THE MINERALOGICAL AND PETROGRAPHIC APPROACH TO THE POTTERY ANALYSIS AT DIFFERENT OBSERVATION SCALES

GERMANA BARONE
Dipartimento di Scienze Biologiche, Geologiche ed Ambientali, Università di Catania, Corso Italia 57, 95129 Catania

In recent years, the study of ceramic materials, especially those of archaeological interest, has been addressed by archaeologists, historians, geologists, chemists, physicists, and biologists, often with a multidisciplinary approach.

From an archaeological point of view, ceramics are usually classified according to their macroscopic characteristics together with the definition of their form, type, history, and the site where they were discovered.

Furthermore, in the field of archaeological research, there is a widespread need to use scientific analysis in order to obtain not only a correct characterization of ancient materials but also the economic and social status of the site, the definition of trade routes as well as to establish their age. In this context, the mineralogic and petrographic techniques have also helped to resolve the problems related mainly to the identification of firing processes, the characterization of ceramic coatings, and their production centres.

In other cases, petrological applications have been used to discriminate authentic ceramic materials from false ones, to recall ancient "recipes" in order to reproduce today "antiquated" materials for industrial use and to understand the technological aspects of raw materials and firing conditions.

In addition, some studies are underway to test non-destructive and innovative methods to investigate the complex processes that lead to the production of ceramic materials.

In studies of this type, ceramic materials are often considered homogeneous objects. Instead, it can be said that ceramics are highly heterogeneous material due to several factors linked to; a) the compositional and granulometric variability of the raw materials; b) the production process (based primarily on the experience of the potter); c) the firing or baking conditions (the technological level of the oven which determines the maximum temperatures, the reducing or oxidizing atmosphere, and the more or less homogeneous heat distribution inside the furnace); d) the transformations occurring during or after use (*e.g.*, length of time and conditions of burial or immersion).

The characterization of heterogeneity requires an approach that takes into account the different scales, from centimetres to nanometres, with which the processes are, recorded (Fig. 1). Observations, therefore, must be carried out using several complementary methods that are useful for a correct interpretation of the archaeological and archeometrical data.

In addition to the more classical methods (optical and electronic scanning microscopy, X-ray fluorescence and X-ray diffraction), a number of innovative methodologies play an increasingly important role, as in some examples also studied by the Research Group at Catania University.

In the case of studies aimed at determining the manufacturing centres of ceramic materials, it is also crucial to compare the results obtained from analysing the raw materials. The heterogeneity of the ceramic, on the one hand, complicates its study whereas, on the other, it highlights some of the characteristics that help in the study of its provenance, as well as in those related to production processes.

This close correlation between heterogeneity and the provenance of the source is particularly evident in the study of coarse ceramics when the inclusions have traits that can be traced back to particular geological areas, since the raw materials were generally found close to the production site. For example, the inclusion of metamorphic rocks in samples, for which a Sicilian production is hypothesized on archaeological basis, suggests the productions in the Peloritana area (Barone *et al*., 2011c).

In other cases, the presence of enigmatites in certain ceramics determines with certainty the provenance from Pantelleria (Barone *et al*., 2010). Help can also be derived from mineral chemistry data which, for example in the case of volcanic pyroxenes, allowed the discrimination of materials produced in Campana, Mt. Etna, Aeolian, or Iblei sites (Barone *et al*., 2010).

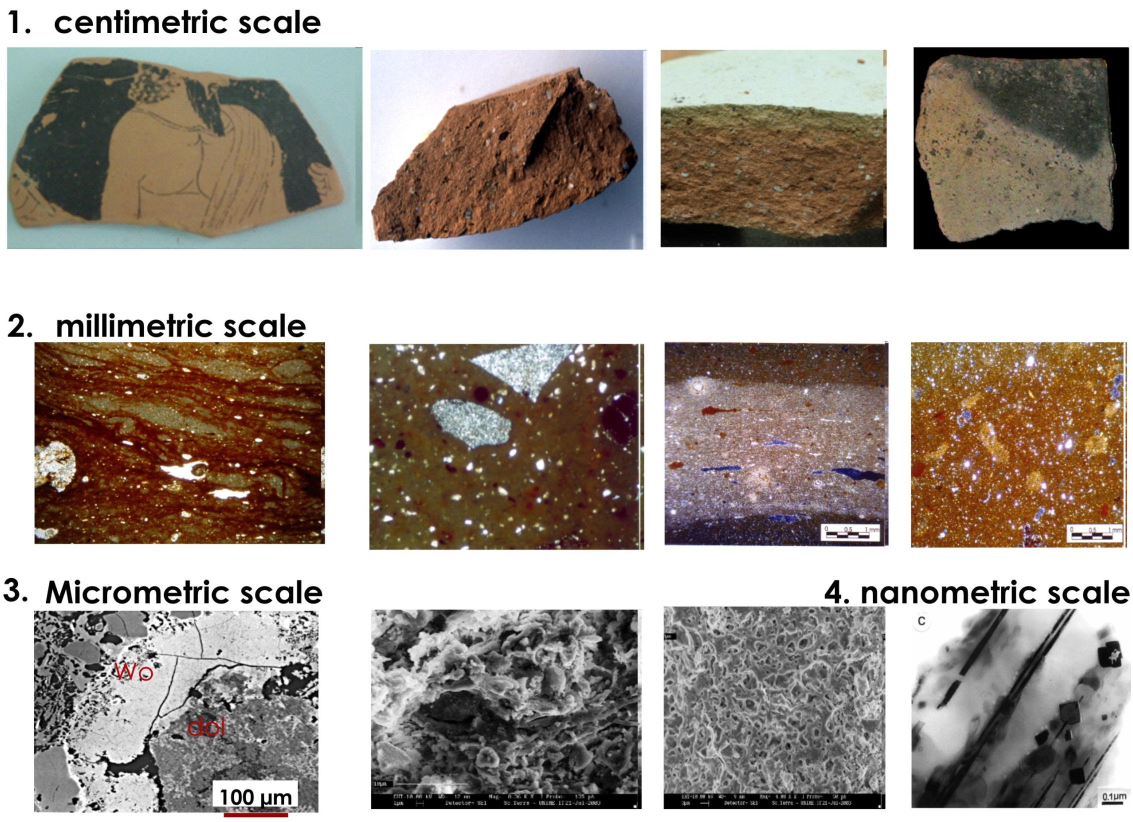

Fig. 1 - Different observation scales heterogeneity related to raw materials and production processes of the archaeological pottery.

Where pottery does not have a strong petrographic heterogeneity, as in the case of fine ceramics, the study of its origins is more complicated. In this case, the chemical analysis of the product and the comparison with reference materials of a certain local production (laboratory tests made with clay sediments, kiln scrap, common ceramic) provides indispensable information (Barone *et al.*, 2005). Sometimes, however, advanced statistical processing methods have to be used. For example, fine potteries from Gela, Agrigento, and Syracuse produced with Pio-Pleistocene clays, which is widely used in eastern and southern Sicily, have been investigated with neural networks (Mazzoleni, Personal Communication).

Heterogeneity is often accentuated during the firing process. In fact, reactions lead to the nucleation and the development of new phases and to compositional and textural re-arrangement. These reactions, that depend on composition, clay grain size, inclusions, firing temperature, and reducing or oxidizing conditions inside the furnace (Riccardi *et al.*, 1999), can be observed on different levels.

On a nanometric scale, thanks to small angle neutron scattering (SANS) study, it was possible to point out that when firing temperatures rised the reactions that occur, starting with CaO rich clay sediments, developed new phases with fractal geometric surfaces (Nittmann *et al.*, 1985; Cultrone *et al.*, 2001) characterized by an increased fractal dimension linked to the firing temperature (Botti *et al.*, 2006; Barone *et al.*, 2011b).

On the contrary, in ceramics made from clay with a low calcium content, the fractal geometry model is not applicable given that up to 1000 °C firing temperatures the reactions are much simple and do not lead to a profound restructuring of the ceramic body. Comparing the variations observed in the parameters obtained with the SANS (Rg and alpha), taken from laboratory tests at different temperatures and on archaeological ceramics, allowed us to estimate firing temperatures even for non-carbonate materials (Barone *et al*., 2011b).

A micro-millimetre scale identifies microdomains reactions that can be observed with SEM (Riccardi *et al*., 1999) whereas optical micro observations show heterogeneity from their b-fabric and optical state (Whitbread, 1995).

In many cases, at a centimetric level heterogeneities appear as combustion spots, the so-called "black heart" or superficial cleansing. The latter is typical of some ceramics produced in Gela and is the desired result of complex processes that occur thanks to the choice of raw materials and firing conditions. As the results of the XRD quantative analysis have shown, along with the thermogravimetric analysis carried out on laboratory test, clarification is obtained through the presence of the NaCl in the raw material which, at about 500 °C, reacts with Fe_2O_3 forming volatile compounds which are then found as sublimates inside the interior walls of the furnaces (Barone *et al*., 2012).

In conclusion, given the wide heterogeneity that ceramic products have on different scales, it is not in many cases possible to indicate, as often requested by archaeologists, the quantity of samples to be analysed to have a representative result of the ceramics. This is shown in a research (Barone *et al*., 2011a) in which it was estimated that only in the case of fine ceramics micro sampling may be representative thanks to the comparison of whole sample quantitative mineralogical composition, obtained with non-destructive neutron diffraction analysis (TOF-ND), and XRD analysis of micro sampling of different minimum quantities of fine and coarse ceramics.

Therefore, as we have already said, non-destructive and portable analysis (*e.g.*, pXRF, Raman, FT-IR) are of particular importance, allowing for: a) numerous analysis of the same sample; b) analysis on a larger range of samples, thus making the results statistically more valid; c) selection of samples on which to make a destructive analysis.

REFERENCES

Barone, G., Lo Giudice, A., Mazzoleni, P., Pezzino, A. (2005): Chemical characterization and statistical multivariate analysis of ancient pottery from Messina, Catania, Lentini and Siracusa (Sicily). *Archaeometry*, **47**, 745-762.

Barone, G., Belfiore, C.M., Mazzoleni, P., Pezzino, A., Viccaro, M. (2010): A volcanic inclusions based approach for provenance studies of archaeological ceramics: application to pottery from southern Italy. *J. Archaeol. Sci*., **37**, 713-726.

Barone, G., Bartoli, L., Belfiore, C.M., Crupi, V., Longo, F., Majolino, D., Mazzoleni, P., Venuti, V. (2011a): Comparison between TOF-ND and XRD quantitative phase analysis of ancient potteries. *J. Anal. At. Spectrom*., **26**, 1060-1067.

Barone, G., Crupi, V., Majolino, D., Mazzoleni, P., Teixeira, J., Venuti, V., Scandurra, A. (2011b): Small angle neutron scattering as fingerprinting of ancient potteries from Sicily (Southern Italy). *Appl. Clay Sci*., **54**, 40-46.

Barone, G., Mazzoleni, P., Ingoglia, C., Vanaria, M.G. (2011c): Archaeometric evidences of the 4^{th}-2^{nd} century BC amphorae productions in north eastern Sicily. *J. Archaeol. Sci*., **38**, 3060-3071.

Barone, G., Mazzoleni, P., Spagnolo, G., Aquilia, E. (2012): The transport amphorae of Gela: a multidisciplinary study on provenance and technological aspects. *J. Archaeol. Sci*., **39**, 11-22.

Botti, A., Ricci, M.A., De Rossi, G., Kockelmann, W., Sodo, A. (2006): Methodical aspects of SANS and TOF neutron diffraction measurements on pottery. The case of Miseno and Cuma. *J. Archaeol. Sci*., **33**, 307-319.

Cultrone, G., Rodriguez-Navarro, C., Sebastian, E., Cazalla, O., De La Torre, M.J. (2001): Carbonate and silicate phase reactions during ceramic firing. *Eur. J. Mineral.,* **13**, 621-634.

Nittmann, J., Daccord, G., Stanley, H.E. (1985): Fractal growth viscous fingers: quantitative characterization of a fluid instability phenomenon. *Nature*, **314**, 141-144.

Riccardi, M.P., Messiga, B., Duminuco, P. (1999): An approach to the dynamics of clay firing, *Appl. Clay Sci*., **15**, 393-409.

Whitbread, I.K. (1995): Greek transport amphorae: A petrological and Archaeological study. The British School at Athens, ed. Fitch Laboratory Occasional Papers, 4, 453 p.