# ESTIMATE OF FIRING TEMPERATURES THROUGH BONE-BASED CHALCOLITHIC DECORATED POTTERY

*C. Odriozola* and J. M. Martínez-Blanes*

Instituto de Ciencia de Materiales de Sevilla-CSIC, Avd. Américo Vespuccio 49, 41092 Sevilla, Spain

Guadiana River Chalcolithic middle basin (Badajoz, Spain) pottery was in many cases decorated with bone, which suffers a hydroxyapatite to β tri-calcium phosphate transformation while firing. The evolution of physico-chemical characteristics of bone decorations and experimentally heated fossil bone as a function of temperature through 1) major XRD planes, and 2) OH librational mode at 630 $cm^{-1}$ in the FTIR spectra let us establish a correlation between the physico-chemical features and firing temperature, allowing the estimate of firing temperatures for bone decorated pottery. What is a reliable criterion to differentiate over potters behavior and skill during the pottery production.

***Keywords:*** *bone-based decoration, chalcolithic, decorated pottery, firing temperatures*

## Introduction

Within the context of pottery technology, one of the applications of scientific methods of analysis is the determination of firing temperatures employed in the production of ceramic vessels [1]. The firing temperature of prehistoric pottery are of major interest because they provide information on the performance of the bonfire-kilns used and, on the firing behaviour of the potters understood as a segment of the production process within the behavioural chain [2]. Apart from its direct archaeological significance, this information is valuable when full-scale replicas of pottery firing schedules are used in order to acquire further data on the technology and econometrics of pottery production on recent prehistory.

Traditional studies of firing temperatures estimates the firing temperature either through the study of the minerals and the new-formed mineral phases which result from the firing process by means of X-ray diffraction and thermal analysis, as well as by petrological examination. The mineralogical temper scale can only indicate an upper or lower limit for the firing temperatures, on the basis of the new-formed mineral phases with temperature – wollastonite, mullite, ghellenite, cristoballite, etc. These upper and lower limits seems to be a poorly approach, which indeed does not allow the formation of ceramic temperature-based groups, because it can not discriminate within the different temperatures that undergoes in most of the mineral phase transformation process, in result of what one can expect spans as 50–200°C [3], being a greater accuracy extremely rare.

In this paper we have developed a protocol to estimate the firing temperature of pottery, based on the evolution of the hydroxyapatite pattern upon temperature-bone paste incrusted as a part of the decoration of the Bell beaker pots within other decoration forms of 3rd millennium BC prestige pottery [4–6] – by traditional analytical techniques – XRD and thermal analysis. Monitoring the transformation process of hydroxyapatite to β-tricalcium phosphate with temperature, and based on the evolution of the width of the hydroxyapatite main XRD peaks: *hkl* 211, 122, 300 and 202, we can reliably estimate the firing temperature with much more accuracy than the estimate based on pottery temper transformation.

We must keep in mind that we are not estimating the real firing temperature of the analyzed pottery sherds, what we are really estimating is the equivalent firing temperature – i.e. the firing temperature, which if maintained for about an hour, is equivalent in its effect on the mineralogy and microstructure to the actual firing temperature maintained for only a few minutes [3]. In order to obtain significant equivalent firing temperatures we have submitted the samples and reference materials to heating schedules similar to those registered anthropologically, defined as differential heating rates since Smith [7] cleared out that structure is by no means the major parameter of firing technologies – i.e. what allows the identification of distinct 'simplified' firing behaviors is the schedule and scale. What makes the equivalent firing temperatures more equivalent if we can develop heating rates and firing schedules similar to those registered during fieldworks on actual primitive societies.

* Author for correspondence: carlos@icmse.csic.es

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*Akadémiai Kiadó, Budapest, Hungary*
*Springer, Dordrecht, The Netherlands*

As usual, many of the Bell Beaker pots recovered are decorated with a white incrusted paste, which has been characterized principally as calcium carbonate in France [8], NE Spain [9] and the Spanish Meseta [10], whereas recent studies made over the Beaker pots from the middle Guadiana River basin have shown the use of a bone paste [11].

We have studied the bone-based decorated pottery from two of the largest 3rd millennium BC settlements throughout all of Iberia that are found within the Spanish middle Guadiana River basin (Badajoz, Spain) (Fig. 1): La Pijotilla (80 ha) [12] and San Blas (30 ha) [13]. Although we have worked-out with bone decorated pottery the scope of this work goes further and can be used to determine firing temperatures of bone-tempered pottery from any historical period, and applied even in other scientific fields as forensic science, for determining more accurately the cremation temperature of bone specimens than by color code or as a real model for the thermo-chemical characteristic of bone to compare with new biomaterials in material science field [14, 15].

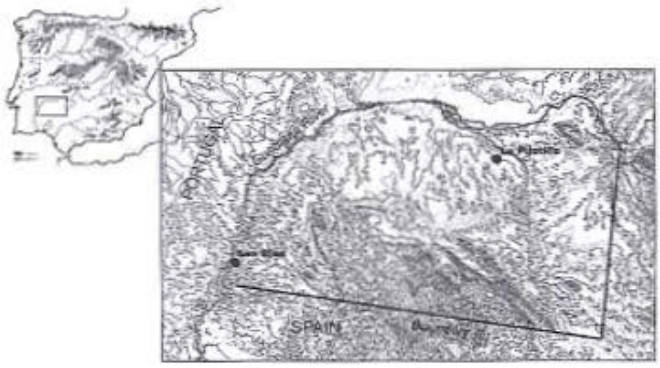


**Fig. 1** The middle Guadiana River basin landscape within Iberia

*Pottery technology*

The technology used by the chalcolithic potters of Southwest Iberia in the decoration stage that follows the drawing of the decorative motifs and themes by incisions or impression involves the application over the gap left by the incisions and impressions of an inlay made of a thick, soft, moist paste, produced by mixing dry powdered bone with a liquid, either water or a fatty agent. The incrustation of this bone paste, as argued by Salanova [8] and recently by Odriozola and Hurtado [11], was carried out before firing, what suggest that the bone paste was made with fresh bone, or cooking bones which may not have started the hydroxyapatite to β tri-calcium phosphate transformation process [16, 17].

The bone paste was incrusted before the firing of the pot and, as the exclusive result of the interactions that took place upon firing; the bone suffered a transformation process to β-tricalcium phosphate at around 600–900°C. This transformation is responsible for the materialization of the FTIR band at 630 $cm^{-1}$. These stages are otherwise responsible for the sharpening of the peaks in the XRD diagram [*hkl* 211, 112, 300]. In this sense, we are able to see different width in the XRD peaks [*hkl* 211, 112, 300] due to the different conditions that took place in the manufacturing processes of these decorated pots. So far it is possible to think of the thermally altered bone as a by-product of the firing behavioural activities or potter skills [18] in the control of the firing conditions.

## Experimental

*Materials*

29 samples of different species (continental style Bell beaker, incised and impressed pots) of bone-based incrusted paste pottery are studied in this work. The decorative techniques of all the incised Bell beaker sherds correspond to continental style beakers. In the case of non-Bell beaker decoration, the technique can be either incised, impressed or a mixture of both, in which case the impressions are generally dots and in few cases genuine impressions.

Some bone artefacts – recovered from San Blas site – are used in this paper as reference material in order to compare their physicochemical characteristics with those of the incrusted bone pastes. We have mainly use an unidentified faunal bone found in trench E9, near a wall bastion at San Blas and a little bone bowl with continental style beaker decoration to perform the experimental firing schedule.

*Methods*

FTIR spectra were collected as a test to ensure the bone nature of the samples as proposed by Odriozola and Hurtado [11] and to discard a non-biogenic nature of the incrusted paste. Thus FTIR spectra were collected from the bone-based incrustations using a Nicolet 510P Fourier Transform infrared spectrometer with a DTGS detector. Data was recorded in the transmission mode from pellets of the powdered samples dispersed in KBr, by co-adding 64 scans at 4 $cm^{-1}$ resolution. The system was previously $N_2$ purged to reduce atmospheric $CO_2$ and $H_2O$ absorption.

The samples were studied by X-ray diffraction (XRD), and thermal analysis (TG/DTA) in order to monitor the transformation process suffered by the bone – hydroxyapatite as the major mineral component of bone [19] – to β-tricalcium phosphate when fired. On the suggestions of Odriozola and Hurtado [11] that pointed out a possible correlation between

the firing temperature or maximun-firing temperature reached by a pot during its behavioural activities and the evolution of its XRD pattern with temperature by the decrease of the FWHM of the major diffraction planes of bones [20].

In order to try out this correlation 18 aliquots of each bone specimen used as reference material were placed in a ceramic crucible and heated isothermally in a static linear heating schedule of 10°C $min^{-1}$ in a RHF 1600 Carbolite Furnace. Each aliquot was heated in the furnace using this heating rate and cooled out of the furnace once they have reached the desired temperature (between 100 and 500°C in 100°C steps and between 500 and 1150°C in 50°C steps) without soaking time. Later in turn X-ray diffractions patterns of the heated aliquots were recorded from a Philips X'Pert Pro diffractometer with a θ–θ goniometer, using the following measurement conditions: 1/8° for divergence slit and 1/4° for antiscattering slit, with a copper anode at 40 kV and 40 mA (λ=1.5406 Å) equipped with a X'Celerator detector and a Kβ filter (Ni). The diffractograms were recorded in the scanning ranges 2θ from 29.5 to 35.5° with a step size of 0.033° and a counting time of 200 s per step. The powdered white paste was suspended in ethanol and poured into a Zero background holder (silicon single crystal) upon the evaporation of the solvent.

The deconvolution of hydroxyapatite major X-ray diffraction planes *hkl*: 211, 112, 300, 202, and the measurement of FWHM was developed with the Philips Profit 1.0c software package for both: experimentally heated bone samples – used as reference material – and the archaeological recovered bone-based paste – coming the 3rd millennium BC decorated pottery. Thus deconvolution provides a precise measurement of the evolution of the FWHM of the samples and the reference material.

We have calculated the regression curve that fits our FWHM reference material data, achieving an equation where to substitute the experimental FWHM values of the bone-based paste and later in turn calculate the equivalent firing temperature for each pottery sherd.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out simultaneously in an automatic thermal analyzer system (Setaram TG-DTA 92). Samples of about 30 mg were packed loosely into a platinum holder and were thermally treated at a heating rate of 10°C $min^{-1}$ in air flow (400 $cm^3$ $min^{-1}$). The mass loss was estimated graphically and the temperature range was found as the intersection with the TG curve of the bisecants to its respective tangents.

Anthropological studies carried out over actual primitive societies have shown that neither the maximum temperature reached nor the thermal profile of the firing can be used to differentiate open fire structures from kilns [7, 21]. As Smith [7] pointed out the difference between the thermal profiles of firings is the behaviour of craftsmen operating the firing. Two different behaviours were detected in extensive fieldworks [7, 21] with independence of the firing structure type, and fuel used. Based on the firing schedule, two types of firings can be characterized, those firings with a very fast heating rate, short soaking times, and maximum temperatures of 700–800°C; and those characterized by slow-medium heating rates, moderate soaking time, and maximum temperatures of 800–900°C.

We have chosen the medium-low heating rate (10°C $min^{-1}$) – without soaking time except for the one at 1150 that was cooled down in the furnace – for the experimentally heated bone on the basis that the firing structures found at San Blas site at different spaces (characterized as bonfire pits with medium-heavy insulation).

The chemical analysis of the white incrustation was obtained with an EDS EDAX Eagle III μ-XRF. After focusing with an optical microscope, a 40 μm area was analyzed using 40 kV $K_\alpha$ radiation produced by an Rh tube. Quantification was performed in the standardless mode provided in the software of the instrument in order to avoid misleading results caused by the non-homogeneous nature of the samples. Quantitative data were reported after averaging five measurements.

## Results and discussion

The presence of the FTIR band at 630 $cm^{-1}$ corresponding to hydroxyl librational mode, jointly with the X-ray diffractograms (hydroxyapatite: ICDD pdf 9-432) has ensured the burned-bone nature of all the studied incrusted paste samples [11].

We have tried out to correlate the area of the hydroxyl librational mode band at 630 $cm^{-1}$ with temperature and crystallinity as suggested Odriozola and Hurtado [11]. But unfortunately due to sampling considerations [22] the only fact is that the appearance of this band trusts that samples are heated bone; and no correlation has been found between the area of this FTIR band and the crystallinity or the temperature reached by samples.

The evolution of the reference material major X-ray diffraction pattern planes – *hkl*: 211, 112, 300 – with temperature shows a correlation between temperature and FWHM [13] what indeed indicates that higher crystallinities are reached with higher firing temperatures. The materialization of this relationship: firing-crystallinity is appreciated in Fig. 2 by the sharpening of the X-ray diffraction peaks with increasing temperature.

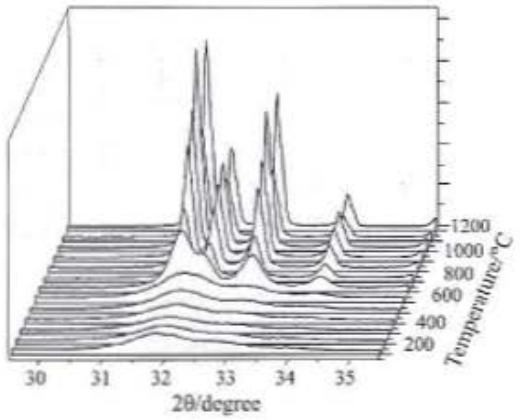


**Fig. 2** 3D plot of the evolution of X-ray diffraction pattern of hydroxyapatite (reference material) to β-tricalcium phosphate

It can be noticed in Fig. 2 that a mineral phase transformation from hydroxyapatite bone mineral (dahalite) to β-tricalcium phosphate ($Ca_9(PO_4)_6$ with apatitic structure) starts around 600°C [5, 13]. What entails a shape transformation on the X-ray diffractogram, where the overlapping broad peak corresponding to *hkl* planes: 112 and 211 evolves with temperature to two sharp and well defined peaks, what in turn allows the measurement of FWHM of the four major planes of the XRD pattern with temperature (Fig. 3).

It has been necessary to deconvolute XRD patterns where the *hkl* 112 and 211 were overlapped in order to measure the FWHM of these peaks. However, no measures of FWHM were made for temperatures under 500°C due to low levels of precision in the deconvolution process, as can be seen in Fig. 3.

We have proceeded to deconvolute and measure FWHM over the XRD pattern with the Philips Profit 1.0c software package. The line shape selected for the fitting is Pearson VII curve (E1), where the fitting parameters: diffraction angle 2θ (*hkl* 211: 31.774°; *hkl* 112: 32.197°; *hkl* 300: 32.902° and *hkl* 202: 34.049°), as well as the line shape value (1.6), were fixed; and intensity, FWHM and asymmetry were optimized to obtain the best fit.

$$y=\frac{1}{\left[1+4\left(\frac{x-x_c}{\mathrm{FHWM}}\right)^2\left(2^{1/\lambda}-1\right)\right]^{\lambda}} \qquad \text{(E1)}$$

where $I$=Intensity, $x_c$=peak position (2θ) and λ=value of the shape parameter.

Once we have the FWHM values of the planes *hkl*: 211, 112, 300, 202, obtained from the deconvolution and measurement of XRD peaks, we have plotted FWHM values *vs.* temperature and proceed to fit the values. Obtaining a fitting equation for our reference material (Fig. 4). The curve that fits better our values was a sigmoidal, which is the typical graphical expression for most of the solid-state reaction kinetics (E2).

$$y=\frac{A_1-A_2}{1+e^{\frac{x-x_0}{d_x}}}+A_2 \qquad \text{(E2)}$$

where $A_1$, $A_2$, $x_0$ and $d_x$ are fitting parameters; $x$ is FWHM and $y$ is temperature.

It can be observed in Fig. 4 that some plots have less data points, this is due to the proximity of *hkl* planes 211 and 112 and the difficulty on an accurate deconvolution what indeed forced to remove some unreliable data points from the fitting. However (E2) provides really good fitting for all of the four peaks fitted (*hkl* 300: $\chi^2$=0.00028; $R^2$=0.99343; *hkl* 202: $\chi^2$=0.00029; $R^2$=0.98603; *hkl* 112: $\chi^2$=0.00013; $R^2$=0.99817 and *hkl* 211: $\chi^2$=0.00015; $R^2$=0.99683). Thus the accuracy of the fitting on each of the four peaks provides an accurate estimate of the temperature.

While monitoring the transformation process to β tri-calcium phosphate, we did not found relationship be-

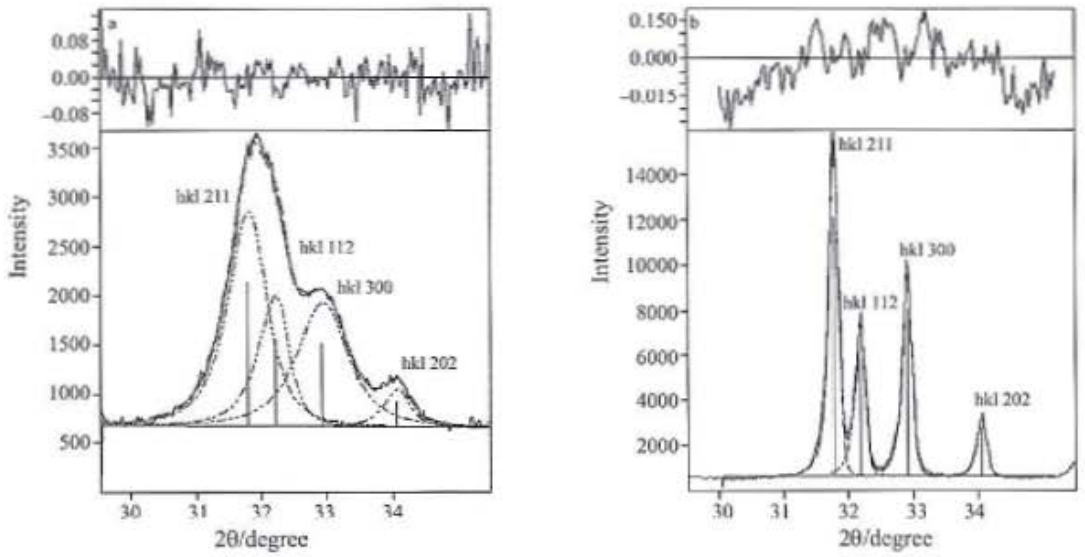


**Fig. 3** X-ray peaks deconvolution of the reference material; a – XRD pattern at 600°C; b – XRD pattern at 900°C

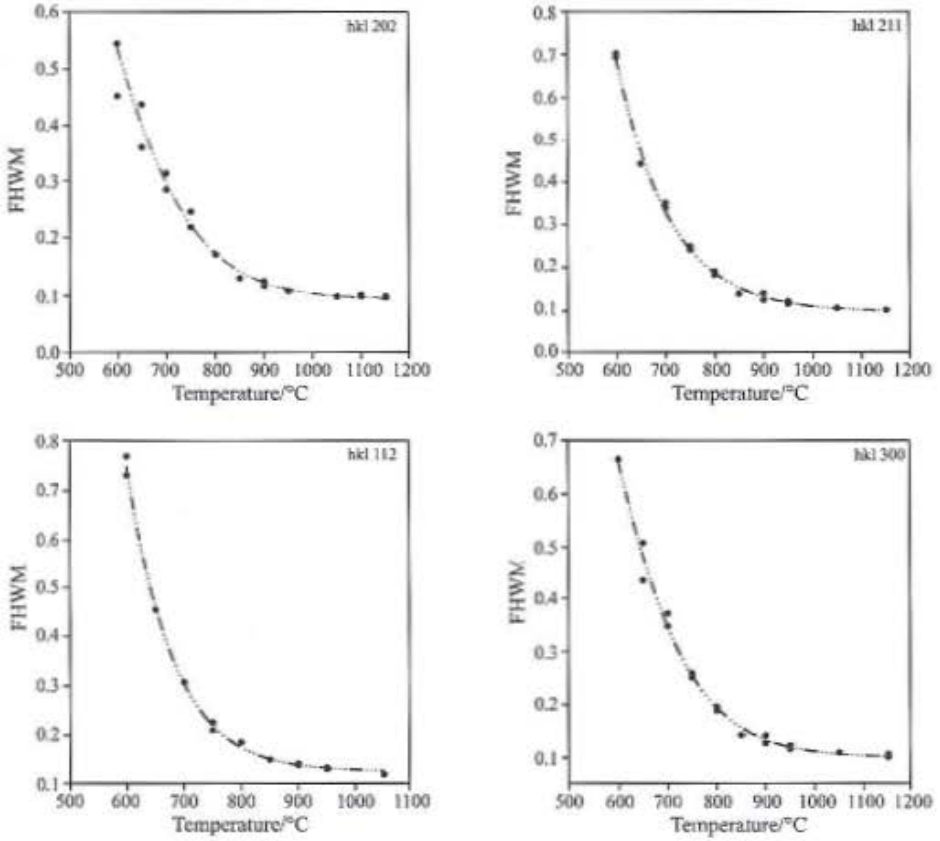


**Fig. 4** Scattered plot of FWHM *vs.* temperature. Showing a sigmoidal fit

tween the Ca/P ratio and the transformation of bone with temperature. A priori, it was suggested a decrease in the Ca/P ratio with temperature [23]; experimentally measured values with EDS X-ray microprobe show that this ratio stays constant with temperature (1.89 mass%) for all the heated aliquots. And that the variations among samples is due to the different sampling area – tooth, large bone, etc. – or in the bone-based incrustation to the different animal species of bones used. But it also depends on the bone tissue calcification and age of each individual, for human – healthy female and male between 15 and 55 years old – fresh femoral neck bone Ca/P ratio ranges from 1.86 to 2.48 mass% [24].

In Fig. 5 it is shown the TG-DTG and DTA of the reference material were possible to see how bone loses around 25% of its mass when heated, this loss is not correlated with the Ca/P ratio that stays constant as suggested by Grupe and Hummel [23], in turn it is correlated to a water loss, in a first stage, the combustion of organic matter in a second one, and finally the loss of carbonate groups at around 600°C, (the carbonate loss is about 5% what indeed matches the mean value of carbonate content in bone tissue).

It is time now to calculate the equivalent firing temperature of our samples, by just replacing the measured FWHM value of the samples in the Eq. (E2)

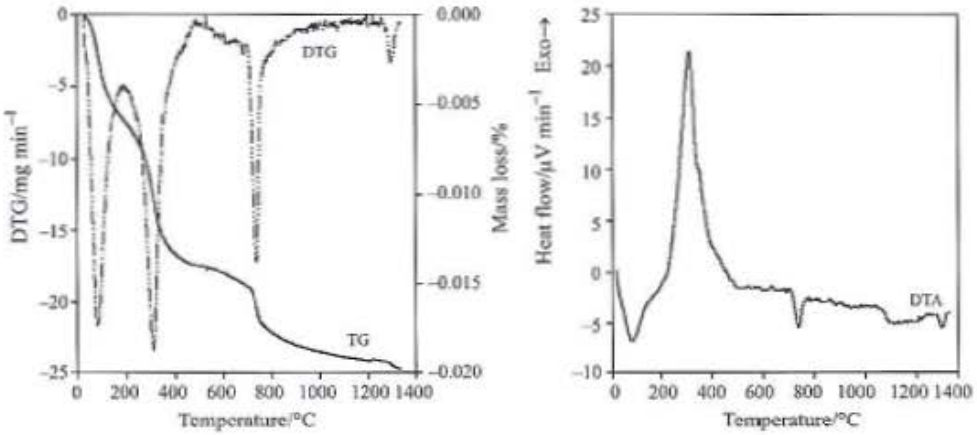


**Fig. 5** TG-DTG and DTA plots of the reference material-fossil bone

resulting a temperature for our pots. To calculate the equivalent firing temperature, we have calculated it for each plane, and taken the mean value of these four values as the equivalent firing temperature.

The real difficulty in the pottery manufacturing process lay in the control of the firing conditions. In many cases, this control would have depended upon the potters behavioural activities [25], including the interpretation of the sensorial characteristics of the firing: when is the pot fired, does it need more fuel, is the colour not red or black enough, etc. and would have varied according to the potter's skill, age and experience [18]. The presence of burnt bone in different degrees based on the FWHM of XRD pattern is probably due to the potter's behaviour or skill in the control of the firing conditions.

Specialised potters of actual primitives societies produce really standardized pots in shape and chemical composition. Bell beaker pots are a prestige item and therefore should be considered a specialized attached production. One would expect of such a production a really homogeneous product with low degrees of variation. What includes the firing conditions – schedule and scale – as a segment of the behavioural chain. Thus the calculated firing temperatures should be grouped around a temperature, depending on the number of specialized potters, what in turn reflects the organization of production.

The plotted histograms (Fig. 6) of firing temperatures of San Blas and La Pijotilla follows two tendencies: one centred about 700°C and a second one about 825°C. Contrary to what one would expect we found a bimodal tendency that do not match neither a concrete site nor a style. In turn we found a well-defined firing condition in San Blas with little variation. While in La Pijotilla we found two tendencies in firing conditions.

This variation on the firing patterns of La Pijotilla (mean 771±45 and 820±15°C) can be explained by

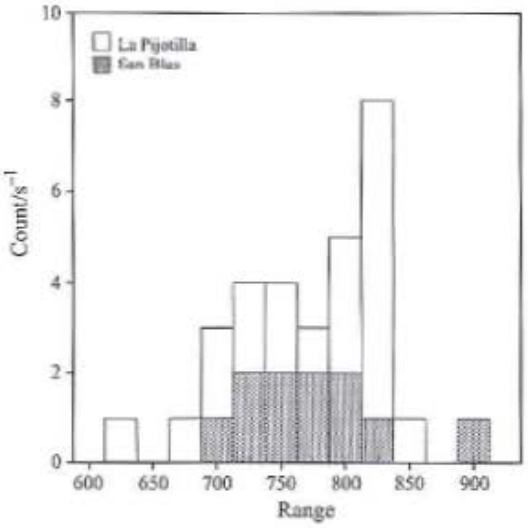


**Fig. 6** Temperature histograms of La Pijotilla and San Blas sites

several factors that affect the recovered sherds at this site: *i*) they are all survey sherds and therefore they can be a product of several workshop upon time (Bell beaker phenomena lasted for several centuries); *ii*) they do not follow a stylistic pattern; and *iii*) difference in firing conditions may reflect different provenances. While in San Blas all sherds are continental style Bell beaker pots coming from the same chronological context and therefore the firing conditions are much more homogeneous (mean temperature 777±54°C), although the number of analyzed sherds is small they are all the sherds found at these two sites.

## Conclusions

The increase of bone crystallinity and its mineral phase transformation with temperature can be used as a protocol for achieving firing temperature of bone-based decorated pottery as shown above. It provides accurate measures of firing temperatures based on the evolution of the XRD peak FWHM with temperature, this protocol provides a more accurate firing temperatures than the mineralogical temper scale that can only indicate an upper or lower limit, based on the new-formed mineral phases with temperature.

This accuracy accounts for a mean standard deviation value of 60°C what can be envisaged as a good accuracy if compared with the mineralogical temper scale accuracy.

This simple protocol can be straightforward used in the archaeological research; as it provides a useful and reliable criterion to differentiate between productions and their organization.

Within San Blas site it is possible to observe how only a firing behaviour is detected, while La Pijotilla we have detected two firing behaviours. This can be explained in terms of style, chronology and production organization.

Further research must be done by incrementing the number of samples and studied sites in order to really try out this protocol in a more complex landscape formed by more sites.

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