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Pottery firing temperatures: a new method for determining the firing temperature of ceramics and burnt clay

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A B S T R A C T

A new method for determining the maximum firing temperature of ceramics and burnt clay is presented. The technique relies on measuring the magnetic susceptibility on a step-wise re-fired sample. The validity of the method has been tested by determining firing temperatures of two sets of clay samples fired at temperatures ranging from 400 to 1000 °C. Aliquots of the same samples have been studied petrographically by optical microscopy on thin sections and analyzed by powder X-ray diffraction in order to monitor structural and mineralogical changes as a function of temperature. The method is demonstrated on samples from four geographically widely different sites and it is applied to a larger set of ceramics of Late (ca. AD 900–AD 1450) and Inca (ca. AD 1480–AD 1532) periods from the Northwestern Argentine region, dating to a limited period of time prior to the fall of the Inca Empire. The method is shown to be a powerful tool in revealing archaeological information about the change in firing technologies in the pre-Hispanic societies in the Andean area through time.

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1. Introduction

There has been a long debate about how to determine the maximum firing temperature of archaeological ceramics and the archaeological meaning that can be ascribed to such data (see e.g. Gosselain, 1992; Livingstone Smith, 2001; Tite, 1995, 2008). It is agreed in the literature that the simplistic ‘open firing’ versus ‘kiln firing’ discussion leaves out much of the complexities of the firing procedure, although either of these assumptions may be viable or at least practical archaeological approximations. In general the analytical methods applied to determine firing temperatures involve establishing a relationship between the firing temperature and changes in mineralogy and possibly in the microstructure of the pottery, such as porosity, clay matrix, progressive sintering, and vitrification (e.g. Tite, 1995: 37–38). The maximum firing temperature experienced by a vessel is important archaeological information pertinent to understanding the technological procedures applied by the ancient potters (Rice, 1987; Rye, 1981). The maximum firing temperatures are relevant in relation to establishing which kiln technology was utilized in a society and in order to distinguish between such technologies either in space or in time. Examples of the archaeological uses of firing temperature information are the introduction of Spanish colonial reign in Peru (Chatfield, 2010), the continuity of clay source use in Italy (Terenzi et al., 2010), differences in geological clay sources in Bulgaria (Jordanova et al., 2001), and for assessing duration, firing temperature and oxygen tension in ceramics production in Italy (Benedetto et al., 2002).

The firing temperature of archaeological ceramics has been estimated by a number of different methods. Amongst the methods working on a larger temperature scale are: 1) observations of the thermal expansion and dilation of regularly shaped samples of the ceramics (Roberts, 1963; Tite, 1969); 2) measurements of the coercive force and saturation magnetization (Coey et al., 1976); and 3) X-ray diffraction measurements of the layer spacing in the clay mineral illite (Maggetti and Rossmanith, 1981). Other methods have also been invoked, such as the study of sintering and vitrification of the clay matrix by observing the microstructure by SEM (Chatfield, 2010; Maniatis and Tite, 1981; Musthafa et al., 2010; Velraj et al., 2008); monitoring the intensity of Mössbauer lines (Hayashida et al., 2003a, 2003b; Lumbra...
et al., 2003; Shimada et al., 2003a, 2003b, 2003c, 2003d); the use of colour coordinates (Mirti, 1998; Mirti and Davit, 2004); ESR signal, penetration of high frequency radiation, and Vickers hardness. Comprehensive reviews are provided by Heimann and Franklin (1979) and Tite (1995, 2008). Disadvantages of several of the methods include limited accuracy and applicability over a limited temperature range only. In general, any method is also susceptible to the uncertainty introduced by the firing history. Besides the maximum temperature, this includes parameters such as the heating rate, duration of the firing, the cooling rate, and possibly also re-firing events. Furthermore, the temperature can be a complicated function of time, which may not necessarily constitute a good approximation to the preferred laboratory step-function.

This paper describes a novel method for the determination of the maximum firing temperature for ceramics and burnt clay. The method can be applied to samples as small as a few milligrams of archaeological ceramics. Results of the method have previously been reported (Rasmussen, 2003; Rasmussen and Hjermind, 2006), but the method itself has not been described and validated in detail. Here we report a validation experiment extending from 400 to 1000 °C from which we estimate an uncertainty of the method of ±25.8 °C (1 sigma). In order to further validate the method, it has been applied to 4 sherds from widely different archaeological sites around the world, and to 36 sherds coming from six different but closely spaced archaeological sites located in the Southern Abaucán Valley in the Province of Catamarca, Argentina.

2. Description of the method

The main raw material for ancient ceramic production is often clay, which consists of clay minerals mixed with a variety of other minerals. Upon firing they undergo characteristic reactions such as dehydroxylation, decomposition, and transformation. Precisely which stable and/or metastable neoformation phases are produced during the firing depends upon the mineralogy of the raw material, its grain-size distribution, maximum firing temperature, duration of the firing, and the redox conditions in the atmosphere of the kiln (Cultrone et al., 2004; Jordan et al., 2008; Moropoulou et al., 1995). The magnetic properties of a ceramic vessel often changes upon firing due to a combination of destruction of some of the original minerals and the occurrence and growth of neoformation mineral phases. A wide range of clay compositions are found worldwide, which makes the accurate determination of firing temperature inherently difficult. However, in most cases a change in the mineralogical assemblage is introduced upon firing and very often these changes cause a change in the magnetic susceptibility of the bulk sample. The magnetic susceptibility is a material parameter defined as the proportionality factor (χ) between the induced magnetization (J) and the externally applied magnetic field (H): J = χH. The magnetic susceptibility is dimensionless in the SI-unit system.

The size of the change in magnetic susceptibility is a function not only of which minerals are destroyed and which are formed, in each case depending on the passing of a specific threshold temperature, but also on the grain-size which the neoformation minerals grow to. Once the ceramic vessel is cooled from its maximum firing temperature, the processes of neoformation of minerals will normally not be reversed, and the high temperature mineral assemblage will to a large degree be preserved after archaeological time. It is therefore from the outset likely, if not completely predictable how, that the maximum firing temperature can be read off a curve of the magnetic susceptibility as a function of re-firing temperature.

2.1. Details of the method

A solid sample of ceramic material is dried for at least 24 h at 120 °C, cooled, weighed and measured in quadruple for magnetic susceptibility on a Kappabridge KLY-2 magnetic susceptibility meter. The susceptibility of the empty sample holder is measured and subtracted from the sample values. The Kappabridge is calibrated twice a day using a standard sample of known susceptibility. Generally the reproducibility is better than 1% relative and the limit of detection is ca. 1 x 10^{-6} SI-units. The average magnetic susceptibility is calculated using the sample weight and assuming a standard density of 2.5 g cm^{-3}. A constant density is assumed because it is inherently difficult to measure density of oddly shaped archaeological ceramic samples and because an error in the estimation of the density will only parallel-shift the curve of the magnetic susceptibility versus re-firing temperature by a fixed amount, which will not in any way affect the determination of the firing temperature as described below. The method has been used for samples between 10 mg and 5 g in weight. The measuring sequence starts by firing the sample in a Carbolite 1100 CWf oven at 200 °C (±1 °C) for 24 h, after which it is cooled to room temperature and measured in quadruple for magnetic susceptibility. This treatment is repeated in 20 °C steps from a temperature of 200 until ca. 1000 °C, for increasingly smaller times, ending up with a firing time of 30 min for temperatures above 900 °C.

The susceptibility data are subsequently plotted as a function of the re-firing temperature. Examples of such graphs are shown in Fig. 1; the samples are taken from widely different archaeological sites in Iran, Denmark, Argentina, and Israel. In the plot, the sudden discontinuity marks the point when the original maximum firing temperature is exceeded. A similar behaviour when superseding the original firing temperature, but with changes in the colour coordinates, has previously been reported by Mirti (1998). In order to establish this threshold temperature unambiguously and more accurately than just attempting to read it off the susceptibility versus temperature curve, the square of the first derivative is plotted as a function of stepwise re-firing temperature. The derivative is calculated as (S_i - S_{i-1})/△T, where S_i and S_{i-1} are two consecutive susceptibility measurements and △T is the temperature difference (in this study 20 °C). The squared derivative of the data is also shown in Fig. 1. The determined maximum firing temperatures are indicated with arrows in Fig. 1.

3. Results

3.1. Validating the method through an experimental approach

In order to validate the method, we have applied it to two sets of clay samples fired at specific temperatures in a laboratory oven, a Carbolite 1100 CWf with ±1 °C temperature control. For the two series (termed series 1 and A), the same yellow-burning ‘blue’ clay from the locality Solkaer near Haderslev in Denmark was procured in the field and formed into 1 x 1 x 2 cm bricks, each pair (series 1 and A) incised with the firing temperature. The 14 samples were dried at 120 °C for 48 h, followed by another drying at 200 °C for 5 days in order to avoid cracking of the samples while firing to higher temperatures. The samples were then fired at temperatures 400, 500, 600, 700, 800, 900 and 1000 °C for progressively shorter times, reflecting the diminished need for equilibration at higher temperatures (see Table 1). The fired samples were then divided into 4 subsamples, each being weighed with 0.1 mg accuracy, and on average weighing 1.4 g.

The samples from Series 1 were measured for firing temperature with stepwise re-firing times of ca. 16 h per step from 200 to 600 °C. From 600 to 700 °C the re-firing time was 4 h, from 700 to 850 °C it...
Fig. 1. Examples of experimental determination of the maximum firing temperatures. Four samples have been selected from archaeological sites from widely different geographical and geological settings: (a) a sherd from a Medieval vessel from Viborg, Denmark; (b) an iron age sherd excavated by Henrik Thrane in the 1950’s in Luristan, present day Western Iran; (c) a sample of Inca ceramics from the Catamarca region in Northern Argentina; (d) sample of a scroll jar found in locus 41 in Qumran, on the West Bank of the Dead Sea. Left diagrams show the measured magnetic susceptibility as a function of stepwise re-firing temperature. Right diagrams show the squared first derivative calculated from the data in the left diagram. The maximum firing temperatures are determined as the first large deviation from zero of the squared first derivative and are indicated with arrows.
was 2 h, from 850 to 950 °C 1 h, and from 950 to 1060 °C the stepwise re-firing time was 0.5 h. After the completion of the first series a complete replication of this procedure was carried out with the samples of Series A. The determined firing temperatures are listed in the last column of Table 1, and an example of the data is shown in Fig. 2, where both the magnetic susceptibility and the squared first derivative of the magnetic susceptibility are plotted against the stepwise re-firing temperature. The original firing temperature is easily identifiable in both plots (indicated by arrows). Fig. 3 shows the firing temperatures determined in this way as a function of the known firing temperatures. The straight line is a regression line calculated using the data from both series of samples simultaneously. The correlation coefficient of $R^2 = 0.99$ and the average uncertainty (1 sigma) of ±25.8 °C are quite satisfactory, especially when compared to the uncertainties of the previously used methods for determining firing temperatures of ceramics.

In order to examine the mineralogical changes in the samples of the artificial re-firing series, aliquots were subjected to powder X-ray diffraction (PXRD) analysis. The data were collected on a PANalytical X’Pert PRO diffractometer using Ni-filtered CuKα-radiation (tube voltage 45 kV, tube current 40 mA, average wavelength 1.5418 Å) and a solid-state PIXcel detector. The sample was placed in a stainless steel holder, and data were collected in Bragg-Brentano (reflection) geometry, with the sample rotated at 2 revolutions per second to minimise preferred orientation. Data were collected over the range 5–70 degrees 2-theta using a continuous scan for a total data collection time of 10 min. A selection of the PXRD patterns is shown in Fig. 4 and the main mineral phases are listed in Table 2.

Thin sections produced from another set of aliquots were studied petrographically. The minerals identified by optical microscopy are listed in Table 2 and optical micrographs of six of the test samples are shown in Fig. 5. In a sample only tempered at a temperature of 200 °C (KLR-7933) muscovite, microcline, Na-feldspar, and calcite were identified by optical petrography. These phases have disappeared in the samples fired at higher temperatures, i.e. 900 °C (KLR-7947 and 7948) and 1000 °C (KLR-7949 and 7950), where we identify gehlenite, wollastonite, akermanite, and diopsides, all of which are neoformation mineral phases (Molera, 1991, 1996; Bearat, 1992; Buxeda i Garrigós and Cau Ontiveros, 1995; Cultrone et al. 2001). The PXRD patterns support and complement the petrographic observations, showing clearly the destruction of calcite at higher firing temperatures and the accompanying rise of gehlenite and wollastonite (Fig. 5).

The nucleation and growth of hematite has previously been reported in pottery production using a mixture of clay and calcite (Duminuco et al., 1998; Dondi et al., 1999; Nodari et al., 2007),
a composition that is very similar to the raw material used in this experiment. In the case of our test series, however, it is evident from the PXRD patterns that hematite (and also magnetite) is not observed, at least to the detection limit of the technique, which is estimated conservatively to be 2–3%. When both calcite and Fe are present during firing, it is also established that the neoformation minerals gehlenite (Ca$_2$Al(AlSi)O$_7$), wollastonite (CaSiO$_3$), and diopside (CaMgSi$_2$O$_6$) can incorporate Fe. In wollastonite this does not alter the magnetic susceptibility, but in gehlenite the incorporation of Fe can increase the magnetic susceptibility drastically. As shown by Nöller and Knoll (1983), the magnetic susceptibility of Fe-gehlenite can reach $36.5 \times \text{10}^{-3}$ (in emu), which is in agreement with the measured susceptibility for the test samples in this study. The mineralogical origin for the change in magnetic susceptibility in the case of our test series is therefore thought to be the gradual formation of Fe-gehlenite, possibly augmented by small amounts of neoformation hematite. Both minerals occur only in relatively minor amounts — gehlenite in amounts sufficient to be detected by PXRD, and hematite, if it is present at all, below the detection limits of that technique.

3.2. Archaeological application of the method

Concerning the existence of any mineralogical or other constraints on the applicability of the method, we note that we have tested it so far on samples from over fifty different archaeological sites and only in a few percent of the cases has the method failed to show any sudden change in magnetic susceptibility. Fig. 1 shows examples of maximum firing temperatures determined on samples originating from widely different geographical areas and geological conditions: Denmark, Israel, Luristan (Iran), and Argentina. In each case a maximum firing temperature can easily be found (indicated by arrows).

To examine further the applicability of the method, we have determined firing temperatures for a series of ceramic samples ($N = 36$) from the Northwestern Argentine region, where we for archaeological reasons expect to find two different kiln technologies. The Late Period in Northwestern Argentina is traditionally characterized as a time of marked regional development, increased socio-political complexity, inequality, economic stratification, and an increasing number of internal conflicts (warfare) (González, 1977; González and Pérez, 1972; Ottonello and Lorandi, 1987; Raffino, 1983, 1991; Tarragó, 2000). Craft specialization is widely represented in the archaeological record of the pottery production (De La Fuente, 2011a, 2011b). Late Period ceramic forms in the Southern Abaucán Valley, Catamarca, are mainly bowls, ollas, and funerary urns. These ceramics are well-fired in fully oxidizing atmospheres mostly through the utilization of kilns (De La Fuente, 2011a; Feely et al., 2010). The arriving of Incas in the region led to a reorganization of the pottery production visible through new forms of labor (mit’a), the introduction of extremely standardized new forms such as aríbalos (jars) and plates, together with the application of different ceramic paste recipes, and probably the use of firing procedures different than those used before by the ancient potters of the Late Period (Espinoza Soriano, 1970, 1975, 1987; D’Altroy, 1992; D’Altroy and Williams, 1998; Hayashida, 1999; Murra, 1980, 1982; Spurling, 1992). Like in the Late Period, Inca pottery is generally well-fired in fully oxidizing atmospheres and kilns appear to have been located near the Inca residential sites (De La Fuente, 2011a).

The samples used in this study are from six different but closely spaced Late (ca. AD 900–AD 1450) and Inca (ca. AD 1480–AD 1532) periods.
while SaCat12, SaCat13, and CV2 are Late Period sites with abundant archaeological sites geographically located in the southern sector of Abaucán valley in the Province of Catamarca (see KMZ, connecting with several other sites through the Inca road, by optical microscopy in thin sections and mineral phases by XRD of a selection of fired test samples.

Table 2
Main mineral inclusions and rock fragments identified by optical microscopy in thin sections and mineral phases by XRD of a selection of fired test samples.

<table>
<thead>
<tr>
<th>Lab no.</th>
<th>Temp. °C</th>
<th>Mineral identified in thin-sections</th>
<th>Mineral phases identified by PXRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>KLR-7940</td>
<td>500</td>
<td>Quartz and rock fragment inclusions: mostly fractured, size fine/medium, very abundant; plagioclase: albite, size fine, trace; calcite (primary): very coarse, trace; argillaceous inclusions: size coarse/very coarse, presence; igneous rock fragments: granites, size medium, trace; amphibole: hornblende, size very fine, trace; Fabric: anisotropic, formed by clay aggregates (2.5 YR 3/8); % inclusions: 10%; Distribution: fair; Pores: elongated.</td>
<td>Quartz, muscovite, microcline (K feldspar), calcite, feldspar (Na-component), ilomite.</td>
</tr>
<tr>
<td>KLR-7941</td>
<td>600</td>
<td>Quartz and rock fragment inclusions: size medium/coarse, very abundant, rounded; plagioclase: size fine/medium, moderated, some specimens altered to sericite; argillaceous inclusions: size fine, presence; microcline (K feldspar): size fine, presence; igneous rock fragments: size fine/medium, presence; pyroxene: size fine, presence; calcite (primary): size very coarse; trace; opaque minerals: size fine, trace; Fabric: anisotropic, formed by clay aggregates and very fine quartz (2.5 YR 3/7); % inclusions: 15%; Distribution: poor; Pores: elongated.</td>
<td>Quartz, muscovite, calcite, microcline (K feldspar), feldspar (Na-component), diopside.</td>
</tr>
<tr>
<td>KLR-7944</td>
<td>700</td>
<td>Quartz and rock fragment inclusions: size medium/coarse, very abundant, rounded; plagioclase: size fine, moderated with inclusions altered to sericite; muscovite: size very fine, trace; igneous rock fragments: size medium/coarse, presence; amphibole: brown hornblende, size fine/medium, trace; calcite (primary): size coarse/very coarse, trace; pyroxene: size very fine, trace; Fabric: anisotropic, formed by clay aggregates and very fine quartz (2 YR 4/10); % inclusions: 20%; Distribution: poor; Pores: elongated and sub-rectangular.</td>
<td>Quartz, muscovite, calcite, microcline (K feldspar), feldspar (Na-component), diopside.</td>
</tr>
<tr>
<td>KLR-7946</td>
<td>800</td>
<td>Quartz and rock fragment inclusions: size fine/medium, mostly rounded, very abundant; plagioclase: size very fine/medium, presence; microcline (K feldspar): size medium, trace; igneous rock fragments: size fine/medium, trace; amphibole: brown hornblende, size fine/medium, trace; calcite: size medium/coarse, trace; argillaceous inclusions: size fine, trace; Fabric: anisotropic, partially micaceous (2.5 YR 4/10); % inclusions: 10%; Distribution: fair; Pores: elongated with microfractures.</td>
<td>Quartz, gneissite, wollastonite, akermanite, anorthite, diopside, quartz low, traces of hematite.</td>
</tr>
<tr>
<td>KLR-7948</td>
<td>900</td>
<td>Quartz and rock fragment inclusions: size fine/medium, very abundant, fractured; igneous rock fragments: granites, size medium, trace; argillaceous inclusions: probably sandstone, size medium, trace; plagioclase: albite, size fine/medium, some specimens altered to sericite; amphibole: brown hornblende, size fine, trace; Fabric: isotropic, with very fine quartz at the bottom (5 YR 6/12); % inclusions: 15%; Distribution: fair; Pores: elongated.</td>
<td>Quartz, gneissite, wollastonite, akermanite, anorthite, diopside, quartz low, traces of hematite.</td>
</tr>
<tr>
<td>KLR-7949</td>
<td>1000</td>
<td>Quartz and rock fragment inclusions: size medium/coarse, very abundant, mostly rounded – there are polycrystalline quartz inclusions; plagioclase: size very fine, presence; igneous rock fragments: size medium/coarse, trace; amphibole: size fine, presence; microcline (K feldspar): size fine, trace; Fabric: isotropic, formed by clay aggregates (5 YR 6/10); % inclusions: 10%; Distribution: poor; Pores: elongated.</td>
<td>Quartz, gneissite, wollastonite, akermanite, diopside, quartz low, traces of hematite.</td>
</tr>
<tr>
<td>KLR-7950</td>
<td>1000</td>
<td>Quartz and rock fragment inclusions: size fine/medium, very abundant, low sphericity, and very fractured; plagioclase: size fine, moderate; microcline (K feldspar): size fine/medium, presence; amphibole: hornblende, size fine, presence; pyroxene: size fine, trace; argillaceous inclusions: size medium, trace; Fabric: isotropic (5 YR 6/10); % inclusions: 15%; Distribution: fair; Pores: elongated.</td>
<td>Quartz, gneissite, wollastonite, akermanite, diopside, quartz low, traces of hematite.</td>
</tr>
</tbody>
</table>

References: Size (Orton et al., 1993; Wentworth scale (φ scale) modified from Folk, 1965); % abundance (semi-quantitative): very abundant (40–60%), abundant (20–30%), moderate (10–20%), presence (5–10%), and trace (<1%); % inclusions (Mathew et al., 1991); Distribution (Barralough, 1992); Matrix description (Freestone, 1991).
designated Inca–Diaguita Chileno and recovered at Costa de Reyes N° 5, are non-local ceramics coming probably from Chile.

An extensive ceramic petrology study carried out on 150 Inca and Late Period sherds showed mainly the presence of felsic minerals (quartz, alkali, and plagioclase feldspars), and igneous rock fragments (granite), complemented with muscovite and biotite minerals, few volcanic rock fragments (mainly andesite), accessory minerals like amphibole and clinopyroxene, and opaque minerals such as hematite and magnetite (De La Fuente, 1999, 2004, 2011a; see also Chatfield, 2010; and Hayashida et al., 2003b for descriptions of Inca ceramics from Peru). Additionally, for Inca ceramics we determined the presence of calcite (primary and secondary calcite) and the unique presence of grog (De La Fuente, 2011a). Preliminary multi-elemental chemical characterization by NAA shows that the ceramics are non-calcareous ceramics, with Inca ceramics forming a chemically very homogeneous group, and with the presence of some compositional variation for the Late Period sherds (De La Fuente et al., in press).

The maximum firing temperatures determined are listed in Table 3. For one sample only (DLF-038) the data were inconclusive and no firing temperature could be determined, which is probably due to a complex thermal history or one or more re-firing events. As pointed out also by Heimann and Franklin (1979), Livingstone Smith (2001), and Tite (2008), the precise functionality of the heating and cooling history, and any additional firing events to comparable or even higher temperature than the initial firing temperature, must influence the results of any method for determining firing temperature. As can be seen in Fig. 8, the distribution of firing temperatures shows two distinct peaks: one at 830 °C and one at 950 °C. Archaeological reasons for the presence of two distinctly different firing temperatures could be many, e.g. burning in two different types of kilns (Shimada et al., 1994, 2003b; Wagner et al., 1999; Hayashida et al., 2003b), the use of different types of fuel such as wood, grass, straw or dung (Sillar, 2000a, b), different people or families operating the same kiln, etc. In general terms it is likely that the firing temperature experienced by a vessel is dependant on the position it had in the kiln during firing, estimated by Mirti (1998) to be as large as 50 or even 100 °C (cf. Gosselain, 1992; Livingstone Smith, 2001). However, it seems unlikely that two distinct peaks 120 °C apart can result from inhomogeneous kiln temperatures. We therefore believe that the two peaks arise from two different firing practices.

4. Discussion

It could be asked if this method can be applied to clays with compositions other than those resembling the South Danish clay of the test series, the examples from the Middle East, and the Andean ceramics tested here. The prerequisite for the method to work is that one or more minerals with a sizable magnetic susceptibility are
either destroyed or neo-formed upon firing. The destruction of calcite or the neoformation of wollastonite, for instance, will not lead to a significant change in magnetic susceptibility. However, if hematite or Fe-gehlenite (as seen in South Danish example) or any other Fe-rich mineral exhibiting a magnetic susceptibility is formed, the method will be applicable. Similarly, the method will work if for instance Fe-rich carbonates or oxides, like e.g. siderite or goethite, are destroyed upon firing. Even in cases without destruction or neoformation of minerals, processes such as recrystallization, crystal size growth or magnetic domain growth are likely to provide enough change in magnetic susceptibility for the method to work (see Shimada et al., 2003a, 2003b). There can undoubtedly be found examples, where the method will fail: e.g. for samples consisting of pure calcite, pure quartz, or haphazard mineral assemblages where the decrease in susceptibility from the destruction or neoformation of a mineral is counterbalanced by an exact similar increase in magnetic susceptibility of other minerals. However, such cases must be rare. We have tested the method on ca. 50 different sites in Europe, the Middle East and in South America and encountered only a few percent of the samples where the method has failed to yield a sudden change in susceptibility. Consequently, we believe that the method is applicable for the majority of archaeological red clays.

What, then, is the archaeological usefulness of establishing the firing temperature? First, it must be noted that under normal conditions the original firing temperature in a kiln is higher than the temperature exposure over a cooking fire or in a cooking oven (Chatfield, 2010; Hayashida et al., 2003b; Livingstone Smith, 2001; Rice, 1987; Rye, 1981; Tite, 1995, 1999, 2008). Therefore the archaeological conjectures revolve around the technology and conditions in the kiln producing the ceramics. In the ideal case a method like the present can help discriminating ceramics from different kilns either at different sites or at different times, and thus act as an indirect tool for provenancing ceramics. On a larger time scale the method can be used to track developments of kiln technologies.

Andean pottery was mostly fired using open methods such as open firings or bonfires (Chatfield, 2010), although some cases have been reported on the utilization of kilns, simple kilns, and insulated bonfires (Feely et al., 2010; Shimada et al., 1994, 2003b; Wagner et al., 1999; Hayashida et al., 2003b). The advantages and disadvantages of these opposed firing procedures have been stated and

**Fig. 6.** Powder X-ray diffraction patterns in the range 29–38 degrees 2-theta of the test series samples fired at 700, 800, 900, and 1000 °C. From the bottom up: KLR-7943 (700 °C, black curve), KLR-7945 (800 °C, red), KLR-7948 (900 °C, blue), and KLR-7949 (1000 °C, green). The positions expected for peaks of calcite, wollastonite, magnetite, gehlenite, hematite and quartz are indicated with arrows. Gehlenite and wollastonite are neoforming minerals whereas calcite is disappearing with increasing temperature. There is no indication of magnetite in any of the patterns. Peaks attributable to hematite are hardly discernable, and it can be present only in minute amounts at elevated temperatures, if at all.

**Fig. 7.** Late and Inca periods archaeological ceramics analysed in this study: (a) and (b) Inca Provincial sherds, Costa de Reyes N° 5, Sector B; (c) Inca-Diaguita sherds, Costa de Reyes N° 5, Sector B; (d) Late Period sherds, Sanagasta Culture, SaCat12 and SaCat13 sites.
Table 3
Results of the determination of maximum firing temperatures of the samples from the Catamarca region in Northern Argentina. DLF-No and KLR-No are field and laboratory designations. The uncertainty of the measured firing temperatures are ca. ±25 °C (1 sigma). The fourth column indicates the archaeological site, and the last column describes the type of ceramics.

<table>
<thead>
<tr>
<th>KLR-No.</th>
<th>DLF-No.</th>
<th>Measured firing temperature [°C]</th>
<th>Site</th>
<th>Sample description</th>
</tr>
</thead>
<tbody>
<tr>
<td>KLR-7573</td>
<td>DLF-005</td>
<td>830</td>
<td>SaCat 12</td>
<td>Sanagasta, rim frag., bowl</td>
</tr>
<tr>
<td>KLR-7574</td>
<td>DLF-006</td>
<td>950</td>
<td>SaCat 12</td>
<td>Sanagasta, rim frag., bowl</td>
</tr>
<tr>
<td>KLR-7575</td>
<td>DLF-015</td>
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Fig. 8. Experimentally determined maximum firing temperatures of 35 ceramic samples from six different sites in Northern Argentina (data in Table 3). The uncertainty in the determination is ± ca. 25 °C. The distribution shows two distinct peaks, at 830 and 950 °C.
950 °C, is the largest group consisting of 10 sherds: four Inca sherds, five Sanagasta sherds, and one Sausal sherd. G3 (850 °C) consist of two Inca sherds, one Inca Provincial and one Inca/Driguita Chileno. G4 (870 °C) holds two Inca sherds, one Sanagasta, and one Sausal. G5 (890 °C) consists of one Inca sherd and two Late Period sherds. G6 (930 °C) holds one Inca sherd and two Late Period Sanagasta style sherds. The isolated cases are 3 sherds of lower firing temperatures: one Inca sherd (770 °C), one Inca/Driguita Chileno sherd (790 °C), and one Late Period Sanagasta style sherd (810 °C). Then two sherds with higher firing temperatures: one Inca sherd (910 °C) and one Late Period Sanagasta style sherd (1030 °C).

While there is no systematic separation between Late and Inca period sherds according to the determined maximum firing temperatures, it is obvious that Late Period sherds in general exhibit lower maximum firing temperatures than the Inca sherds (for similar results see Hayashida et al., 2003b). Inca sherds, except for two cases, have maximum firing temperatures above 850 °C.

There is also a clear difference between the Inca Provincial sherds and the two Inca/Driguita Chileno sherds, the latter exhibiting firing temperatures lower than or equal to 850 °C. The differences observed in the maximum firing temperatures between Late and Inca Period sherds are probably related to changes in the firing procedures and kiln technologies which occurred with the appearance of the Incas in the region, which led to a new organization of the whole pottery production. In general there is observed higher and more homogenous maximum firing temperatures of the Inca sherds, which is in accordance with the use of kilns and a better control of temperature and firing atmosphere. Late Period sherds appear to have been fired in conditions exhibiting larger variations in temperatures, probably due to the use of insulated bonfires and even open fires. Perhaps some of the Late Period vessels could have been fired using the new firing procedures and kiln technology brought to the region with the Incas, since it is known that Incas used local labourers to intensify the production of pottery (Hayashida et al., 2003b: 162); however, safe conclusions in this respect requires further investigation. In one particular case a pottery kiln was excavated near Costa de Reyes N° 5 site, where there was found wood used for fuel dating from the Late Period. Whether this was due to the use of old wood, possibly reused timber, or the kiln was indeed in operation in the Late Period remains to be seen.

Therefore the use of the decomposition or neoformation of mineral phases detected by measurements of magnetic susceptibility has proven a powerful tool in revealing archaeological information about the changing firing procedures utilized by the pre-Hispanic societies in the Andean area through time. In the present context, we believe that our data from the Late Period and Inca ceramics exhibit the potential of the method to determine firing temperatures for a broad range of samples with a so far unprecedented accuracy.

5. Conclusions

A new methodology for determining the maximum firing temperature of ceramics and other burnt clay materials using stepwise re-firings and measurements of the magnetic susceptibility has been presented. The method has been validated for two series of clay samples fired at 400, 500, 600, 700, 800, 900, and 1000 °C. The correlation coefficient between the known firing temperature and the experimentally determined firing temperatures was found to be $R = 0.99$ ($R^2 = 0.98$), which is a very satisfactory agreement. The uncertainty in estimating the firing temperature in this validation experiment is determined to be ±25.8 °C (1 sigma). The mineralogical changes responsible for the sudden change in magnetic susceptibility after re-firing exceeding the original firing temperature in the validation series samples are probably the neoformation of Fe-gehlenite and possibly hematite, as shown by powder X-ray diffraction measurements. The method has been demonstrated to work on ceramic samples from very diverse geological clay sources from Denmark, Luristan, Israel, and Argentina. The method has been applied to a set of samples from two cultures which likely had different firing technologies, the Late (ca. AD 900–AD 1450) and the Inca (ca. AD 1480–AD 1532) periods in the Catamarca region in Northern Argentina. The determined maximum firing temperatures exhibit a two-peak distribution that can be understood in relation to the archaeological context.

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Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jas.2012.01.008.
Paidós, Buenos Aires.
Revolución de Mayo, XVII Congreso Nacional de Arqueología Argentina, Men-...


