Rock magnetic, petrographic and dielectric characterization of prehistoric Amerindian potsherds from Venezuela

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ABSTRACT

Rock magnetic, petrographic and dielectric analyses were carried out, in a number of archeological ceramic potsherds, in order to characterize the different manufacturing techniques used by Prehistoric Venezuelan Amerindian potters. Samples were excavated in 7 Venezuelan islands and ascribed to distinct cultural groups on purely stylistic grounds (i.e. Valencioide, Ocumaroide, Dabajuroide and Unknown). Mean coercivity values were determined through a direct signal analyses (DSA) applied to isothermal remanent magnetization (IRM) acquisition curves. Logarithmic plots of these mean coercivities are the best quantitative means to classify diverse ceramics. The mean coercivity values seem to group the samples according to the manufacturing development. These values also seem to discriminate the samples provenance, indeed, this plot displays a good grouping of data for samples presumably manufactured by the same culture but excavated at different locations. Thermomagnetic cycles supply helpful information about original ceramic firing conditions. The irreversibility parameter (IP) for thermomagnetic curves (heating and cooling), serves as an indicator of the amount of organic matter burnt during original pottery firing. The IP for a number of pottery samples from Venezuelan islands and mainland, with ages ranging between 300 BC to 1500 AD, might suggest a possible increasing trend in time towards the complete reversibility line of IP = 0. Most samples, independently of age and cultural group, have IP values that suggest that most open fires, used by primitive Venezuelan Amerindian potters, had enough ventilation and oxidizing atmospheres. A scatter plot of maximum current depolarization temperatures versus natural remanent magnetization (NRM) suggests a complex non-linear relationship between these two parameters most likely due to the fact that both, dielectric and rock magnetic data, are linked to pore-related features.

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1. INTRODUCTION

Aboriginal ceramics can be regarded as cultural markers that allow the characterization of human social groups. Since archeological potsherds are easily found in large amounts and spread over large regions, their study provides some insight about technological, historical-cultural and artistic aspects of ancient people. Indeed, the geographic location where a ceramic vessel or figurine was manufactured, as well as the methods and raw materials used for its craftsmanship, are of foremost importance to archeologists since this information yields evidence for trade and cultural links in ancient times (*Shepard, 1980* and *Orton et al., 1993*).

Archeological provenance studies, using rock magnetic properties, have been previously applied to obsidian samples from the Mediterranean region (*McDougall et al., 1983*), Argentinian and Chilean Patagonia (*Vasquez et al., 2001*) and central Mexico (*Urrutia-Fucugauchi, 1999*). *Beatrice et al. (2008)* have combined magnetic properties, derived from hysteresis loops, with colour surveys to characterize burnt clays and archaeological tiles from Pompeii and Gravina di Puglia, Italy. *Rasmussen (2001)* combined Magnetic Susceptibility and Luminescence measurements for provenance studies of pottery at three different sites in Denmark. *Mooney et al. (2003)* used magnetic susceptibility and isothermal remanence in provenance studies at archaeological ochre quarries in Australia. In Venezuela, *Costanzo-Álvarez et al. (2006)* and *Rada et al. (2008)* have formerly carried out provenance studies for a collection of potsherds from some Venezuelan islands.

In *Costanzo-Álvarez et al. (2006)* it was employed, for the first time, a two-fold magneto/dielectric technique (i.e. rock magnetic properties and thermally stimulated depolarization currents technique or TSDC). They concluded that conventional petrographic analyses agree with clusters of data identified in scatter plots of initial magnetic susceptibility (*MS*) versus saturation isothermal remanent magnetization (*SIRM*), and natural remanent magnetization (*NRM*). *MS*, *SIRM* and *NRM* appear to describe clay sources whereas other properties, such as high temperature *MS* and dielectric TSDC parameters, seem to relate to different steps of pottery fabrication (i.e. clay preparation, finishing and firing).

Apart from these preliminary provenance studies, some of the latest archeometric research projects in Venezuela include the determination of paleointensities for a set of Venezuelan potsherds (*Brandt and Costanzo-Álvarez, 1999*), X-ray fluorescence, instrumental neutron activation analysis and prompt gamma activation analysis (*Kasztovszky et al., 2004* and *Sajo-Bohus et al., 2005*).

In Venezuela, archeological pottery samples are one of the very few vestiges of the pre-hispanic past providing valuable information about the country's first inhabitants. In this study we attempt to completely characterize, via petrographic, rock magnetic and dielectric analyses, a set of potsherds, from some Venezuelan islands, with ages between 1060 AD and 1530 AD. This group includes those samples previously studied in *Costanzo-Álvarez et al. (2006)* and *Rada et al. (2008)*. The potsherds analyzed in these studies (Table 1) were excavated in archeological sites in Los Roques Archipelago (Dos

Table 1. Pottery samples analyzed in this study. Radiocarbon non-calibrated ages were determined on organic matter from the ceramic pieces archaeological context (*Antczak and Antczak, 2007*).

Archipelago/ Island	Culture	Site	Age (AD)	Number of Samples	Number of Specimens
Los Roques	*Ocumaroide*	Domusky Norte	1060 ± 90	2	21
		Dos Mosquises	1430 ± 80	6	30
	Valencioide	Cayo Sal	1200 ± 100	2	13
		Dos Mosquises	1430 ± 80	4	20
	Unknown	Dos Mosquises	1430 ± 80	2	10
La Orchila	*Valencioide*	Los Mangles	1370 ± 80	2	13
Las Aves	*Dabajuroide*	Isla del Tesoro	1530 ± 80	2	14
		Curricai	1530 ± 80	2	11
La Blanquilla	*Unknown*	Cuevas de la Cabecera	1130 ± 120	5	45

Mosquises, Cayo Sal and Domusky Norte), Las Aves de Sotavento Archipelago (Curricai and Isla del Tesoro), La Orchila (Los Mangles) and La Blanquilla (Cuevas de la Cabecera) islands (Fig. 1). We extend the previous works by adding new experimental data and re-examining prior results using new methods. In this fashion, the irreversibility parameter of thermomagnetic curves (*IP*), previously used as an indicator of the amount of organic matter burnt during original pottery firing for three representative samples of the Dos Mosquises (*Rada et al., 2008*), is applied here to the whole set of samples. In *Costanzo-Álvarez et al. (2006)* the ceramic samples were dielectrically characterized, in this study this technique is employed on the whole set of samples. The IRM curves of all the studied samples are analyzed here using an alternative approach to decompose them (*Aldana et al., 2011*). The parameters derived from this decomposition, mainly the mean coercivities, could help to discriminate between cultural groups. With this analysis we try to distinguish not only geographical, but also cultural aspects, identified by stylistic analyses, of the studied potteries.

In this work we also compare thermomagnetic data from these samples with their mainland counterparts from La Calzada, Valle de Quíbor, El Jobal, La Cabrera, Laguna Iboa, Aguerito, El Cedral, Tucuragua, Urumaco and Las Dos Puertas (*Brandt and Costanzo-Álvarez, 1999*).

2. ARCHEOLOGICAL SAMPLES

The most common Fe-minerals in clay, the main ingredient used in pottery making, are: hematite (Fe_2O_3), goethite (a-FeOOH), limonite (hydrated Fe-oxide), magnetite (Fe_3O_4), pyrite (FeS_2), marcasite (FeS_2) and siderite ($FeCO_3$). Grain-sizes of colloidal particles vary between 1 and 5 μm. According to *Shepard (1980)*, each human group had a preferred location to collect their clays. After collection, they were dried out, ground and compacted with water. The resulting paste was then mixed with coarser grains of ground-up pottery or rocks. This step, known as temper, was meant to avoid cracks during drying. Venezuelan potters used ground-up seashells, sand, quartz, vegetal ashes and charcoal for tempering purposes. After being modelled, the surface of the piece was smoothed down by hand or by using rudimentary tools. In some instances, a fine coating of clay and water was also applied over the surface of a vessel to produce a smooth finishing called the slip. Decorations were carved or painted with plant or mineral-based pigments. Inorganic pigments were made mainly of hematite and limonite combined with water and an organic binder. The last step of pottery-making was the firing. During an initial (low heat) dehydration period, water was driven off to avoid rapid formation of steam and breakage. That is why Amerindian prehistoric potters used to maintain a slow heat at the very beginning of the firing process. Throughout the oxidation stage that follows dehydration, the carbonaceous matter was burned out from the clay. Finally, at higher temperatures, the vitrification stage was characterized by a process in which the pottery constituents began to soften and fuse together. Temperatures attained by prehistoric Venezuelan Amerindian potters were not high enough for true vitrification though. An incipient vitrification might start between 800 and 900°C depending on the amount and kind of impurities in the clay. Primitive pottery makers in Venezuela did not have kilns. Instead they used shallow pits or bonfires (i.e. open firing or clamping). Temperatures attained via such firing conditions usually ranged between 600 and 850°C. The times of heating were variable and the temperatures of extraction from the heating sources possibly went from 125 to 800°C.

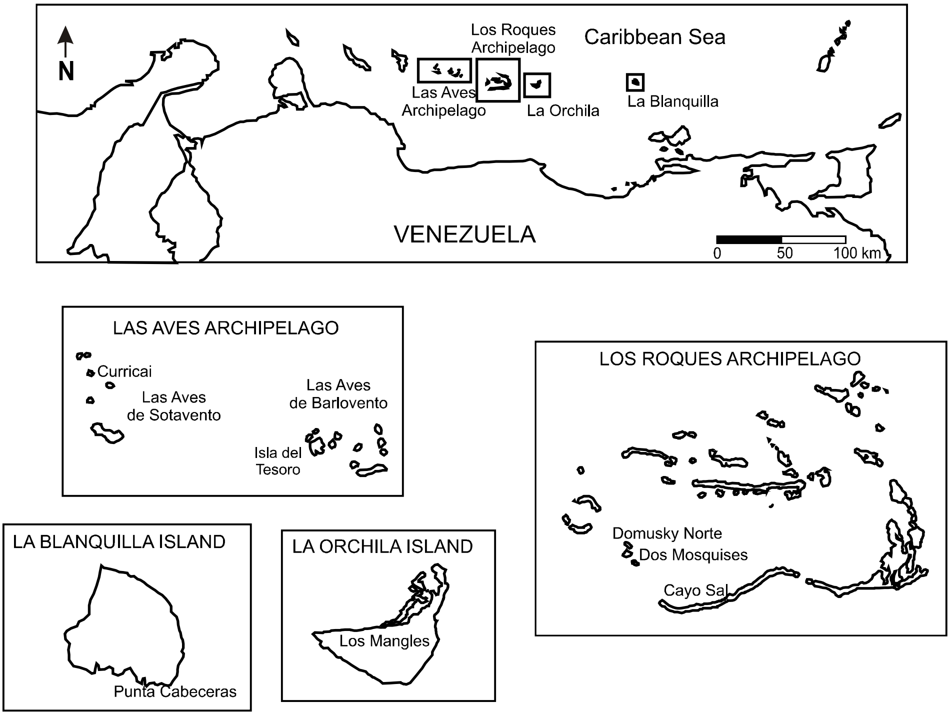

Fig. 1. Sketch map of northern Venezuela showing the islands and archipelagoes with the location of archeological sampling sites.

Most vessels show dark spots produced by irregular burning which may indicate that they were used for cooking purposes. Some others display dark cores resulting from an oxidizing atmosphere that was not hot enough to burn away all the organic components.

Our study is focused on a set of 27 fragments of unoriented potsherds (fragments of bowls) (Table 1) collected in Domusky Norte (2), Dos Mosquises (12) and Cayo Sal (2) from Los Roques Archipelago; Curricai (2), and Isla del Tesoro (2) from Las Aves Archipelago; Los Mangles (2) from La Orchila and Cuevas de la Cabecera (5) from La Blanquilla (Fig. 1). According to their stylistic features these samples have been categorized into five cultural groups, namely *Dabajuroide*, *Valencioide*, *Ocumaroide*, Dos Mosquises *Unknown* and La Blanquilla *Unknown*.

Potsherds from Las Aves Archipelago (Curricai and Isla del Tesoro) (Fig. 1) have been identified as ceramics from the *Dabajuroide* group (*Antczak and Antczak, 2007*). This pottery is characterized by its highly ornamented geometric decorations. The *Dabajuroide* pottery manufacturers inhabited western Venezuela as well as the Netherland Antilles (i.e. Aruba, Bonaire and Curaçao) between 600 and 1500 AD (*Cruxent and Rouse, 1958*; *Rouse and Cruxent, 1963*).

Potsherds from Los Roques Archipelago and La Orchila Island (figure 1) have been associated with *Valencioide* and *Ocumaroide* cultural groups (*Antczak and Antczak, 2007*). Both cultural groups inhabited the north-central part of Venezuela between 800 and 1500 AD (*Cruxent and Rouse, 1958*; *Rouse and Cruxent, 1963*). There is also a third ceramic style that shows no resemblance with none of the other two, and therefore was called *Unknown* pottery.

The *Valencioide* pottery shows highly stylistic uniformity, elaborated shapes and colours indicating a well established manufacturing technique. It is made mostly of fine-grained and well-sorted grit tempered clay, ussually finished with a reddish slip (Fig. 2a). Anthropomorphic figurines are characteristic of the *Valencioide* culture and they are widely found in northern mainland Venezuela (*Cruxent and Rouse, 1958*; *Rouse and*

Fig. 2. Figurines from Dos Mosquises: **a)** Standardized and **b)** Heterogeneous from the collection of the Unidad de Estudios Arqueológicos (IERU, Universidad Simón Bolívar). Pictures courtesy of A. Antczak.

Cruxent, 1963). This ceramic group was excavated in Cayo Sal and Dos Mosquises (Los Roques Archipelago), and also in Los Mangles (La Orchila Island) (*Antczak and Antczak, 2007*).

On the other hand, the *Ocumaroide* ceramic is characterized by poor manufacturing techniques that translate in rudimentary figurine shapes, rough surfaces, stylistic diversity and colours grading from brown to reddish brown (Fig. 2b). Moreover, the paste is coarse-grained with large fragments of rocks and shells that were used for tempering (*Antczak and Antczak, 2007*). This pottery was unearthed in Domusky Norte and Dos Mosquises (Los Roques Archipelago) (*Antczak and Antczak, 2007*).

The Dos Mosquises *Unknown* group has unique stylistic characteristics that do not coincide with neither of the other two excavated in Los Roques. They reveal the use of advanced manufacture techniques similar to those that characterize the *Valencioide* group (*Antczak and Antczak, 2007*), namely thick reddish slips covering fine-grained cores with colors ranging from light gray to salmon red.

Pottery samples from La Blanquilla (Fig. 1) show an advance manufacturing technique, with light grey cores covered with a dark gray slip and fine-grained grit temper. No figurines have been found in this island and this ceramic style has not been associated with any known cultural groups, although it possibly were produced by an eastern Venezuela prehistoric society.

Since most of these islands are arid and sandy, lacking of clay deposits, sources of freshwater and fertile soils, the archeological sites excavated have been interpreted as temporary campgrounds established by Amerindian groups from mainland Venezuela. They probably visited the islands seasonally until the times of the European contact in the 16th century (*Antczak and Mackowiack-Antczak, 1999* and *Antczak and Antczak, 2007*). Cultural strata are quite homogeneous and rarely thicker than 60 cm. Thus archeological stratigraphy renders useless in establishing relative ages between different potsherds collected in a single location. Visual analyses of the different ceramics reveal colors and textures that vary widely between islands. Non callibrated ^{14}C dates (*Mackowiak-Antczak and Antczack, personal communication*) reveal a range of ages that goes from a maximum of 1060 ± 90 AD up to a minimum of 1530 ± 80 AD.

In this work we also compare thermomagnetic data for the samples collected at the Venezuelan islands with their mainland counterparts from La Calzada (1) (260 ± 20 BC), Valle de Quíbor (1) (105 BC), El Jobal (1) (350 ± 130 AD), La Cabrera (1) (450 ± 250 AD), Laguna Iboa (1) (670 ± 560 AD), Aguerito (1) (760 ± 320 AD), El Cedral (10) (1150 ± 250 AD), Tucuragua (1) (1385 AD), Urumaco (1) (1410 ± 110 AD) and Las Dos Puertas (1) (1600 ± 110 AD) All ages, except El Cedral (dated by context), are non-calibrated ^{14}C dates (*Brandt and Costanzo-Álvarez, 1999*).

3. ROCK MAGNETIC, DIELECTRIC AND PETROGRAPHIC EXPERIMENTS

Rock magnetic characterization of pottery samples includes high temperature susceptibility cycles, analyses of isothermal remanent magnetization (IRM) acquisition curves and natural remanent magnetization (*NRM*).

Sample preparation for rock magnetic experiments (except for themomagnetic ones) involved the careful selection of the homogeneous inner part of irregular potsherds, in order to avoid possible magnetic contamination from the outer surface of the vessels (i.e. pigments from the painting and/or slip) as well as from the firing heterogeneities. These fragments were then cut as squared specimens of 1 × 1 × 0.3 cm (approximately 10 g) and embedded into a mixture of magnetically innocuous plaster of Paris. After drying (for about 24 h) cores of 2.5 cm in diameter and 2.5 cm heigh were drilled into the Plaster of Paris matrix around each specimen. One specimen per sample was used for each experiment.

NRM was measured in a Molspin minispin rock magnetometer with a sensitivity better than 1×10^{-7} emu/cc at 24 s.

IRM acquisition curves, between 1 and 1000 mT, were obtained using an ASC IM-10-30 impulse magnet with exchangeable coils. We have used an alternative method to analyse these IRM curves, based on a Direct Signal Analysis (DSA) decomposition (*Aldana et al., 1994, 2011*). To apply this method, the experimental IRM is described as the sum of *N* elementary curves, each one modelled according to the expression proposed by *Robertson and France (1994)* and hence characterized by their mean coercivities, $B_{1/2}$:

$$IRM\left(B\right) = \frac{Mr}{DP\left(2\pi\right)} \int_{-\infty}^{\infty} \exp\left[-\left(\frac{\left(\log B - \log B_{1/2}\right)^2}{2\left(DP\right)^2}\right)\right] d\left(\log B\right) . \qquad (1)$$

In the equation above, *Mr* is the inferred saturation magnetization, $B_{1/2}$ the field which causes half of the saturation IRM and *DP* the dispersion parameter. Hence, we approximate the experimental curve by the superposition of *N* of these elementary IRM curves as:

$$IRM\left(B\right) = \sum_{i=1}^{N} \frac{Mr_i}{DP_i\left(2\pi\right)} \int_{-\infty}^{\infty} \exp\left[-\left(\frac{\left(\log B - \log\left(B_{1/2}\right)_i\right)^2}{2\left(DP_i\right)^2}\right)\right] d\left(\log B\right) \qquad (2)$$

We select a window wide enough for the $\log\left(B_{1/2}\right)_i$ values to include all the possible magnetic phases present in the sample. The result of the adjustment is a spectral histogram of the contribution Mr_i or heights of each elementary curve to the experimental IRM. From this histogram, the number of main contributions, their widths and mean coercivities, associated with the number and type of magnetic minerals, can be obtained. Detailed description of the method is described in *Aldana et al. (2011).*

Curie temperature analyses were performed using a Bartington MS2, a MS2W probe and a SM2WF furnace that allows continuous susceptibility readings of a 1.5 g ground sample with temperature. Thermomagnetic cycles go from room temperature up to 700°C (heating curve) and then back to 30°C (cooling curves).

In this study, the irreversibility parameter of thermomagnetic curves (*IP*) (*Böhnel et al., 2002*) was calculated, to quantify the resemblance between heating and cooling curves. This was done not only for the samples of the islands but also for 23 ceramic

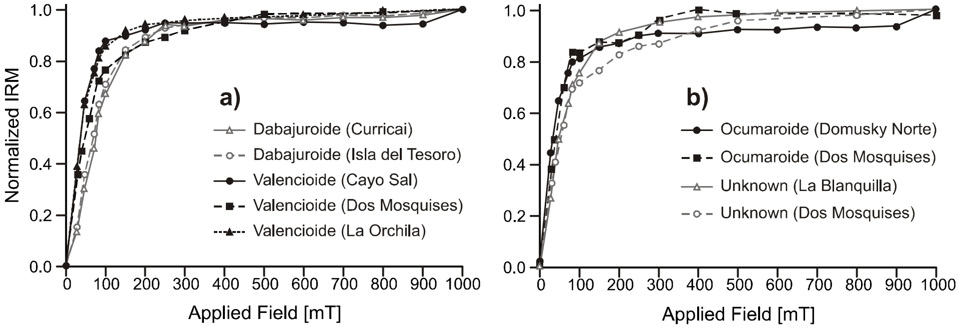

Fig. 3. IRM acquisition curves for potsherd samples of each cultural group: **a)** *Dabajuroide* and *Valencioide*, **b)** *Ocumaroide*, *Unknown* La Blanquilla and *Unknown* Dos Mosquises.

samples from Venezuelan mainland archaeological sites (*Brandt and Costanzo-Álvarez, 1999*). The *IP* is the difference of areas below heating and cooling curves, normalized by the area under the heating curve. Therefore, an $IP = 0$ indicates complete reversibility, whereas $IP < 0$ means that the heating curve runs over the cooling one and $IP > 0$ occurs for the opposite situation.

Finally we carried out a dielectric characterization for 24 of the total number of samples analyzed in this study. The technique of thermally stimulated depolarization currents (TSDC), used for such a purpose, examines the variation with temperature of the depolarization current given by a sample previously polarized, under the influence of an external electrostatic field, at a temperature T_p sufficiently high to allow the orientation of fragment or bond dipoles and charges (*Aldana et al., 1994*). The principle of this technique is based on the strong dependence on the temperature, *T*, of the dielectric relaxation time, τ, of dipoles (bound charges causing dipolar relaxation) and free charges. The relaxation processes depend on textural, morphological, and chemical characteristic of the studied samples because these characteristics affect the temperature-dependent mobility of bound and free charges in the system. The TSDC technique is appropriated to study relaxation phenomena in any materials because electron clouds in atoms, molecules, solids, and other materials are sensitive to an external electrostatic field, and corresponding reorientation of dipoles or location of free charges can be frozen. As a thermal analysis method, TSDC uses the molecular mobility, of the entire molecules or their fragments, as a means of accessing structural information that cannot be obtained by other techniques. It also gives access to thermodynamic and dynamic parameters such as entropy, Gibbs free energy, and enthalpy variations, as well as activation energy of relaxation and relaxation time (*Gunko et al., 2007*). This technique is also particularly suited to materials having a polar character, such as pore and adsorbed water, polar organics, bio-objects, etc. (*Suárez et al. 2003, 1999*). Integration of *NRM* and TSDC data has been previously used as an alternative stratigraphic tool to characterize lithologies (*Costanzo-Álvarez et al., 1999*). It is noticeable that in this case two techniques, based on distinc physical properties (i.e. magnetic and dielectric) albeit similar process of polarization and thermal relaxation to equilibrium, were combined.

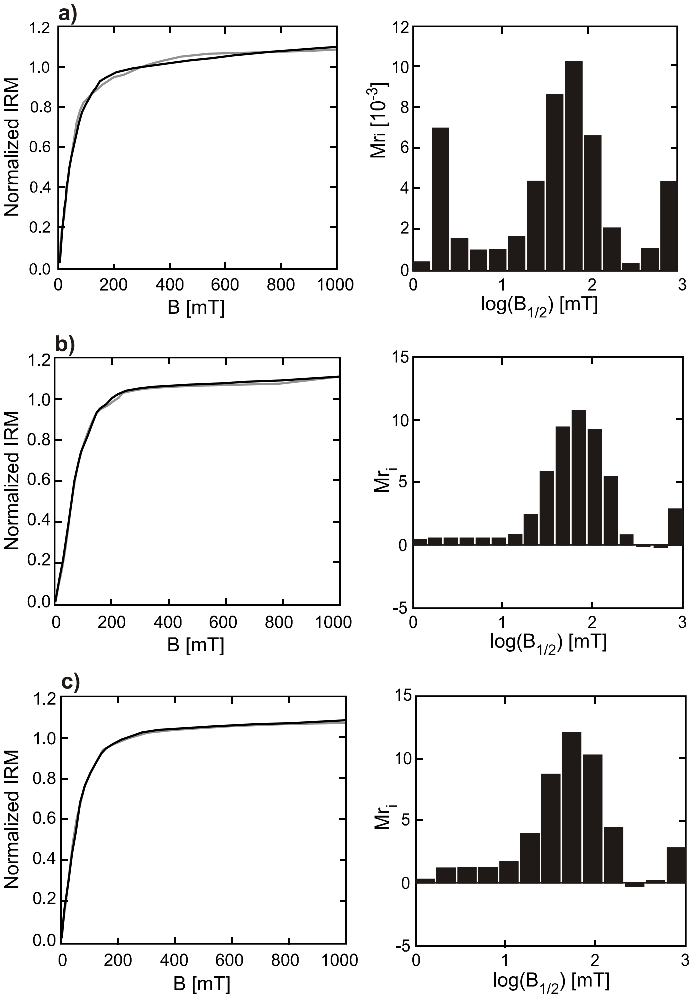

Fig. 4. Results of the DSA decomposition of IRM curves for representative potsherds samples from: **a)** *Valencioide* (Dos Mosquises), **b)** *Dabajuroide* (Isla del Tesoro) and **c)** *Unknown* (la Blanquilla). The experimental IRM curve (gray), the fitted curve (black) and the resultant spectral histogram after applying the DSA are presented in each case.

The depolarization spectrum obtained in a TSDC experiment is composed of electrical current peaks produced by the relaxation process of dipolar entities with different characteristics or heterogeneities (*Suárez et al., 2003*). One of the advantages of this technique is its high sensitivity, leading to the detection of very low electrical dipole concentrations, and its very low equivalent frequency (~ 10^{-3} Hz), allowing multicomponent peaks to be resolved accurately. The method permits the isolation of a particular relaxation from its neighboring peaks by carefully choosing the polarization conditions. For this study, disc-shaped ceramic samples (20 mm in diameter and 250 μm thick) were polarized at room temperature ($T_p \sim 300K$) and cooled afterwards to liquid nitrogen temperatures, at a 55°C/min rate, in order to freeze the polarization state. Such polarization was achieved by applying an electrical field of ca. 5×10^5 V/m. To generate the depolarization current, the electrical field was withdrawn and the temperature was increased at a 0.07K/s linear rate. The TSDC experiment was performed employing a Cary Vibrating Reed Electrometer model 401 with sensitivity of 10^{-17} A, signal to noise ratio better than 500 and fully automatic current-temperature data acquisition. In this work we used the maximum current depolarization temperatures for the most conspicuous peaks identified in the TSDC spectrum of each sample analyzed. To analyze the influence of physisorbed moisture (contribution of water dipoles) to the TSDC spectra, drying and rehydration treatments were performed. The samples were rehydrated in a water-saturated atmosphere at room temperature during three days. For the dehydration treatments, water was evaporated in vacuum ($p \approx 10^{-4}$ Pa) at room temperature and the spectra were recorded after 30 min, 26 h and 75 h of outgassing, and after heating to 320K during 5 min followed by 24 h more of drying.

Petrographic analyses were carried out previously (*Costanzo-Álvarez et al., 2006* and *Rada et al., 2008*) for some representative samples of each ceramic group.

4. RESULTS AND DISCUSSION

The IRM acquisition curves (*Costanzo-Álvarez at al., 2006*; *Rada et al., 2008*) for some of the studied samples are shown in Fig. 3. Results of the DSA decomposition of IRM curves for some representative potsherds samples are presented in Fig. 4. In order to compare the $B_{1/2}$ values of all the samples, the envelopes of the spectral histograms of all the studied samples are summarized in Fig. 5. The results revealed up to 3 main magnetic components with coercivity values that range between 1–4 mT, 20–80 mT and 200–600 mT (Fig. 5).

Fig. 6 shows a logarithmic plot of mean coercivity values, for the middle range interval 20–80 mT, in terms of the cultural group. This middle range appears to be shared by all the samples in Fig. 5. The mean coercivity values seem to group the samples according to their manufacturing development. Samples with values lower than 40 mT correspond to more primitive manufacturing techniques (*Ocumaroide,* group 1 in Fig. 6). Additionally, these values also seem to discriminate the samples provenance: values lower than 60 mT correspond to samples from central and eastern Venezuela ceramics (La Blanquilla *Unknown*, *Valencioide* and *Ocumaroide,* groups 1 to 4 in Fig. 6), while those with higher values were produced in western Venezuela (*Dabajuroide*, group 5 in Fig. 6).

Previous analysis of thin section photomicrographs for each ceramic group indicated that the samples from western Venezuela (*Dabajuroide*) have a characteristic high percentage of angular-shaped and poorly sorted fragments of volcanic rocks and feldspars (*Costanzo-Álvarez et al., 2006*). On the other hand, the samples from central and eastern Venezuela have a mixed source of igneous and metamorphic rocks (*Costanzo-Álvarez et al., 2006*; *Rada et al., 2008*). Additionally, *Valencioide* samples present much smaller deformed mica and metamorphic quartz grains than *Ocumaroide* ones. They also show

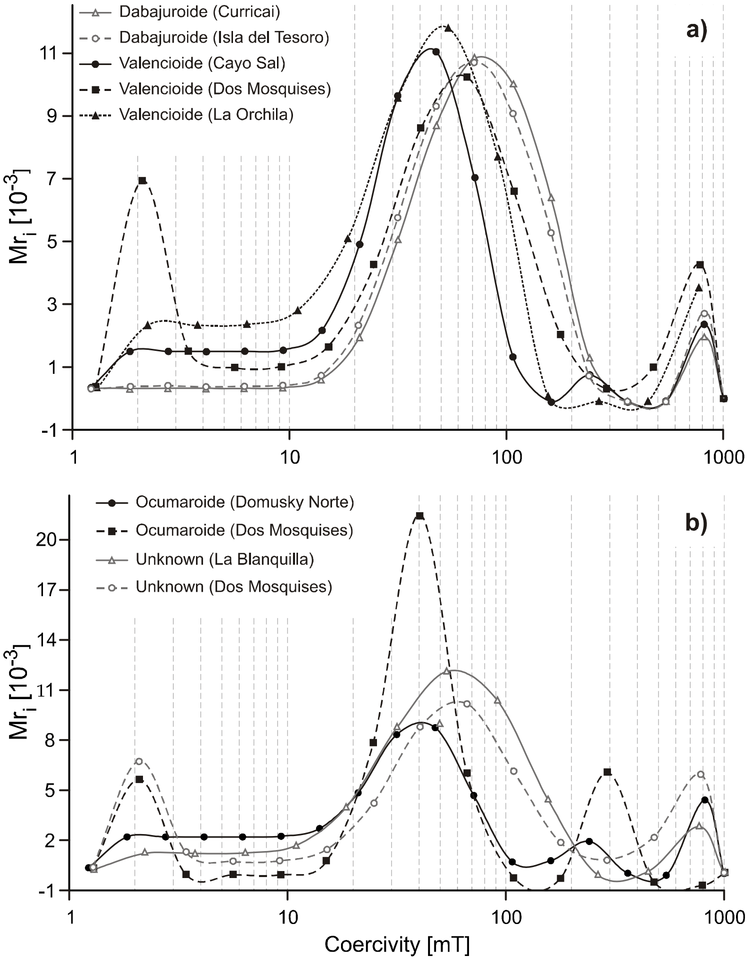

Fig. 5. Envelope of the spectral histograms resulting after applying the DSA to the IRM acquisition curves of Fig. 3: **a)** *Dabajuroide* and *Valencioide*, **b)** *Ocumaroide*, *Unknown* La Blanquilla and *Unknown* Dos Mosquises. The results exhibit a middle range of coercivities between 20 and 80 mT that seems to be shared by all the samples.

superficial alteration of amphiboles, biotites and feldspars, revealing two sedimentary sources, namely metamorphic rocks (most likely from the coastal central mountain range in northern Venezuela too) and a weathered granodiorite. Mineral grains and fragments of rocks in these ceramics are much better sorted than their *Dabajuroide* and *Ocumaroide* counterparts. This observation coincides with the data trends observed in Fig. 6. Indeed, whereas *Valencioide* mean coercivity values lie mostly within the swathe of 40 to 60 mT, *Dabajuroide* (Curricai and Isla del Tesoro) and *Ocumaroide* (Dos Mosquises and Domusky Norte) lie between 60–70 mT and 20–40 mT, respectively.

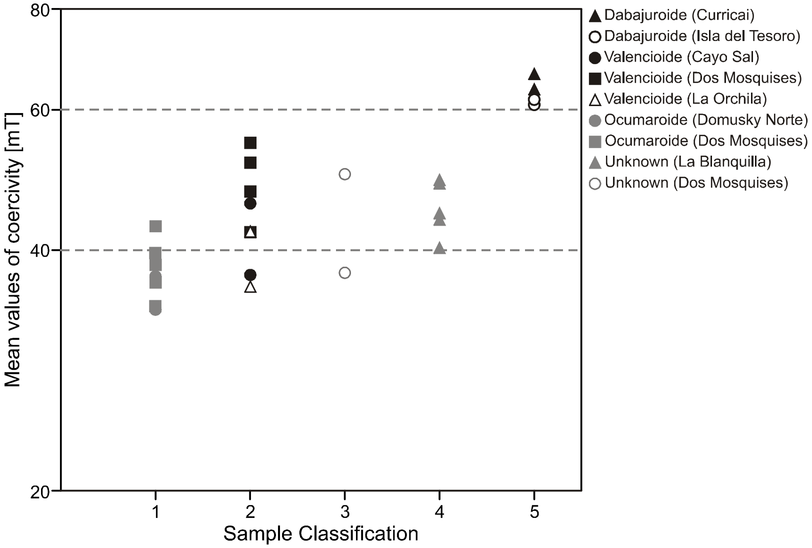

Fig. 6. Mean coercivity values, between 20 and 80 mT, according to the sample classification represented by numbers: 1 - *Ocumaroide* samples (Dos Mosquises and Domusky Norte), 2 - *Valencioide* potsherds (Dos Mosquises, Cayo Sal and La Orchila), 3 - *Unknown* pottery from Dos Mosquises, 4 - *Unknown* ceramics from La Blanquilla and 5 - *Dabajuroide* samples (Curricai and Isla del Tesoro).

The final stage of pottery making (i.e. firing) is indirectly analyzed here via thermomagnetic analyses. These experiments were carried out on representative samples of each ceramic group (Fig. 7). Thermomagnetic cycles for representative *Ocumaroide* and *Dabajuroide* samples (fig. 7a and b) indicate the formation of secondary magnetite, whereas those for *Valencioide*, Dos Mosquises *Unknown* and La Blanquilla *Unknown* (Fig. 7c,d) show no formation of new magnetite phases during heating. Ti-poor magnetite seems to be the chief magnetic mineral in most of these samples with Curie temperatures ranging from about 400 and 525°C for Dos Mosquises *Unknown* and *Dabajuroide* potsherds, and up to about 570°C for *Ocumaroide* and *Valencioide* pottery.

Rada et al. (2008) have previously proposed that the irreversibility parameter for thermomagnetic curves (*IP*) could be employed as an indicator of the amount of organic matter burnt during original pottery firing. Open fires used by most prehistoric potters generally had insufficient ventilation. These conditions produced an atmosphere with a low supply of oxygen preventing entire fuel combustion and causing reducing gas accumulations. Therefore, these ceramics did not get sufficient oxygen and for that reason, the organic matter was not entirely burnt. When thermomagnetic experiments are carried out in the laboratory, the organic remnants result into secondary magnetite formation that generates a cooling curve with an area larger than the heating one. This experimental result translates in an $IP > 0$ (Fig. 7a,b). On the other hand, for open fires with good ventilation, there is enough oxygen to completely burn the fuel creating an atmosphere where carbonaceous matter is wiped out. Potsherds fired in such conditions

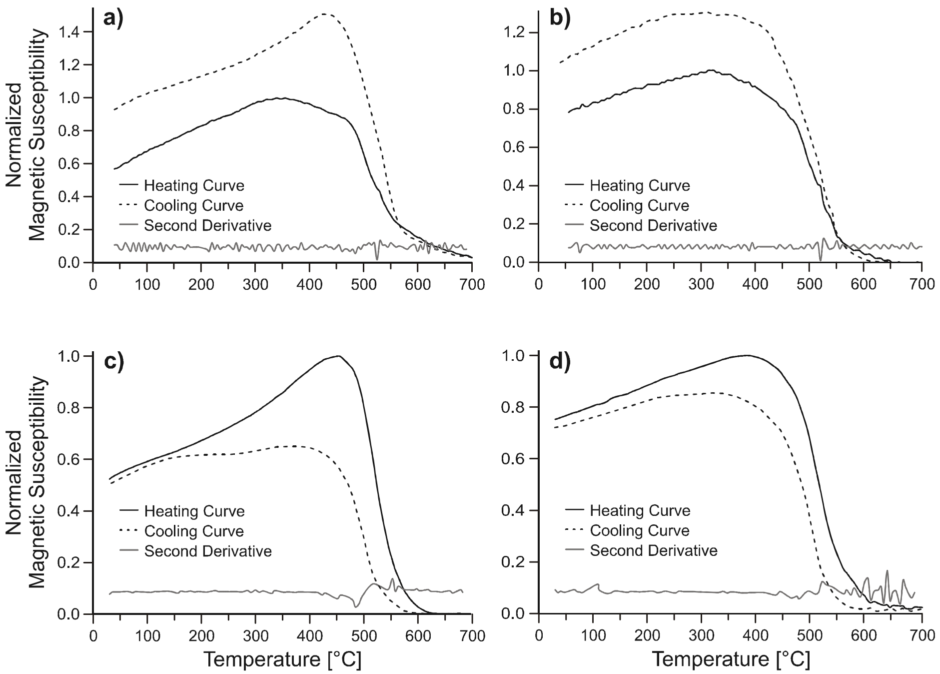

Fig. 7. Normalized magnetic susceptibility curves measured in air for continuously increasing (solid curve) and decreasing (dotted curve) temperatures for representative pottery samples of each cultural group: **a)** *Ocumaroide* (Domusky Norte), **b)** *Dabajuroide* (Curricai), **c)** *Valencioide* (Dos Mosquises), and **d)** *Unknown* (Dos Mosquises). The second derivative for the heating curve is also shown (gray curve).

should display more reversible thermomagnetic behaviors ($IP \leq 0$), with almost no secondary magnetite formation (Fig. 7c,d).

According to our results, the firing atmospheres for *Ocumaroide* and *Dabajuroide* potteries were the most reducing ones ($IP > 0$), whereas the *Valencioide*, La Blanquilla *Unknown* and Dos Mosquises *Unknown* firing atmospheres had sufficient oxygen ($IP < 0$), most likely due to the achievement of better firing/manufacturing techniques. Thus, the *IP* for thermomagnetic cycles, applied to archaeological ceramics analyses, could be used as a cultural index that measures how advanced the firing techniques of Amerindian prehistoric potters were.

Fig. 8 displays the *IP* for a number of thermomagnetic curves, plotted against ages of 37 archaeological samples, that include 14 potteries from this study plus another 23 potsherds from Venezuelan islands and mainland (after *Brandt and Costanzo-Álvarez, 1999*). Ages, determined by radiocarbon and archaeological context, range from 300 BC to 1500 AD. There is a high scattering of the data probably caused by the large errors that exhibit most of the ages available (e.g. El Cedral samples that have been dated on stylistic grounds). The variety of firing atmospheres attained in the open fires used by different Venezuelan Amerindian cultural groups might have also contributed to such a scattering.

However, although far from being clean cut and in spite of the lesser amount of data in the old range date, it appears to be a trend that relates historic times with the advancement of firing techniques; namely a progressive approach of the *IP* from negative values, starting at 300 BC, towards the complete reversibility line of $IP = 0$ at ca. 1500 AD. Most samples, independently of their ages and cultural groups, show *IP* ranging within a swathe that goes from −0.3 up to −0.1. This result suggests that open fires used by Venezuelan Amerindian potters throughout different historical times, had in general enough ventilation and a good supply of oxygen. Only the youngest (between 1200 and 1500 AD) ceramics, from the *Dabajuroide* (Curricai) and *Ocumaroide* (Dos Mosquises and Domusky Norte) groups, have anomalous high *IP* values typical of open fires with poor ventilation and reducing atmospheres.

In Fig. 9 we present, as an example, the TSDC spectra for potsherd samples for the Dos Mosquises Island, polarized at high temperature ~ 300K (*Valencioide, Ocumaroide and Unknown)*. Finally, Fig. 10 compares, for the archeological samples from different

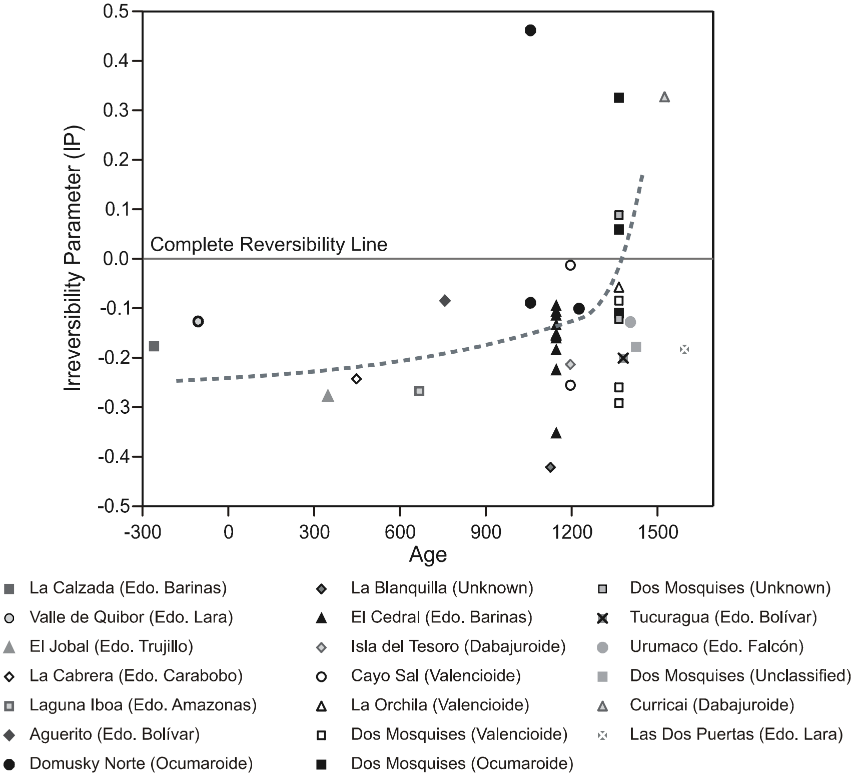

Fig. 8. Scatter diagram of the irreversibility parameter for thermomagnetic curves versus age (^{14}C and context) for 37 archaeological samples that include 14 potteries from this study plus another 23 potsherds from Venezuelan islands and mainland. $IP = 0$ indicates complete reversibility. $IP < 0$ means that the heating curve runs over the cooling one and $IP > 0$ occurs for the opposite case.

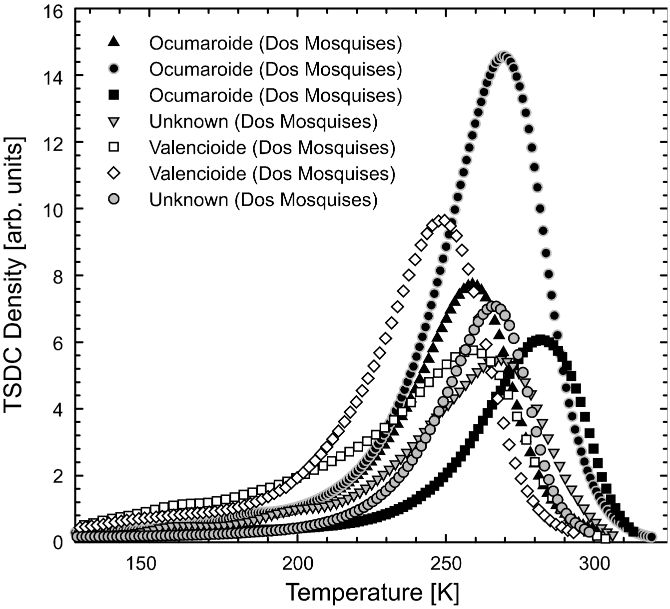

Fig. 9. TSDC spectra for potsherd samples for the Dos Mosquises Island, polarized at high temperature ~ 300K (*Valencioide, Ocumaroide and Unknown*).

Venezuelan Islands, rock magnetic properties (*NRM*) with the TSDC data (maximum current depolarization temperatures of the spectra). This scatter plot suggests a complex nonlinear relationship between two physical independently parameters. Also, the data seem to cluster into two major groups. One of these groups is defined, according to the logarithmic plot, by a narrow temperature window from 280K to 290K and a wide *NRM* range from ~ 8 mT to 200 mT. This cluster includes samples from La Blanquilla *Unknown*, Curricai *Dabajuroide*, Domusky Norte *Ocumaroide* and La Orchila *Valencioide*. Conversely, the other cluster is delimited by a wide temperature window (from 240K to 275K) and a narrow range of *NRM* (from 80 to 200 mT). It includes Isla del Tesoro *Dabajuroide*, Cayo Sal *Valencioide* and Dos Mosquises *Valencioide* and *Unknown* samples. Only two data points, corresponding to the *Ocumaroide* samples from Dos Mosquises, lie on a completely different third cluster. Although there is not a clear explanation for such an anomalous behavior, it is noticeable the fact that independent rock magnetic scatter plots, that provide information about magnetic granulometries and firing atmospheres (i.e. mean coercivities in figure 6 and *IP* versus age in Fig. 8), also show a poorly constrained grouping of the *Ocumaroide* data from Dos Mosquises. Moreover, in some cases such as those presented in Fig. 8 there is a complete departure of these *Ocumaroide* data from the main trends defined by the rest of the pottery samples, quite similar to the behavior shown in the scatter plot of Fig. 10.

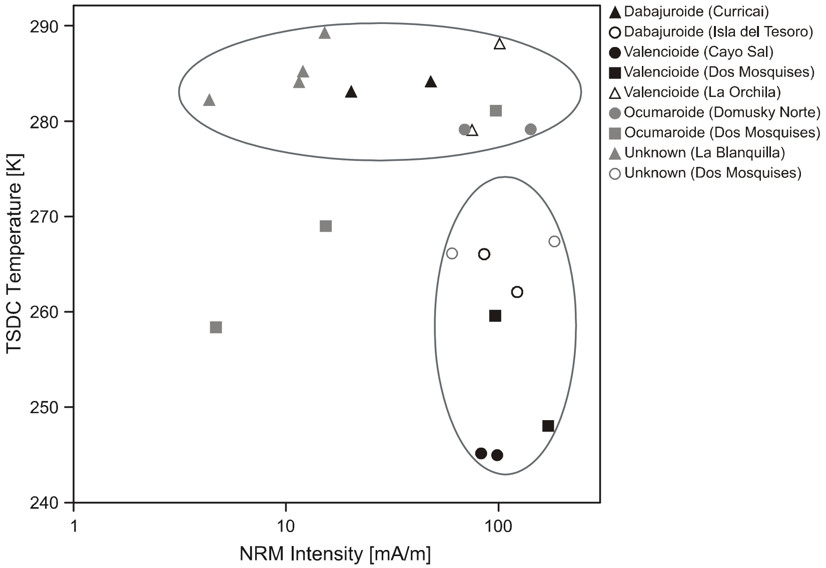

Fig. 10. Scatter plot for TSDC data for 24 samples polarized at room temperature ~ 300K) versus *NRM* values. This plot shows two main clusters of data that go from a wide spectrum of *NRM* values and a reduced range of TSDC data (*Unknown* La Blanquilla, Curricai *Dabajuroide*, unclassified Dos Mosquises, Domusky Norte *Ocumaroide* and La Orchila *Valencioide*) up to a narrow range of *NRM* and a wide range of TSDC values (Isla del Tesoro *Dabajuroide*, Cayo Sal *Valencioide* and *Valencioide* and *Unknown* Dos Mosquises).

The results of hydration and drying treatments on the TSDC spectra for one of the studied samples are depicted in Fig. 11. As can be observed, after dehydration, the dielectric signal (i.e. intensity of the TSDC curves) diminishes. The opposite effect was observed after the rehydration of the sample, i.e. an increase in the dielectric signal and hence of the polarisable entities responsible for the observed spectra. In fact, the area of the TSDC spectrum after dehydration treatments was 44% of the hydrated sample. These results indicate that the observed spectra could be mainly due to the relaxation of moisture trapped in the microporosity of the material (*Costanzo-Álvarez et al., 1999*). It is important to notice that, due to its low equivalent frequency (10^{-4}–10^{-2} Hz) that leads to an enhanced resolution of these relaxations, the TSDC technique has been widely used to investigate hydration properties of heterogeneous systems. In fact, it has been used to investigate in detail the dynamics of low-temperature relaxations of water molecules loosely bound and hydrogen-bonded to chemical groups as carbonyl and silica groups and also the influence of microporous on these relaxations (*Frank et al., 1996*; *Suárez et al., 1999*; *Alcañiz-Monge et al., 2002*, among others). *Alcañiz-Monge et al. (2002)* have studied the phenomenon of water adsorption in microporous carbons using activated carbon fibers (ACF) as the adsorbents. They have found that the water adsorption in the micropore structure of ACFs is influenced by the micropore size distribution. *Suárez et al. (2003)* have also studied the dynamical properties of water relaxation in porous rock

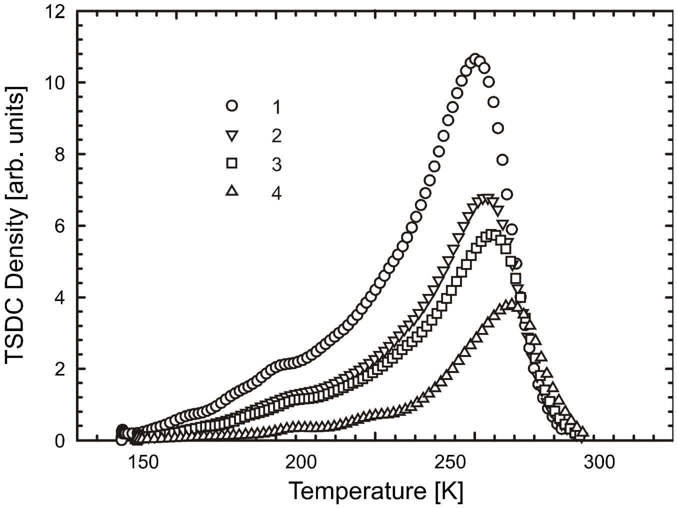

Fig. 11. Example of dehydration treatments for one of the studied sample. For dehydration, water was evaporated in vacuum ($p \approx 10^{-4}$ Pa) at room temperature and the spectra were recorded after (1) 30 min, (2) 26 h, (3) 75 h of outgassing, and (4) after heating to 320K during 5 min followed by 24 h of drying.

samples. They have found that the TSDC temperature polarization spectra ranging from 100 to 300K, were associated to water clusters confined into the pores. In the present work, the relaxations seem to respond adequately to petrophysical properties such as the mean pore radius. In poorly consolidated rocks, pore characteristics will be related to granulometric parameters. Therefore, it could be argued that the main correlation shown in Fig. 10 is due to the fact that both, dielectric and rock magnetic data, are linked to pore-related features. At temperatures of ca. 350°C, the edges of the clay start to soften and to adhere to each other (sintering). Since this process does not necessarily affect magnetic minerals in the same way it does in clays, a less defined correlation between dielectric and rock magnetic data should be expected as firing temperatures approach to vitrification levels. However, in most cases, Venezuelan Amerindian ceramics are relatively non vitreous wares. In other words, in this kind of materials clay particles have suffered only partial fusion of their edges due to incipient heating at peak temperatures lower than 850°C.

Finally, it is important to point out that in this study we have integrated the results of previous works by *Brandt and Costanzo-Álvarez (1999)*, *Costanzo-Álvarez et al. (2006)* and *Rada et al. (2008)*. This study was intended to gain more insight regarding the different manufacturing techniques used in Prehistoric Venezuelan Amerindian potters. Previous studies in Venezuelan potsherds suggested a possible association between magnetic parameters and geographical location. Our results indicate that the magnetic and dielectric parameters allow discriminating manufacturing techniques and ceramic provenance, aspects that are related to the cultural group. Particularly, the mean coercivities seem to be the magnetic parameter that better discriminates among the cultural groups. To obtain these values, we have applied for the first time in this kind of studies, an alternative method to decompose IRM acquisition curves based on a direct signal analysis of the curve. Also the analysis of a greater amount of samples (37) from different archeological places confirms the *IP* parameter as an indicator of the evolution of firing techniques, as was previously proposed by *Rada et al. (2008)* but based on the analysis of three samples from the same archeological site.

5. CONCLUSIONS

We have performed a petrographic, rock magnetic and dielectric characterization of 27 fragments of prehistoric Amerindian ceramic bowls, from 5 different cultural groups excavated in Los Roques and Las Aves Archipelagos, La Orchila and La Blanquilla islands in Venezuela, attempting to have an insigth about the different manufacturing techniques used by Prehistoric Venezuelan Amerindian potters.

Our results indicate that mean coercivity values seem to be the best quantitative means to classify the distinct stylistic groups of these samples. The mean coercivities were obtained after the deconvolution of the IRM curves using a DSA-based method. This analysis showed that magnetic minerals with mean coercivities in a range between 20 and 80 mT are present in all the samples. Previous petrographic analyses (*Costanzo-Álvarez et al., 2006*; *Rada et al., 2008*) revealed some differences among these ceramics that appear to agree, in some extent, with the mean coercivity distributions plotted according to their stylistic classification.

The irreversibility parameter (*IP*) was obtained from the thermomagnetic curves of these archeological pottery samples. The analyses of these values suggest that $IP > 0$ can be associated to the most reducing firing atmospheres, whereas $IP < 0$ reflect firing atmospheres with sufficient oxygen, most likely due to the achievement of better firing/manufacturing techniques. Hence the *IP* factor could be used as a cultural index that measures the development of the firing techniques employed by the Amerindian prehistoric potters. Indeed, these values were plotted versus age (between 300 BC to 1500 AD) for 37 archaeological samples from Venezuelan islands and mainland. There is a rather unclear increasing trend, from negative values towards the complete reversibility line of $IP = 0$ at ca. 1500 AD. Most samples, independently of their ages and cultural groups, have *IP* between -0.3 up to -0.1 suggesting that open fires used by Venezuelan Amerindian potters had, in general, enough ventilation and a good supply of oxygen.

A scatter plot that compares rock magnetic (*NRM*) with TSDC (maximum current depolarization temperatures) data suggests a complex non-linear relationship between these two physical independently parameters, most likely due to the fact that both of them are linked to pore-related features.

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