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Exploring porosity in ceramics at nanometric scale using Small-Angle Neutron Scattering: from an understanding of historical ceramics towards the design of novel innovative materials

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Abstract: *Ceramics are complex objects and a rich source of information: they constitute a large part of the staple memory of past and present human activities. A deep understanding of traditional ceramics is an essential key to designing new ceramic materials. The demanding synthesis of ceramics with fine-tuned properties, such as enhanced mechanical, electrical, optical or magnetic characteristics, must be associated with cutting-edge analysis procedures in order to improve the engineering process. In this context, we describe a neutron-based non-destructive approach to investigating the nanoporosity of an historical pottery matrix as an effective investigation technique for exploring both traditional and advanced ceramic materials.*

The importance of ceramic materials from both the past and the present is well understood: for instance, in archaeological sites, ceramic findings are considered to be the most important set of data due to their large distribution. The continuous manufacturing process, for example the recycling of vessels and waste pieces found at archaeological excavation sites, has made it possible to create an archive of testimonies which faithfully record the changes in terms of fashion of the day, technical functions and symbols.[1-5] Traditional ceramics are usually composed of clay and silica. Today, although ceramics are often erroneously associated with low-level technology, advanced production techniques are now used involving complex tools and machinery, often coupled with computer-aided process control.[6] Advanced ceramics are also known as "special", "technical" or "engineering" ceramics: while traditional clay-based ceramics have been used for over 25,000 years, the development of advanced ceramics began in the 20th century.[6]

The chemical and mineralogical composition, porosity and microstructure of ceramic mixtures are indeed correlated to the native material composition and firing temperature, which play a key role in determining the provenance of the pottery and its production techniques[7-10] as well as the properties of the ceramic materials.[6,11,12] Depending on the size of their nanopores, materials are usually classified/sorted as follows: microporous (pore sizes less than 2 nm), mesoporous (pore sizes of 2–50 nm), and macroporous (pore sizes over 50 nm).

Archaeometric research on pottery is focused on studying its production techniques, provenance, age, usage and conservation state. Suitable scientific material analyses, able to characterise the chemical and morphological features of the artefacts in order to determine their production techniques, are essential in this research field.[5] More generally, they also constitute a fundamental approach to the study of modern and advanced ceramic materials, making it possible to correlate the morphological-compositional properties with those more directly related to the desired use of such material. We can easily imagine that nanoporosity influences hardness, density, high-temperature mechanical strength, creep resistance and corrosion resistance in structural ceramics as well as in nanocomposite materials used for applications in engine parts, cutting tools, wear components, heat exchangers, and so on.[6,13-15] Moreover, the study of nanoporosity is also fundamental for bioceramics and membranes, where porosity plays a major role, and the open/closed pores ratio is a very important parameter to be controlled.[6,16-18] As indicated by M. Strlic,[19] "*the complex research questions in heritage science require the development of technologies and approaches that are valuable to other fields of scientific endeavour*": in this context, the aim of our paper is to propose a neutron-based, non-destructive approach for the study of specific features of a pottery matrix that could open a route (based on the study of both open and closed nanopores) for exploring both historical and innovative ceramic-based materials.
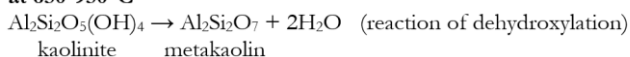
We studied samples from different sites (see SI): fragments originating from the Mediterranean basin and attributed to three main groups - Late Antiquity (5th-7th centuries), Early Middle Ages (8th-10th century) and Middle Age (10th-12th centuries) - from different excavation sites in Torcello, Venice (Italy) in 2012-2013;[20] German sherds dating from the late 13th to 19th century, from several sites located in Central and Eastern Germany, provided by the Landesamt für Archäologie Sachsen in Dresden (Germany). The samples had previously been analysed with different techniques, such as Fourier-Transform Infrared Spectroscopy (FT-IR), Micro-Raman Spectroscopy (μ-Raman), X-ray Diffraction (XRD), and Scanning Electron Microscope coupled with Energy Dispersive X-ray Probe (SEM-EDX).[21,22] Previous investigations established that the samples under consideration were fired between 900°C and 1100°C. Scheme 1

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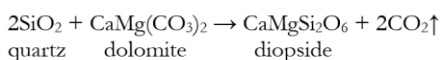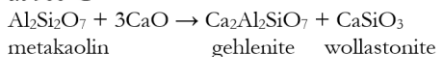   C.P. (X5000HUA) Av. Medina Allende s/n, Córdoba (Argentina)

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summarises the chemical reactions that take place, depending on the firing temperature used.
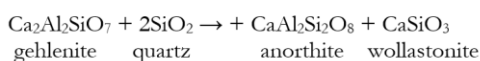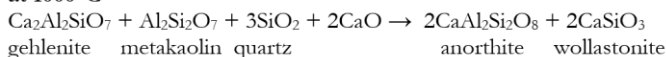
at 650-950°C

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O \quad \text{(reaction of dehydroxylation)}$$
$$\quad\text{kaolinite} \qquad \text{metakaolin}$$

at 900°C

$$Al_2Si_2O_7 + 3CaO \rightarrow Ca_2Al_2SiO_7 + CaSiO_3$$
$$\text{metakaolin} \qquad\qquad \text{gehlenite} \quad \text{wollastonite}$$

$$2SiO_2 + CaMg(CO_3)_2 \rightarrow CaMgSi_2O_6 + 2CO_2\uparrow$$
$$\text{quartz} \quad \text{dolomite} \qquad\quad \text{diopside}$$

at 1000°C

$$Ca_2Al_2SiO_7 + Al_2Si_2O_7 + 3SiO_2 + 2CaO \rightarrow 2CaAl_2Si_2O_8 + 2CaSiO_3$$
$$\text{gehlenite} \quad \text{metakaolin} \quad \text{quartz} \qquad\qquad \text{anorthite} \quad \text{wollastonite}$$

$$Ca_2Al_2SiO_7 + 2SiO_2 \rightarrow + CaAl_2Si_2O_8 + CaSiO_3$$
$$\text{gehlenite} \quad \text{quartz} \qquad \text{anorthite} \quad \text{wollastonite}$$

Scheme 1. Main reactions involving carbonates, calcium oxides and silicates in the 900°C–1100°C temperature range. In this temperature range, the crystalline lattice of clay minerals is destroyed and new phases are formed.

High-temperature crystalline phases are the result of reactions involving carbonates, calcium oxides and silicates (see main reactions in Scheme 1). When the temperature is high enough, the sintering and vitrification processes begin, determining the final colour, hardness, heat resistance and porosity. The latter has been proved to play a key role in the structural parameters of the ceramics and is related to material composition and firing temperature.[23,24] Compounds such as potassium oxides present in illite clay minerals or calcium oxides act as fluxes in the paste, encouraging the sintering process: particle surfaces begin to fuse and stick to each other, and pores become more spherical until they are eliminated, thus increasing the density. Porosity is also reduced due to grain growth at the expense of small grains.[25] Glass formation usually begins at around 1100°C and physical changes such as shrinkage occur because of the loss of open porosity and the development of closed porosity.[10,25-28] The microstructure of the matrix appears more consolidated and the increase in volume due to new phases compensates the shrinkage that occurred at lower temperatures.[29]

Total porosity measurements are therefore needed in order to completely describe the morphological changes occurring during the synthesis process. A conventional laboratory technique for measuring (macro)porosity is the Mercury Inclusion Porosimetry (MIP) analysis. This technique can evaluate porosity, pore size distribution, pore volume, density and other porosity-related characteristics of a material. By applying external pressure, mercury can be forced into the open pores (see SI). The instrument measures the progressive intrusion of mercury into a porous structure under controlled pressure. However, the MIP technique is limited to pores accessible to mercury, namely open pores of a size varying from several tens of μm to a few tens of nm. Figure 1 shows the results of the MIP analysis performed on a selection of the

Mediterranean and German samples. The mean value of the open porosity percentage for the German samples is 12±3, significantly less than the value calculated for the Mediterranean samples (23±2). This is an interesting finding, confirming that the porosity is a critical parameter in the analysis of ceramics.[13]
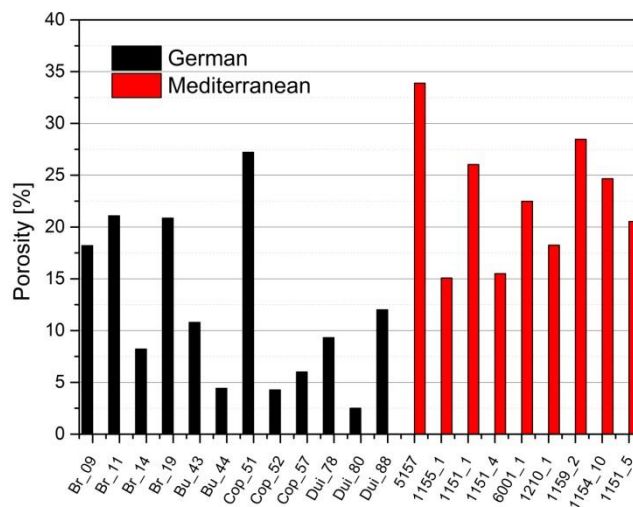

Figure 1. Histogram of open porosity (given as the % ratio between the open pore volume and the equivalent sample volume) as obtained by using Washburn's equation.[30] A description of the samples is provided in the Supporting Information (SI).

Because of the importance of closed porosity as an indicator of synthesis conditions,[10,25-28] and considering the limits of other techniques, In particular the MIP technique, for its determination, we propose Small-Angle Neutron Scattering (SANS) as a powerful investigation tool. SANS is the only technique that could provide new insights when considering how far total porosity is influenced by closed porosity. Thanks to the electroneutrality of the neutron, SANS makes it possible to penetrate deeply into the ceramics, which is extremely useful in cases where pore distribution is peaked at very different size values. Moreover, a very large Q-range, extending over several orders of magnitude, allows us to characterise complex materials over many orders of magnitude in size, which is important when several length scales need to be probed, as is the case for ceramics. The small-angle scattering instrument D11 at Institut Laue Langevin (France) used in this study allowed us to investigate distances from almost 0.6 μm down to few Å (see SI).[31]

At the nanometric scale of SANS investigations, we can distinguish whether our samples are isotropic or anisotropic from the 2D SANS pattern (see Figure 2). From the analysis of the 2D SANS patterns recorded on about 60 different samples, around 70% of the German samples were shown to be isotropic, while around 55% of the Mediterranean samples were anisotropic. Moreover, considering the details of different Q-regions (corresponding to different pore sizes), we observed that anisotropy is mainly determined by pores around hundreds of nm or more.
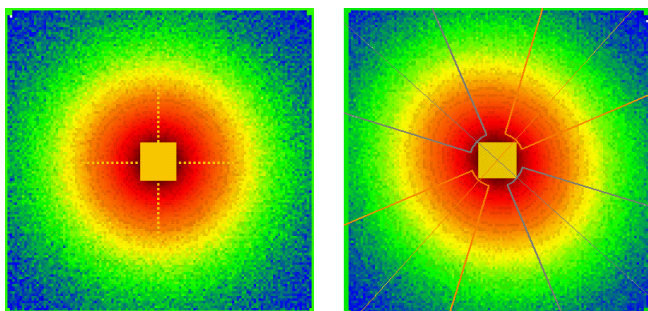
Figure 2. Reduced and normalised SANS signal collected on the 2D detector. On the left, an example of the isotropic image from a German sample; on the right, an anisotropic image from a Mediterranean sample. On the latter, the two different sectors along the two different directions of anisotropy are reported. The rectangles in the centre of the two images are the mask files created to virtually reproduce the beam stop on the detector image.

For isotropically scattering samples an azimuthal average was done over the full 2D detector scattering pattern in order to obtain a 1D scattering curve of Intensity vs scattering vector. Only these data sets have been interpreted and are discussed in this paper. Samples with anisotropic scattering cannot be azimuthally averaged over 360°. A regroupment can only be done in small sectors, which represent cuts from the centre of the scattering pattern with typical angular ranges of 15° to 20°. As such, we lose a lot of information and might introduce systematic errors and put at risk the reliability of our results. We will address a detailed study of the anisotropy in a future publication. We extracted the I(Q) curves by radial integration of the normalised 2D-patterns. The general features of the curves obtained from the two sample groups appeared to be different, as shown in Figure 3, whereas the curves from within the same historical sample group exhibited the same behaviour, underlining the existence of differences between the two groups of potteries. These differences relate to the slope of the curves in the log-log plot, to the position of the bumps in the middle Q region, and to the incoherent scattering value (determining the asymptotic horizontal I(Q) value at higher Q).
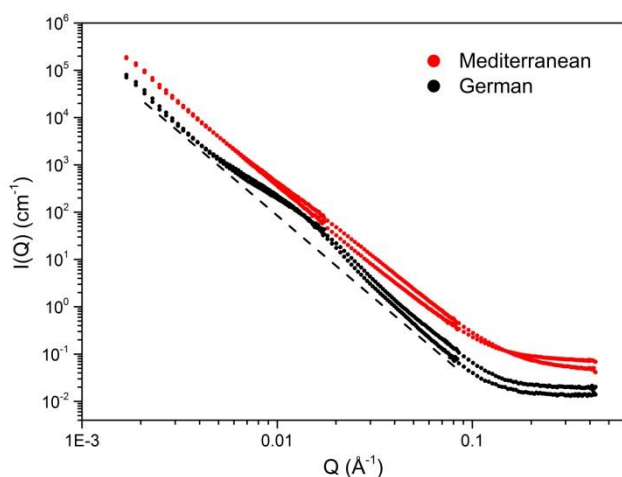

Figure 3. Plot of I(Q) curves for two samples from the German group (black) and two samples from the Mediterranean group (red), to demonstrate the differences that exist between the two groups. All samples belonging to the same group exhibit curves with the shape characteristic of that group. The dashed line is a guide for the eye.

By using a model based on two-phase systems, we calculated the Porod invariant, Q_P: the experimental value of Q_P corresponds to the relative amounts of the two phases (pores and ceramics), where the pore phase accounts for both open and closed pores (see SI). From this analysis of the SANS data, remarkably, we obtained a distribution of the results in two well-distinguished groups, corresponding to the origin of the samples (Figure 4). The mean value of the normalised total porosity for the German samples is 0.21±0.01, which is much less than the value for the Mediterranean samples (0.70±0.05).
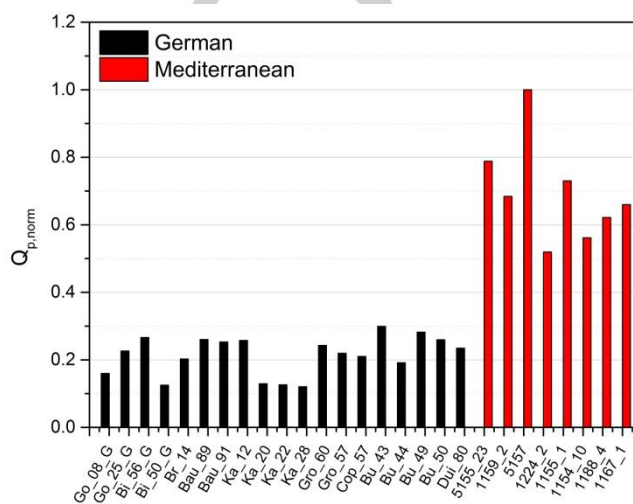

Figure 4. Diagram reporting the Porod invariant, Q_P, for samples from the German group (black lines) and from the Mediterranean group (red lines). Q_P values are normalised to the maximum value. Reported values are significant for the total pore volume (open and closed pores).

Furthermore, the use of neutrons allows us to shed light on the complexity of porosity in ceramics, helping to solve the puzzle of closed and open porosity. Indeed, by using the contrast method[32,33] (see SI) to mask the signal coming from the open pores, we once again observed a marked difference between the two groups. In the German samples, around 90% of the total pore volume was due to closed pores, while for Mediterranean samples the ratio was around 40% (Figure 5).
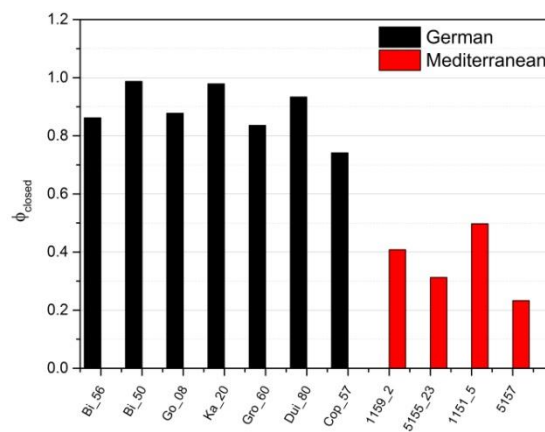

Figure 5. Diagram reporting the ratio between the closed pore volume and the total pore volume, Φ_{closed}, for samples from the German group (black) and from the Mediterranean group (red).

In view of the high cost in terms of experimental time for performing this approach, we limited the number of samples we measured; nevertheless, the trend is evident.

We fitted the whole curves by using an analytic model of flexible cylinders with an elliptical cross section plus a power law (see SI). The power law accounts for the contribution coming from the signal at lower Q, associated with bigger pores of a size out of the range probed by the experiment. This approach allows a study of the form factor correlated to a specific pore shape. The basic idea is to simulate a worm-like chain of contour length L, as a chain of segments of length Lp. In Table 1, we report the average values of the main parameters involved in the fit.

Table 1. Average values for the main shape parameters obtained by worm-like flexible cylinders model for the nanopores.

Samples	Average contour length, L (nm)	Major radius, R_{major} (nm)	Radii ratio, R_{major}/R_{minor}	Average Kuhn length, $2L_p$ (nm)	Tortuosity, L/L_p
Mediterranean	760±50	11±2	8±1	30±10	60±20
German	300±60	16±2	5±1	110±20	5±1

The results show that the pores in the Mediterranean samples are longer than in the German samples. Their shape is more squeezed (they have more or less the same major radius but a very different axis ratio): this is consistent with previous results regarding the anisotropy of the Mediterranean samples. Furthermore, considering the ratio between the contour length L and the unit segment L_p as an indication of pore tortuosity, the Mediterranean samples are significantly more tortuous than German ones.

Moreover, determining the incoherent signal (mainly coming from the hydrogen atoms of water), we found that it was an order of magnitude larger for the Mediterranean samples compared to the German samples. This difference indicates that the Mediterranean samples have extended and very tortuous open pores which trap water molecules (see Figure 6), which is consistent with the evaluation of pore tortuosity and size outlined above.
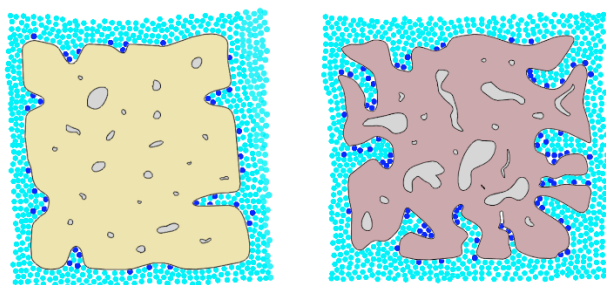

Figure 6. Sketch of the presence of confined water in the open porosity of German (on the left) and Mediterranean (on the right) samples. Dark blue dots are H_2O molecules; light blue dots are D_2O molecules.

The experimental evidence obtained by SANS allowed us to propose a convincing picture of the porosity of the different sample groups by consistently arranging all the pieces of the mosaic of information obtained. 1) The German samples are more isotropic than the Mediterranean ones and the anisotropy is mainly due to porosity in the size range of hundreds of nm or more; 2) the volume of total porosity of the Mediterranean samples is more than three times larger than that of the German samples; 3) the ratio between open and closed pore volume is approximately 1 for the Mediterranean and 1/10 for the German samples; 4) the best model for the form factor of the pores relating to their shape corresponds to flexible cylinders indicating a worm-like morphology. The pores in the Mediterranean samples are more interconnected, more extensive, and they have an articulated and complex shape. In general, they are characterised by a large morphological disorder, in terms of existing mutual interconnections and the irregularity of their shape. In addition, the Mediterranean samples have, in all the size ranges, a more marked porosity than the German ones. This difference is particularly evident for open pores and more relevant in small pores range (whereas in the German samples closed pores dominate). Considering that the small closed pores are probably quite spherical in shape, this justifies the greater isotropy shown by the German samples.

It is reasonable to consider that the differences demonstrated by SANS are closely related to the granularity of the raw materials used in different historical periods, to the geographical areas they are from and to the final use of the ceramic artefacts. On the other hand, it is well known that the main parameters determining the final porosity are firing temperature, raw material composition and other manufacturing technologies, such as the clay refining. The firing temperatures of all the samples investigated were around 900°C and the starting clay materials were kaolin-rich clay (German samples) and Ca-rich clay (Mediterranean samples). Moreover, among the German samples two different origins can be distinguished, namely Central (Thuringia) and Eastern (Saxony) Germany, due to the specificity that the clay used in Central Germany was finer and thinner than that used in Eastern Germany. In order to identify which parameter plays the main role in the determination of porosity and to mimic historical samples, we procured raw materials corresponding to Mediterranean Ca-rich paste and German kaolin-rich pastes from both the Thuringia and Saxony regions, chosen for their similarity with historical samples in terms of mineralogical composition and granularity. From these pastes, we made lab ceramics and performed on them similar SANS analyses as on the historical samples. The results showed that even for samples belongings to the same compositional group, nanoporosity is more marked in those obtained from the finest raw materials. The study of lab ceramic samples in terms of the impact of different synthesis parameters on nanoporosity will be the subject of another paper.

In summary, with this very detailed study of nanoporosity in ancient ceramic samples, we were able to relate the nanoporosity, the open/closed pores ratio, the tortuosity and the form factor of pores to the manufacturing technologies and quality of the starting raw materials. This particular approach, specifically focused on nanoporosity, can open up new prospects for investigations in a plethora of innovative materials,

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bearing in mind that nanoporosity may be an important parameter for improving the engineering of the desired functional properties of advanced modern ceramics.

Acknowledgements

Keywords: ceramics • nanostructures • nanoporosity • small-angle neutron scattering

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