2023 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
Rome, Italy, October 19-21, 2023

A multidisciplinary investigation of an ancient kiln excavated at Costigliole Saluzzo: new archaeometric and archaeomagnetic results

Leite Santos, Y.[1], Tema, E.[2,3], Davit, P.[1], Elia, D.[4], Meirano, V.[4], Fantino, F.[5], Gulmini, M.[1]

[1] Chemistry Department, University of Turin, via Pietro Giuria 7, 10125 Torino, Italy,
yuri.leitesantos@unito.it, monica.gulmini@unito.it, patrizia.davit@unito.it
[2] Earth Sciences Department, University of Turin, via Valperga Caluso 35, 10125 Torino, Italy,
evdokia.tema@unito.it
[3] ALP-CIMaN Alpine Palaeomagnetic Laboratory, via G.U. Luigi Massa 6, 12016 Peveragno
[4] Historical Studies Department, University of Turin, via Sant'Ottavio 20, 10124 Torino,
diego.elia@unito.it, valeria.meirano@unito.it
[5] TTA- Turin Thermoluminescence Analysis, via Felice Cavallotti 33, Cuneo,
tta.fantino@gmail.com

***Abstract* – This study presents the integrated results of archaeological, archaeometric and archaeomagnetic analyses applied to an ancient kiln discovered at the Roman site of Costigliole Saluzzo (northwest Italy). Clay samples from the kiln's inner walls and central pillar were collected for Fourier Transform Infra-Red spectroscopy, X-Ray Powder Diffraction and archaeomagnetic analyses to obtain information about the firing temperatures reached during its use and to determine the direction of the Earth's magnetic field at the time of its abandonment. The analyses highlighted the presence of non-calcareous clayey material. The firing temperatures vary in the different parts of the kiln, reaching a maximum of about 850 - 900 ºC at its central part, making the kiln suitable recorder of the ancient geomagnetic field. Archaeomagnetic results show good magnetic stability and systematic alternating field demagnetization procedures successfully determined the direction of the characteristic remanent magnetization recorded during the last use of the kiln.**

I. INTRODUCTION

The archaeological site of Costigliole Saluzzo is located in Piedmont (northern Italy) (Fig. 1). It has been the subject of numerous archaeological campaigns since 2003, that brought to light an important Roman villa of at least 30,000 m^2. According to the archaeological evidence, the villa was a strategic hub in the road network of the area during the Roman Empire (from the 1st to the end of the 3rd century AD). The villa is divided into several sectors destined for residential and production purposes (storage, processing of agricultural products, cereals milling, clay and metal working, etc.) and for housing of travelers and merchants. A large wine plant has emerged on the site, the first to be discovered in southern Piedmont and one of the best preserved in Northern Italy [1]. Among the other findings, a small circular kiln (Fig. 2), most probably used for pottery production, was recently excavated.

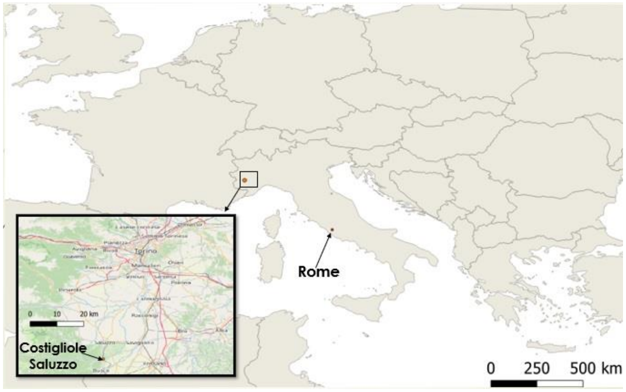

Fig. 1. Location of the Costigliole Saluzzo archaeological site.

In this study, we used a multidisciplinary approach to investigate the excavated kiln, with particular emphasis on the estimation of the firing temperatures reached during its use and on the determination of the archaeomagnetic direction registered during its last firing. X-Ray Powder Diffraction (XRPD) and Fourier

Transform Infra-Red spectroscopy (FTIR) analyses have already proven to be useful approaches for the study of baked clays, based on the mineralogical composition and its change during heating [2]. In many cases, they have been used for the characterization of ceramics and for the assessment of the firing temperatures of ancient pottery [3,4] and kilns [5,6]. In addition, in the case of ancient kilns that have operated at sufficiently high temperatures to acquire a thermoremanent magnetization (TRM), the record of the ancient magnetic field can be determined, offering reference data for the reconstruction of the past secular variation of the Earth’s magnetic field and for the establishment of archaeomagnetism as a potential dating technique [7,8,9] for a given geographical area.

This study aims to show the efficacy of integrated analyses in order to maximize the information obtained from the investigation of such (still *in situ*) clay structures, incorporating not only archaeological information and material science evidence of ancient firing technology, but involving also geomagnetic field reconstructions.

Fig. 2 The remains of the Roman kiln investigated in this study. The sampling points are also visible as white dots.

II. SAMPLING

A total of 15 small pieces of fired clay were collected from different parts of the kiln’s wall and from the central pillar (Fig. 2). For the archaeomagnetic analysis, small plastic discs (~ 20 mm diameter) were glued directly on the baked clay and were oriented *in situ* using a magnetic compass, a solar compass and an inclinometer. Small chunks were then removed, taking care to preserve the oriented disc. The oriented samples were taken to the laboratory, where they were further modelled to obtain small cylinders (about 2 cm in diameter and 2 cm high). From the same samples, small pieces were detached and powdered in sufficient quantity for FTIR and XRPD analyses.

In particular, for FTIR, the powdered samples were mixed with potassium bromide with a 1:50 proportion and compressed into pellets. For XRPD, a few hundred milligrams of each sample were placed in quartz sample holders and pressed with a glass slide. Moreover, a non-baked soil sample from the nearby area was collected and treated with the same procedures employed for the rest of the samples. This soil was considered as representative of the raw material employed to build the kiln. Data obtained for this sample were then compared with those obtained from the samples taken from the kiln remains.

III. METHODS AND RESULTS

A. Firing temperature

When it comes to archaeological ceramics, both FTIR and XRPD analysis can be useful to identify the type of clay and its chemical properties, offering a raw estimation of the firing temperature (mainly in relative values) and enriching the current knowledge on the technical skills of ancient artisans [2,10]. In this study, to obtain the maximum amount of information, both techniques were applied.

FTIR spectra were acquired in the range between 4000 and 600 cm^{-1} with a Bruker Vector 22 spectrometer. OPUS software was used to acquire and manipulate the spectra. The diffractograms were collected using an Analytical X’Pert Pro PANalytical B.V. diffractometer, equipped with a X’Celerator detector using Cu Kα radiation generated at 40 kV and 40 mA. The 2θ range was from 5 to 90° and the diffractograms were elaborated and interpreted using the X’Pert Pro software.

Thermal changes occurring in the clay structure during firing are evaluated from the observation of specific peaks in the FTIR spectra, in particular the hydroxyl stretching vibration pattern in the interval from 3700 to 3400 cm^{-1}, and the silicon-oxygen stretching vibration pattern around 1000-1100 cm^{-1}. In the present study, the spectrum obtained for the non-fired soil is reported in Fig. 3 and it is used as reference for highlighting the variations induced in the material by the thermal treatment. The FTIR spectra obtained from the kiln samples are reported in Fig. 4.

The main Si-O-Si absorption signal is one of the temperature indicators discussed in most FTIR studies on pottery firing technology. In most of the spectra acquired in this study, this signal is centered at 1030 cm^{-1} (Fig 4). However, this very asymmetric and structured band contains contributions from different crystalline and/or amorphous silicate phases, which have effect on the broadening of the signal.

As reported by many authors, a maximum intensity centered at around 1030 cm^{-1} is expected for clays heated at 600 °C, but this stretching band shifts towards higher frequencies and broadens with increasing temperature [11]. The presence of different contributions in this range of the FTIR spectra for the samples under study (highlighted in the inset in Fig. 4) reflects the presence of various silicate species that, in turn, indicate that the samples were exposed to different thermal conditions during the kiln use. Other useful information is obtained from the hydroxyl stretching vibration pattern (3700 - 3400 cm^{-1}).

When exposed to high temperature, the clay is first de-hydroxylated and then decomposed. If the clay minerals are totally decomposed by the heating, then the de-hydroxylation process is irreversible. Nevertheless, depending on the original conditions (heating gradient, maximum temperature and duration of the heating), the clay mineral structure could be (at least partially) preserved and re-hydroxylation can (at least partially) occur. Such conditions are reflected in the spectroscopic characteristics of the hydroxyl pattern in terms of signal intensity, shape of the bands, presence of different components, position and possible shifts.

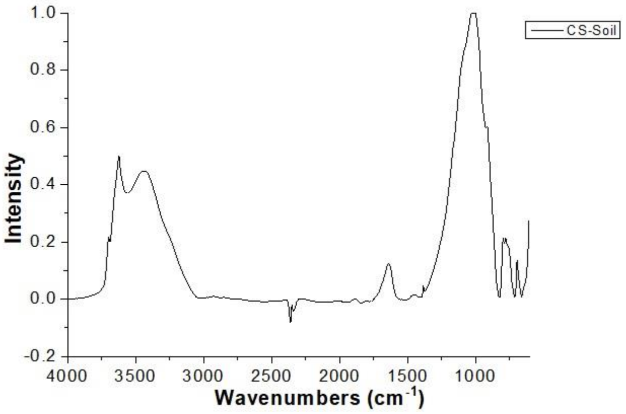

Fig. 3. FTIR spectrum of the soil sample.

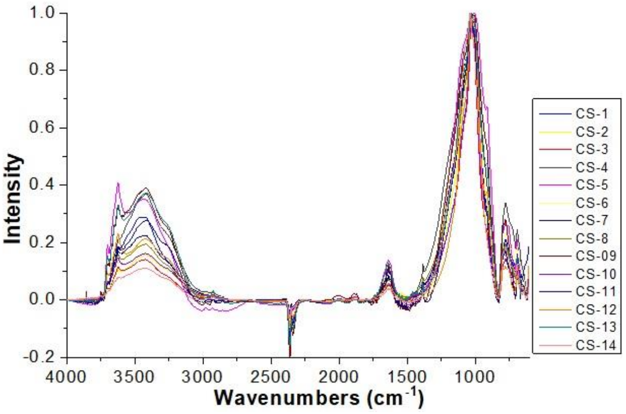

Fig. 4. FTIR spectra of samples collected from different parts of the kiln.

The comparison of the FTIR spectrum of the raw soil (Fig. 3) with the spectra obtained from the kiln samples (Fig. 4) shows that the structures of the clay minerals were not completely destroyed during the use of the kiln. The baked clay was able to re-absorb water and to be re-hydroxylated, at least to a certain extent. The variations (in terms of intensity and shape) of the bands observed in the FTIR hydroxyl pattern of the kiln samples are mainly due to the differences in the extent of the re-hydroxylation process, which in turn suggest that the temperature in the kiln was not homogeneous. Moreover, the spectra offer the possibility to distinguish the samples exposed to higher temperatures from those exposed to lower heating (in terms of relative values), since the re-hydroxylation is expected to be more extensive in the samples exposed at lower temperatures. In particular, our results show that the highest temperature was reached in the central part of the kiln, as the sample collected from the central pillar (sample CS-14) shows the lowest re-hydroxylation (Fig. 4).

The XRPD analyses of the raw soil and of the baked clay collected from the kiln present similar mineralogical phases, but different intensity peak values (Fig. 5). The presence of quartz, clay minerals and feldspars was attested both in the soil and in the kiln samples, but the content of the clay was significantly higher in the soil sample, since the raw material was not subjected to any thermo-induced changes of the crystalline structure of these minerals. The diffractograms suggest that the main clay minerals could be illite and montmorillonite, with minor quantity of chlorite.

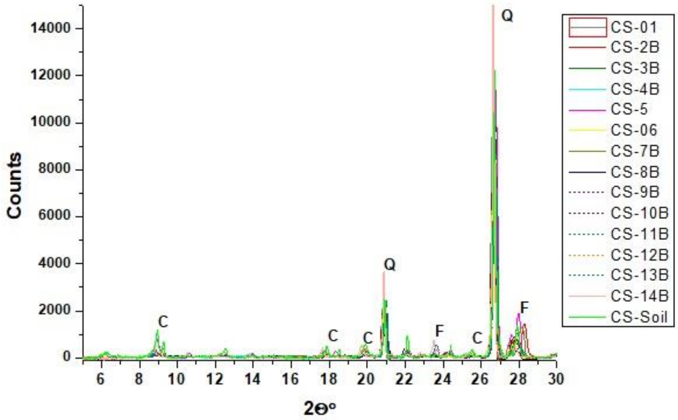

Fig. 5. X-Ray Diffractograms from 5 to 30°, enhancing the comparison of minerals between samples and raw material. Peaks of Quartz (Q), Feldspars (F) and Clay minerals (C) are indicated.

In agreement with the FTIR results, the XRPD patterns of the samples taken from the kiln still show the presence of the signals from the clay minerals, confirming that they were not fully decomposed by the heating of the kiln. In addition, both the soil sample and of the kiln ones featured the absence of the calcite peak around 34° in the XRPD pattern (not shown in Fig. 5) and the lack of the carbonate vibration signals in the FTIR spectra. This indicates that the raw materials used to build the kiln were non-calcareous / carbonate-poor clays.

Estimating the firing temperature for non-calcareous clays is very challenging, due to the lack of the information provided by the reactions that occur to carbonates during heating, characterized by the decomposition of multiple phases and the formation of new phases at different and specific temperature intervals. Although the decomposition/formation reactions also depend on the overall composition of the raw materials, they can give a fairly clear indication of the firing conditions [2,12].

Taking into consideration that the studied kiln was constructed with non-calcareous materials, the focus of data interpretation was thus oriented on the evaluation of the other mineralogical phases that can give some information on firing temperatures, such as feldspars and clays.

The stability of feldspars extends to relatively high temperature, meaning that they do not show any type of transformation in low-fired clay, while the behaviour of K-feldspars is different from that of plagioclases at higher temperatures: K-feldspars do not show evident traces of transformation until 600 °C. Above that temperature, XRPD reflections may generally change in shape and intensity, but they are typically stable up to 850 °C. At even higher temperatures, the (poorly known) reactions that take place are related to the specific type of K-feldspar (i.e. low-temperature microcline, intermediate-temperature orthoclase, high-temperature sanidine) and to the overall composition of the system. Such reflections are expected to disappear from the diffractograms if the temperature exceeds 1100 °C [2].

The presence of both K-feldspars and albite, detected by XRPD in the samples from Costigliole Saluzzo, suggests that this temperature was not reached in the kiln. XRPD also detected the presence of clays. It is known that the structure of clays collapses at temperatures between 850 °C and 900 °C, and it is destroyed between 900 °C and 1000 °C [2]. Therefore, it is very likely that the maximum temperature reached in the kiln has not exceeded 850-900 °C.

By combining the information obtained from both FTIR and XRPD, our results show that the samples obtained from the different parts of the kiln were subjected to variable temperatures. The maximum value that can be set at 850-900 °C was detected in the central pillar, whereas the other samples collected from the different parts of the kiln wall were exposed to lower temperatures, as suggested by the FTIR hydroxyl patterns. Unfortunately, the data for the non-calcareous clay studied here did not permit to confidently establish the value for the minimum temperature to which the clayey raw material was exposed. However, by comparing the FTIR spectra for the kiln samples with that of the soil sample, it is evident that all the samples in the kiln reached the de-hydroxylation stage upon heating. This is reported in the literature to be in a wide range between 525 °C and 725 °C [2], and thus this range shall be considered here as the lower temperature the samples could have been exposed to during the kiln use.

B. Archaeomagnetic direction

Archaeological baked clays fired at temperatures higher than 500 ºC to 700 ºC (exceeding the Curie temperature of the most common magnetic minerals) can reliably register the direction of the Earth’s magnetic field in the past, through the orientation of the magnetic moment carried by the magnetic minerals included in their matrix. They thus consist of a unique source of information about the direction of the ancient geomagnetic field recorded at the time of their last firing. In this study, in order to determine the ancient geomagnetic field registered by the Roman kiln, we have applied standard archaeomagnetic techniques.

First, the natural remanent magnetization (NRM) of 14 samples was measured with a JR-6 spinner magnetometer (Agico) at the CIMaN-ALP paleomagnetic laboratory (Peveragno, Italy). Once the NRM was measured, the samples were stepwise demagnetized with a D-2000 ASC Scientific alternating field (AF) demagnetizer up to 100 mT. During the experiment, a few samples were detached from the plastic cap and glued back again in the most optimal way while others completely lost their field orientation (and were therefore excluded from further analysis).

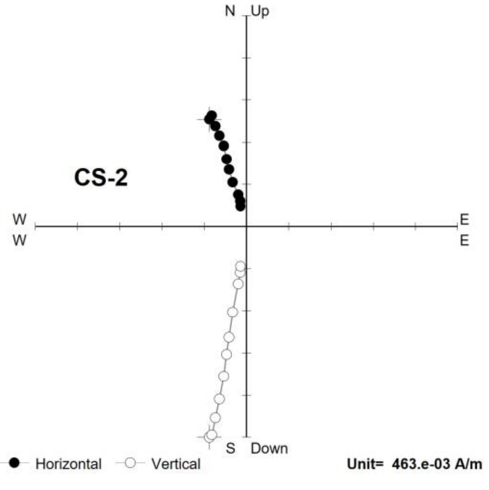

Fig. 6. AF demagnetization results for sample CS-2 represented in orthogonal vector plot (Zijdelveld diagram).

The demagnetization diagrams obtained show a linear and stable magnetic remanence and the characteristic remanent magnetization (ChRM) is well-defined and clearly isolated for most of the samples (Fig. 6). Even though some dispersion can be observed, the equal-area projection of the ChRM directions at sample level shows a general good concentration around the mean value (Fig. 7), which is calculated according to Fisher statistics [13].

These results show that the kiln reached temperatures high enough to record the Earth’s magnetic field during its last use and the obtained archaeomagnetic direction can be added to the Italian archaeomagnetic database, enriching the current knowledge of Earth’s magnetic field secular variation during the Roman times.

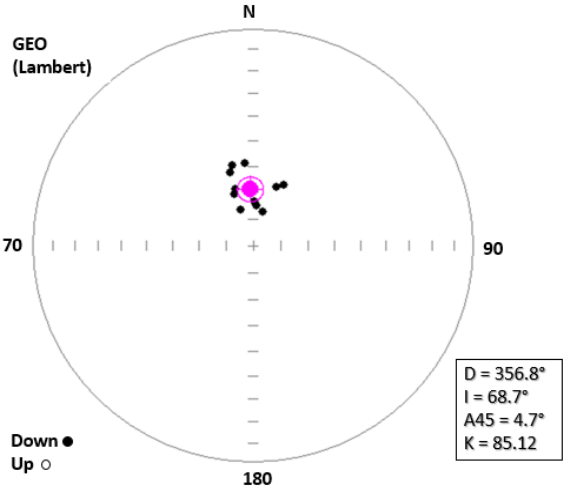

Fig. 7. Equal area projection of the ChRM directions at sample level together with the kiln mean direction as calculated from Fisher statistics (pink dot).

IV. CONCLUSIONS

This study has contributed to the investigation of the ancient kiln excavated at Costigliole Saluzzo, from both archaeometric and archaeomagnetic points of view.

Archaeometric results show that the major mineralogical phases present in the raw material used for the construction of the kiln were quartz, feldspars, and clay minerals, without any significant amount of calcite. The clay phases were only partially decomposed by the temperatures reached during the kiln~~’s~~ use. The temperature distribution in the kiln was rather inhomogeneous, with the highest temperature (around 850-900 °C) detected in the sample obtained from the central pillar. The red colour of the (non-calcareous) samples indicate that the atmosphere in the kiln was oxidizing.

The samples investigated gave information on the maximum temperature reached by the kiln, offered an overview of the distribution of the heat in its various parts and provided the possibility to determine the direction of the Earth’s magnetic field during the kiln last use, thanks to the baked clays still found at the place of their last firing. This study proves that the combination of different disciplines such as archaeology, material science and geomagnetism can contribute to better understand our past from different points of view.

REFERENCES

[1] D.Elia, V.Meirano, “Abitare, coltivare, produrre in Cisalpina. Le scoperte della missione UNITO a Costigliole Saluzzo: la villa romana e l'insediamento tardo-antico”. In: Chiedi alla terra. Scavi e ricerche archeologiche del Dipartimento di Studi Storici dell’Università di Torino, (Ed.) Elia D., Accademia University Press, Torino, 2020, pp. 191-206.

[2] E.Gliozzo, “Ceramic technology: How to reconstruct the firing process”, Archaeological and Anthropological Sciences, 2020, 12, 260. https://doi.org/10.1007/s12520-020-01133-y.

[3] A.Mangone, L.C.Gianossa, G.Colafemmina, R.Laviano, A.Traini, “Use of various spectroscopy techniques to investigate raw materials and define processes in the overpainting of Apulian red figured pottery (4th century BC) from southern Italy” Microchemical Journal, 2009, 92, pp.97-102. https://doi.org/10.1016/j.microc.2009.02.004

[4] C.Germinario, G.Cultrone, A.De Bonis, F.Izzo, A.Langella, M.Mercurio, V.Morra, A.Santoriello, S.Siano, C.Grifa, “The combined use of spectroscopic techniques for the characterisation of Late Roman common wares from Benevento (Italy)”, Measurement, 2018, 114, pp.515-525. https://doi.org/10.1016/j.measurement.2016.08.005

[5] G.Eramo, “The melting furnace of the Derrière Sairoche glassworks (Court, Swiss Jura): Heat-induced mineralogical transformations and their technological signification”, Archaeometry, 2005, 47, pp.571-592. https://doi.org/10.1111/j.1475-4754.2005.00220.x

[6] G.Eramo, “The glass-melting furnace and the crucibles of Südel (1723–1741, Switzerland): provenance of the raw materials and new evidence of high thermal performances”, Journal of Cultural Heritage, 2006, 7, 286-300. https://doi.org/10.1016/j.culher.2006.04.005

[7] E.Tema, F.Fantino, E.Ferrara, S.Allegretti, A.Lo Giudice, A.Re, F.Barello, S.Vella, L.Cirillo, M.Gulmini, “Archaeological, archaeomagnetic and thermoluminescence investigation of a baked clay kiln excavated at Chieri, northern Italy: contribution

to the rescue of our cultural heritage", 2014, Annals of Geophysics, 57, 5, G0548. https://doi.org/10.4401/ag-6611

[8] L.Casas, P.Linford, J.Shaw, "Archaeomagnetic dating of Dogmersfield Park brick kiln (Southern England)", Journal of Archaeological Science, 2007, 34 (2), pp.205-213. https://doi.org/10.1016/j.jas.2006.04.011

[9] E.Tema, P.Lanos, "New Italian directional and intensity archaeomagnetic reference curves for the past 3000 years: Insights on secular variation and implications on dating", Archaeometry, 2021, 63 (2), pp.428-445. https://doi.org/10.1111/arcm.12603

[10] P.Singh, S.Sukanya, "Thermal and spectroscopic characterization of archeological pottery from Ambari, Assam", Journal of Archaeological Science: Reports, 2016, 5, pp. 557-563. https://doi.org/10.1016/j.jasrep.2016.01.002

[11] G.Raja Annamalai, R.Ravisankar, A.Rajalakshmi, A.Chandrasekaran, K.Rajan, "Spectroscopic characterization of recently excavated archaeological potsherds from Tamilnadu, India with multi-analytical approach", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2024, 133, pp.112-118. https://doi.org/10.1016/j.saa.2014.04.188

[12] B.Yan, S.Liu, M.L.Chastain, S.Yang, J.Chen, "A new FTIR method for estimating the firing temperature of ceramic bronze-casting moulds from early China", Scientific Reports, 2021, 11, 3316. https://doi.org/10.1038/s41598-021-82806-z

[13] R.A.Fisher, "Dispersion on a sphere", Proceedings of the Royal Society of London, 1953, A217, pp.295-305.