2022 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
University of Calabria, Italy, October 19-21, 2022

# Implementation of an integrated methodology to assess provenance of ancient ceramic raw materials

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***Abstract* – In the present study a methodology to assess provenance of raw materials used in medieval ceramic has been implemented. It is based on the assessment of the mineralogical composition trend at increasing temperature of clay deposits, as deduced from the firing tests and TG-DSC curves, outcropping in the surrounding of archaeological sites from which ceramic fragments come from. Data are contextualized in the landscape scenario within which the ceramic production centers operated by geo-localizing the sampled clay outcrops and identifying the geographical relationships with the archaeological sites. The methodology was implemented in order to become a best practice in the identification of raw materials used for ceramic productions. This methodological approach has allowed to return an articulated picture of the presence of productions in the region, that during the Middle Ages circulated on a regional as well as extra-regional scale thanks to a network of land and river communication, making it possible to circumscribe any local productions, to define the circulation of raw materials and know-how in the diachrony for a territory such as the Basilicata region, rich in archaeological evidence and densely populated from prehistory to the Middle Ages.**

## I. INTRODUCTION

Chemical and mineralogical composition, provenance and production process of ceramics are the main investigation topics in archaeometry. Clay-dominant deposits are a common source of ceramic raw materials. Each deposit is characterized by a fingerprint. However, comparing the chemical-mineralogical composition of the ceramic fragment with that one of a clay, without considering the chemical and physical transformations during firing process is extremely misleading. For this reason, we implemented a methodology - based on the comparison of the composition of medieval ceramic fragments selected for the study of provenance with the *trend* of the mineralogical composition of clay deposits as temperature increases, contextualized in the landscape scenario within which the production centers operated - that could become a best practice in the identification of raw materials used for ceramic productions.

Several clay-dominant deposits outcropping in Basilicata and belonging to different geological formations were sampled and analyzed to identify the types of raw materials most suitable for the vast production of ancient ceramics, to locate the most likely sources of raw materials, to formulate hypotheses on the circulation of them and/or artifacts, and to discriminate local production from possible "imports".

Ceramic fragments form three archaeological sites form Basilicata (southern Italy) and clay deposits belonging to different geological formations outcropping in Basilicata and sampled in the surrounding of the archaeological sites from which ceramic sherds come have been used to test the methodology. Experimental firing tests on the clay deposits have been performed at different temperature steps. TG-DSC analysis have been carried out on clay samples and correlated to firing tests.

## *II. DISCUSSION AND CONCLUSON*

The determination of the origin of ceramic materials, and of the raw materials used to produce them, is the main field of application of archaeometry. Each deposit can indeed be considered as characterized by a fingerprint. Modifications made by artisans to the original clay – e.g. purification through decanting or sieving procedures or addition of foreign material as a smagrant - during

production must be considered. Following these, the resulting composition of the ceramic mixture will be different from that of the starting material. Therefore, comparing the chemical-mineralogical composition of the ceramic fragment with the one of a clay, without considering the laborious process of "firing" to which a ceramic artifact is subjected before being placed on the "market", is extremely misleading. It is in this perspective that we implemented a methodology that could become a best practice in the research of raw materials used for ceramic productions.

The wide choice and distribution of the raw material "clay" in Basilicata is certainly responsible for the intense ceramic production from the archaeological sites of *Satrianum*, Castello di Moliterno and Santa Maria d'Anglona from the classical period [1] to the medieval period [2,3]. In order to identify the types of raw materials most suitable for the vast production of medieval ceramics, to locate the most likely sources of raw materials, to formulate hypotheses on the circulation of them and/or artifacts, and to discriminate local production from possible "imports", several clay-dominant deposits outcropping in Basilicata and belonging to different geological formations were sampled and analyzed (Fig. 1).

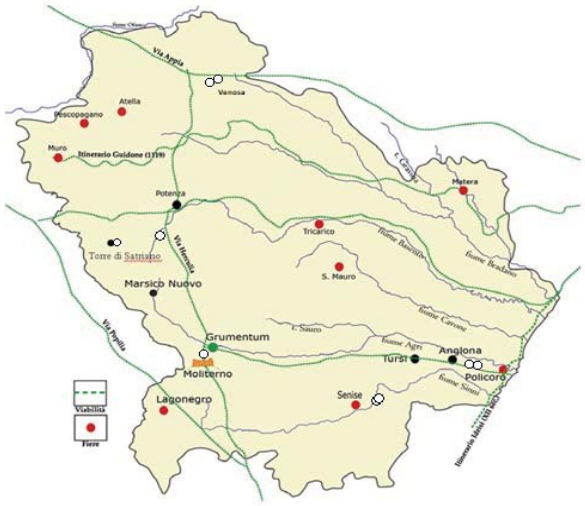


*Fig. 1.● Archaeological sites .○ Clay deposit sampling sites (Annunziata, Gargiulo, 2019)*

In order for clay deposits to be suitable as ceramic raw materials, it is necessary that they are easily accessible and exploitable with the means available in the past, especially in periods of poor circulation of goods and reduced and localized production as in some periods of the Middle Ages. With the help of a Territorial Informative System in a GIS environment and a relational database of raw materials, it was possible to identify the outcrops of clay deposits to sample and compositionally characterize. The illitic "clays" are very abundant in Basilicata and constitute the prevalent clay deposits. TG-DSC curves were acquired - in both reducing and oxidizing environments - from the clay sediments sampled and experimental firing tests were performed at different temperature steps. The final color of the firing test specimen was coded using Munsell Tables. The comparison with the composition of the ceramic material selected for the study of provenance was carried out taking into account the trend of the mineralogical composition of clay deposits as temperature increases as deduced from the firing tests and TG-DSC curves (Figs 2-4) and contextualized in the landscape scenario within which the production centers operated. For brevity, only the Tg-DTA curves of a single sample by type of clay deposits sampled have been reported. The DTA curves give precise indications of the onset of exothermic endothermic transformations that develop in a clay sediment as temperature proceeds. In the DTA curves the first weak endothermic peaks of temperature between 98 and 114°C are associated to dehydration of physically adsorbed water and water molecules bound to exchangeable cations. The second endothermic peaks at about 550 °C are due to the loss of hydroxyl groups and decomposition of kaolinite. The presence of other mineral components in the samples is clearly reflected by the endothermic peaks at about 765 °C associated with the decomposition of calcite. From the TG/DTA curves, the peak temperatures and temperature onsets are mainly influenced by the number and types of components present in the sediment. Finally, low endothermic peaks at temperatures between 880 and 900 ºC and exothermic peaks around 940 ºC appear to be related to phase transformations (formations of neo-minerals such as diopside and gehelenite) and collapse of the clay structure. It is interesting to note that the "matrix" effect as well as the different carbonate composition between the Plio-Pleistocene Clays sediments (Senise locality) and the Sub-Apennine Clays (Venosa and Tursi localities) lead to a decrease in the onset temperatures of calcite dissolution by about 10 °C, respectively. The onset and duration of the interval within which the new phases such as diopside and gehlenite formed also varies among the different sediments: in the Plio-Pleistocene Clays of the Senise locality, the newly formed phases are less abundant, they begin to segregate slightly earlier, and the temperature interval within which the process is completed has a shorter duration than what observed for Subappennine Clays sampled at Tursi and Venosa localities.

The methodological approach based on the comparison of the composition of medieval ceramic fragments selected for the study of provenance with the *trend* of the mineralogical composition of clay deposits as temperature increases, as deduced from the firing tests and TG-DSC curves and contextualized in the landscape scenario within which the production centers operated, allowed to return an articulated picture of the presence of productions in the region, that during the Middle Ages circulated on a

regional as well as extra-regional scale thanks to a network of land and river communication. The integration of the results of the archaeological analysis, the *firing tests*, the geolocalization of the sampled outcrops and the identification of the geographical relationships with the archaeological sites have made it possible to circumscribe any local productions, to define the circulation of raw materials and know-how in the diachrony for a territory such as the Basilicata region, rich in archaeological evidence and densely populated from prehistory to the Middle Age.

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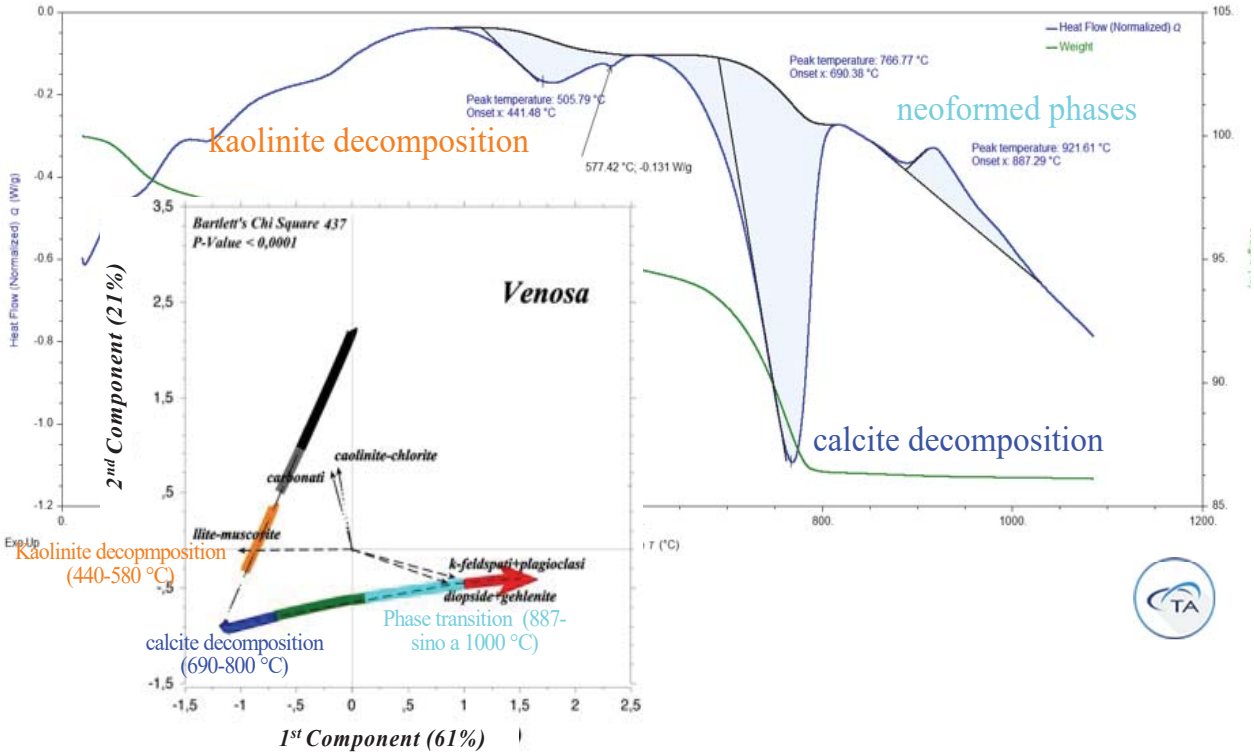


*Fig. 2 . TG-DTA curve e firing test of clay deposits sampled at Venosa (V1). PCA output was generated using a matrix input constituted by abundances of mineralogical phases detected by powder XRD after firing samples for one hour in oven at different temperatures.*

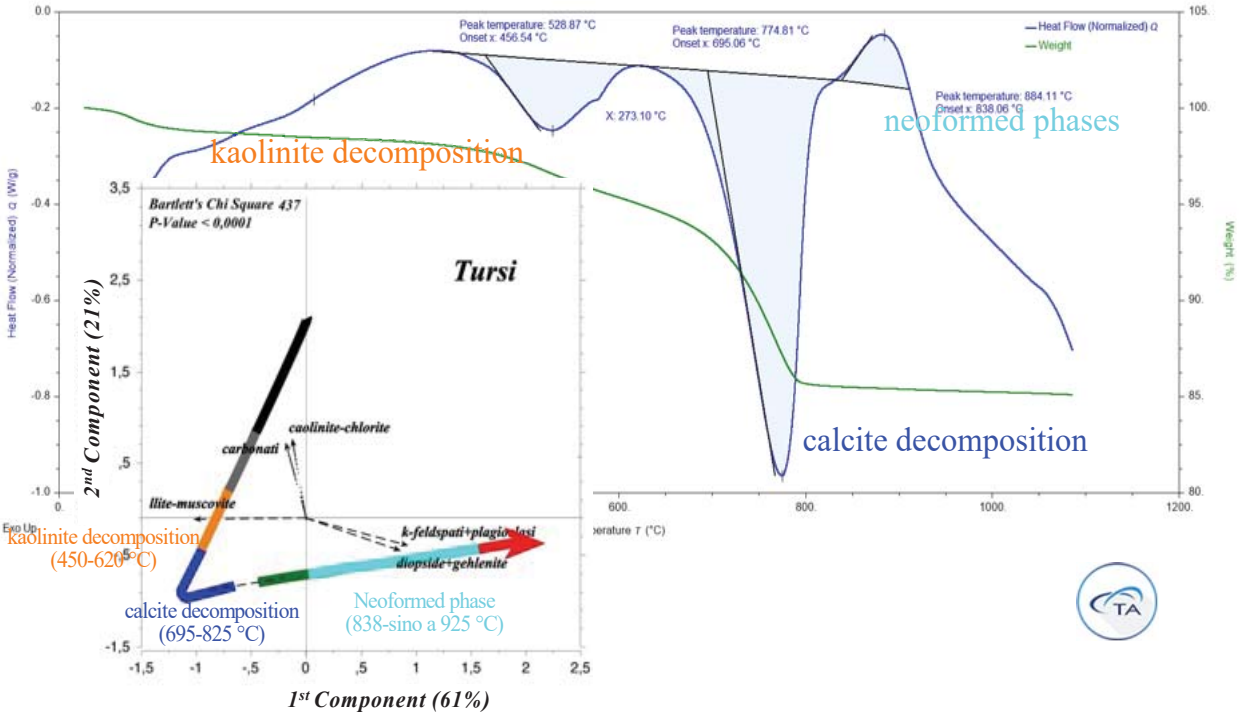


*Fig. 3. TG-DTA curve e firing test of clay deposits sampled at Tursi (C1). PCA output was generated using a matrix input constituted by abundances of mineralogical phases detected by powder XRD after firing samples for one hour in oven at different temperatures.*

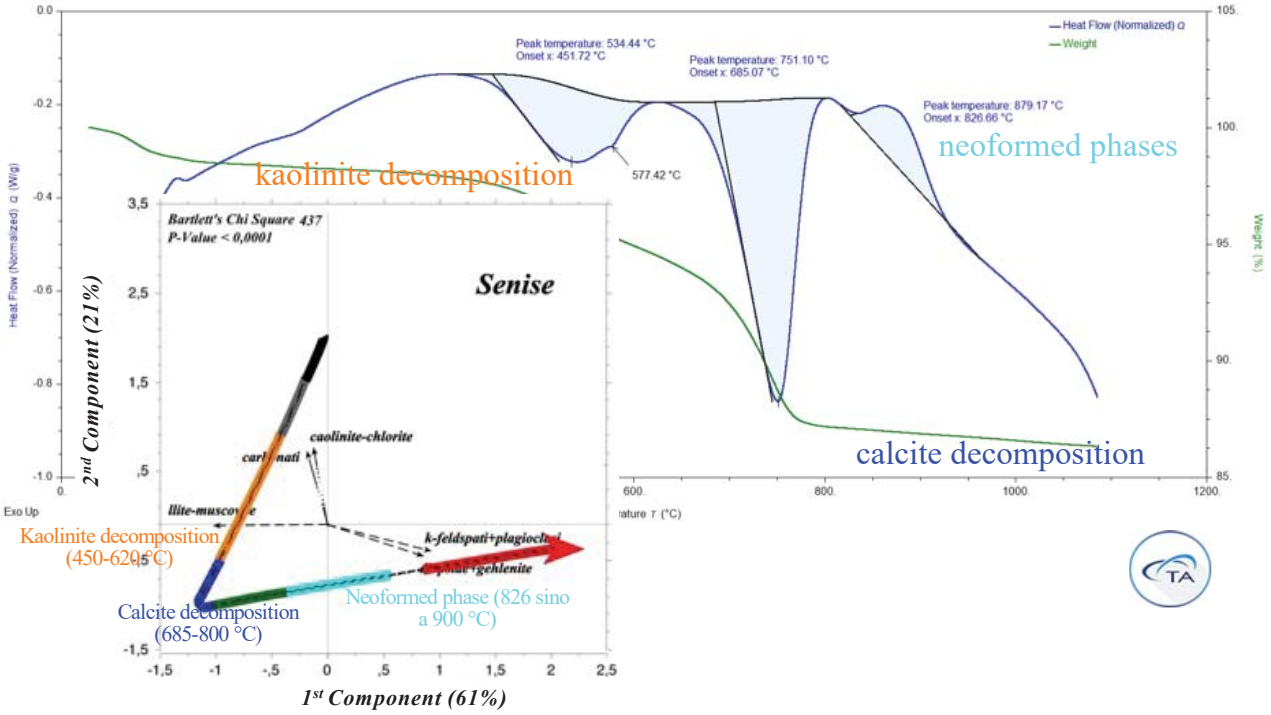


*Fig. 4. TG-DTA curve e firing test of clay deposits sampled at Senise (Senise 4). PCA output was generated using a matrix input constituted by abundances of mineralogical phases detected by powder XRD after firing samples for one hour in oven at different temperatures.*