body section, as its cumulative pore volume curve is shown in Fig. 3A.

The cumulative pore volume curves of neck and body fragments for CazV2 and CazV3 vessels were distinctive (Fig. 3B and C). The pore radii <1000 Å of CazV2 body (CazV2P4) were sealed partially (12%) with respect to the same size of neck. However, volumes of larger pores of the body were preserved because they were similar to those in the neck (similar distribution for higher than 1000 Å pore radius). The partial seal of the smallest pores of the body can be due to the presence of soot, as it was observed with the naked eye, indicating potential use of heat and cooking and as result, probable substances could also have closed the pores partially.

CazV3 vessel analysis (Fig. 3C) showed a different behaviour with respect to the CazV2 vessel (Fig. 3B). Pores larger than 600 Å of the body (CazV3P6) were partially sealed, whereas, pores smaller than 600 Å showed a similar distribution to the neck.

The porosity of the neck and the body sections was different for the three potteries analysed in this work (Table 1). In all cases, the values of the neck (34.4, 41.7 and 42.7%) were higher than the ones of the body (31.7, 37.9 and 41.3%) for the CazV1, CazV2 and CazV3 samples, respectively. The difference in percentages between the neck and body was in the range of 3.3–9.1%.

The cumulative pore volume, the pore size distribution curves and the porosity allowed finding different textural behaviours between the neck and body sectors of the same vessel, which can be attributed to multiple reasons such as manufacture process, pottery function and uses included, sealing – intentional or not – for diverse types of contents (liquid or solid), and post-depositional effects.

4. Conclusions

The use of the mercury intrusion porosimetry (MIP) technique favoured a better understanding of textural archaeological pottery analysis for investigating more about the technology of the potteries of the Hualfin Valley.

MIP has revealed remarkable differences of the cumulative pore volume between *fine* and *ordinary* ceramics. Fine ceramics showed a narrow pore size distribution while the ordinary ceramic showed a wide variation of pore sizes.

The application of this technique to sherds of diverse sectors of the same vessel allowed observing textural differences (pore volume, pore size, and porosity), which can be attributed to different circumstances such as techno-functional implications and circumstances as a result of the use of the piece as a liquid or solid container and subsequent abandonment (sealed, solid or liquids content), or action (dump, hygienic practices, spoon between the inner walls seal, support-surfaces).

For a comparative study about porosimetry (MIP) of the potteries, and taking into account the results presented in this work, it is recommendable to analyse the sherds from the same sector of the vessels, preferably of the neck. This suggestion for a methodological analysis is done because the pores of the body may or may not be partially sealed along the profile of the vessel, after burn or deposits of substances or when it was manufactured and was intentionally sealed to obtain some specific property (e.g. impermeability).

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