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CRYSTALLOGRAPHIC AND PETROGRAPHIC CHARACTERIZATION OF TWO ARCHITECTURAL TERRACOTTAS FROM THE SANCTUARY OF MARASÀ (LOCRI)

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Abstract. Two fragments of the terracotta revetment plaques of the Western Greek sanctuary of Marasà (Locri) stored up in the National Archaeological Museum of Reggio Calabria (Italy) were studied. One of them has chromatic and granulometric anomalies if compared with similar artefacts while the other has a strong chromatic variability. Polarized light microscopy and X ray powders diffractometry were used for petrographic and crystallographic characterization. The ceramic body of find MRC 7013 contains an unusually high quantity of rocky grains and the groundmass shows the green colours of clay minerals (glauconite, celadonite or berthierine) that is stable only at low temperatures. In fragment MRC 7043 three main areas differentiated by colour were identified. The study confirmed crystallographic differences between the samples due to great temperature's differences during the firing process.

1. Introduction

The Marasà temple (Locri, Italy) was investigated for the first time in 1889-1890 by an Italian-German mission directed by Paolo Orsi and Eugen Petersen (Orsi 1924, 2022). The excavation was resumed in 1954 by Alfonso de Franciscis, who discovered over 4,500 fragments of Archaic architectural terracottas (Franciscis 1979). Other excavations were carried out in the 1970s, 1990s and 2000s (Rubinich 2007). More than 600 clay fragments of various types (antefixes, simas, cassettes, drips, slabs and tiles) belonging to the Marasà temple are kept in the deposits of the National Archaeological Museum of Reggio Calabria (Grillo 2011).

Colour of the ceramic body, generally, ranges from orange-pink to light ochre. Ratio between clayey groundmass and non-plastic inclusions (temper) is within the range limits observed in ceramics that reach such considerable thickness. In some cases, however, the texture is arenaceous, which means that temper's fraction highly predominates, while the colour is green or grey, appearing more similar to a mortar than to a ceramic. In other cases, the paste's colour is not homogeneous suggesting an uneven firing process. Our attention focused on these anomalous types with the intention of clarifying the technological processes that produced them.

Samples were studied from a fragment with inventory number MRC 7013 from which only one sample was collected (TM1) and from another one with inventory number MRC 7043 from which three samples were taken (TM2, TM3 and TM4). Each sample was studied under transmitted polarized light microscope (TLPM). Mineralogical phases were identified using X ray powder diffractometry (PXRD).

2. Materials and methods

Two fragments of the terracotta revetment plaques were studied (Fig. 1 and 3). One sample was taken from find MRC 7013 (Fig. 2) and three samples from find MRC 7043 (Fig. 4, 5, and 6). Sampling was did using a sharp chisel choosing areas already abraded. 30 μm thin sections were prepared and studied with polarized light microscopy. Staining for carbonate investigation were obtained preparing a 5.8 mM aqueous solution of Alizarin Red S and a 47.3 mM aqueous solution of potassium hexacyanoferrate both adjusted at pH=1. These solutions were mixed with ratio 3:2, applied on thin sections for 30 seconds and then rinsed with water (Dickinson 1966). Aliquots of each sample, opportunely grounded, were analysed with Philips PW 1050/39 X ray powders diffractometer. The diffractometer operates in the Bragg-Brentano geometry using Ni-filtered Cu Kα radiation (λ = 1.54056 Å) in the 2θ range 5-80° with a step of 0.05° and a time for step of 5 sec. X'pert HighScore® Software was used for the qualitative interpretation of the patterns.

FIGURE 1. Find MRC 7013.

3. Theory

Clays used for ceramic production is composed by a variety of clay minerals and may contain carbonate (calcareous clay). Furthermore, many other mineral species are usually found in rock's fragments used as temper. The ceramic's firing process produces changes in the starting minerals so that the resulting mineralogical composition is strictly dependent on the maximum reached temperatures (R. Heimann 2019).

The first reactions observed as temperature goes up are kaolinite ($Al_2Si_2O_5OH_4$) dehydroxylation, which happens already below 550 °C, and chlorite group minerals ((Al, Fe, Mg)$_{5-6}$(Al, Fe$_{3+}$,Si)$_4$O$_{10}$(OH)$_8$) dehydroxylation above 650 °C. Decomposition of calcium carbonate ($CaCO_3$) starts at 600 °C. In calcareous clay, CaO reacts with silicate minerals

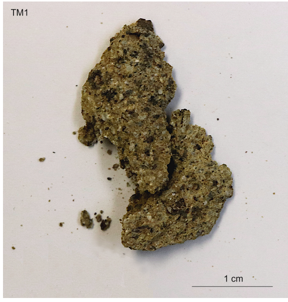

FIGURE 2. sample TM1 from find MRC 7013.

FIGURE 3. Find MRC 7043.

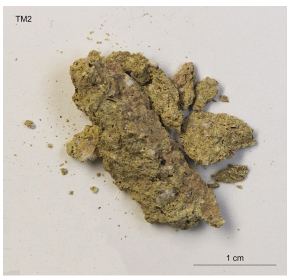

FIGURE 4. Sample TM2 from find MRC 7043.

to produce gehlenite ($Ca_2Al(AlSiO_7)$), diopside ($CaSi_2O_6$), and wollastonite ($CaSiO_3$) starting from 850 °C. K-feldspars disappear below 1000 °C while plagioclase and quartz persist up to 1100 °C (R. B. Heimann and Maggetti 2019). In silica rich clay, mullite ($Al_{4+2x}Si_{2-2x}O_{10-x}$ where $x \approx 0.4$) and tridymite or cristobalite appear at 1000 °C. The transformation from β-quartz to tridymite usually needs a catalyst, such as an alkali element, to occur. Otherwise β–quartz transforms directly to cristobalite (Holmquist 1961; Aasly, Malvik, and Myrhaug 2007; Dapiaggia *et al.* 2015).

FIGURE 5. Sample TM2 from find MRC 7043.

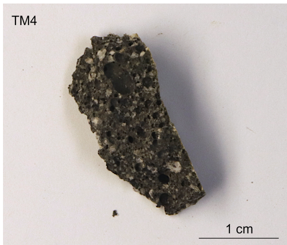

FIGURE 6. Sample TM4 from find MRC 7043.

4. Results

4.1. Find MRC 7013. Find MRC 7013 (Fig. 1) is a revetment's fragment of the sanctuary cell and presents both granulometric and chromatic anomalies. Sample TM1 has a granular and coarse texture. The paste colour by naked eye observation is brown-ochre (Munsell colour system: 10.0 YR 7.00 / 2.0). The granular framework (Fig. 6) is poorly sorted and mainly made up of colourless rocks with a medium-low sphericity, angular or sub-angular shape and medium-fine sandy granulometry (100 – 500 µm) and, secondarily, by black coloured vacuolar grains with high sphericity, sub-angular shape and coarse to very coarse sand grain size (up to 2 mm). The groundmass is green in colour (Munsell colour system: 5.0 GY 6.00/4.0) and constitutes approximately 35% of the total volume (Fig. 6). The light-coloured grains are made up almost entirely of quartz and feldspar. Plagioclases prevail among feldspars, often with the typical polysynthetic twinning. By applying the Michel - Levy method, the amount of anorthite was estimated at 55-60% (labradorite). Alkaline feldspars are present to a lesser extent. The dark coloured component consists of strongly vacuolar volcanic pumice. The groundmass colour can be associated with clay minerals which contain bivalent and/or trivalent iron (glauconite, celadonite, berthierine or chlorite), an indication that the mixture has not underwent firing. Above 400 ° C, indeed, mineralogical transformations take place which lead to striking chromatic changes (Ouahabi *et al.* 2015). Carbonates test with Alizarin Red S red and ferric hexacyanoferrate revealed small quantities of calcite and ferrous calcite respectively. X ray powders diffractometry (PXRD) confirmed the presence of quartz, labradorite, diopside, orthoclase and goethite (Fig. 7).

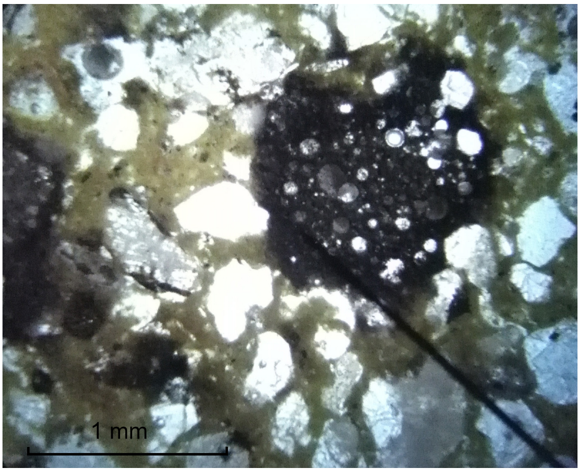

FIGURE 7. Sample TM1, micrograph, // nicols.

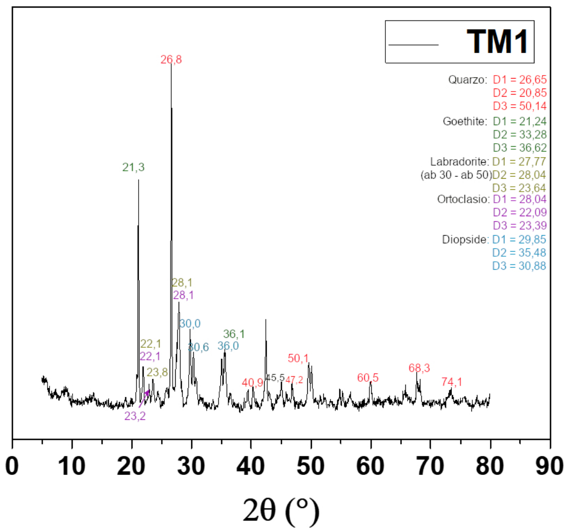

FIGURE 8. PXRD pattern of sample TM1. The three main peaks of the corresponding crystalline species are shown.

4.2. Find MRC 7043. This fragment is decorated with monochrome fish flakes pattern (Fig. 4). The ceramic body's main feature is the marked chromatic unevenness. Three samples were taken in correspondence with the three main chromatic areas and analysed separately.

4.2.1. *Sample TM2.* The texture is granular and highly porose. Colour by naked eye observation is ochre (Munsell colour system: 2.5 Y 7.00 / 2.0).

The granular framework consists mainly of poorly sorted colourless grains with low sphericity, angular or sub-angular shape and grain size from 100 μm to 1 mm and, secondarily, by laminar or elongated chamotte with granulometry of 10-500 μm. The groundmass, which constitutes approximately 50% of the total volume, is yellow-green coloured (Munsell colour system: 5.0 Y 6.00 / 4.0). The rocky grains are made up almost entirely of quartz and feldspar (plagioclase and alkaline feldspar) and, secondly, of pyroxenes. Applying the Michel - Levy method to plagioclases, the amount of anorthite can be estimated at around 55% (labradorite). The presence of calcite and ferrous calcite was highlighted by the carbonates test with red S alizarin and ferric hexacyanoferrate. The groundmass colour is due, partly, to green clay minerals which contain both bivalent and trivalent iron(glauconite, celadonite or their diagenetic alteration products such as chlorite or berthierine), an indication that the mixture underwent firing at low temperatures.

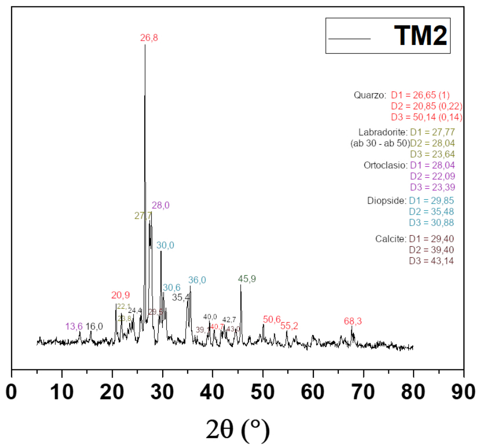

FIGURE 9. PXRD pattern of sample TM2. The three main peaks of the corresponding crystalline species are shown.

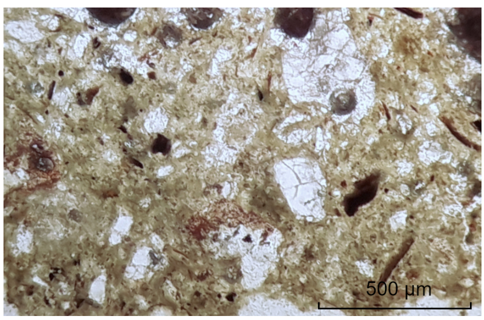

FIGURE 10. Sample TM2, micrograph, // nicols.

PXRD (Fig. 9) confirmed the presence of quartz, labradorite, orthoclase, diopside and calcite (although the peaks are small, they are confirmed by the spectrum of the TM3 sample). The sharp peak at 45.9° could be associated to aragonite, the main peak being masked by that of quartz. associated with aragonite, the main peak being masked by that of quartz.

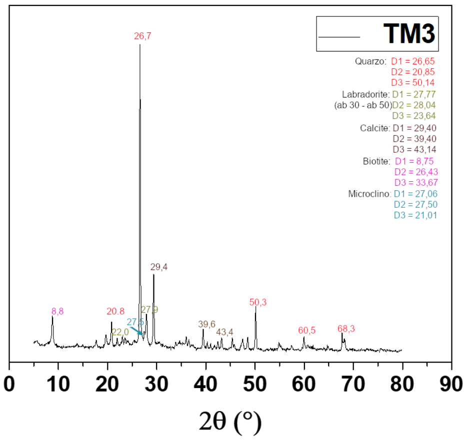

FIGURE 11. PXRD pattern of sample TM3. The three main peaks of the corresponding crystalline species are shown.

4.2.2. *Sample TM3.* The ceramic body's colour by naked eye observation is orange-ochre (Munsell colour system: 7.5 YR 6.00 / 2.0). The granular framework is made up of predominantly light-coloured rocky grains and coarse to medium sand-sized chamotte. It is mainly made up of poorly sorted, colourless grains with low sphericity, angular or sub-angular shape and granulometry from 100 µm to 1 mm and, secondarily, by laminar or elongated chamotte with granulometry of 10-500 µm. The groundmass is orange ochre (Munsell colour system: 5 YR 3.00 / 6.0) and it constitutes approximately 50% of total volume.

The rocky grains are made up almost entirely of quartz and feldspar (plagioclase and alkaline feldspar). Applying the Michel - Levy method to plagioclases, the amount of anorthite can be estimated at around 55% (labradorite). Microcline crystals are visible with the typical tartan texture. There is secondary calcite in microcrystalline form, micrite grains and biotite.

The PXRD (Fig. 11) analysis confirmed the presence of quartz, labradorite, microcline, calcite and biotite.

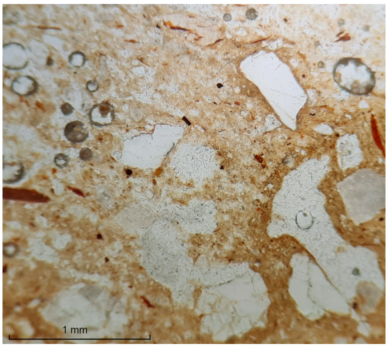

FIGURE 12. Sample TM3, micrograph, // nicols.

4.2.3. *Sample TM4.* Ceramic body's texture is vacuolar, granular and it appears grey-green coloured by naked eye observation (Munsell colour system: 5 Y 5.00 / 2.0). The granular framework consists mainly of light-coloured grains with coarse to medium sandy granulometry. The grain shape is low spheric, angular or sub-angular and the grain size range between 100 µm and 2 mm. The groundmass is greenish brown (Munsell colour system: 2.5 Y 5.00 / 2.0) and it constitutes approximately 50% of the total volume. The granular framework consists almost entirely of quartz and feldspar (plagioclase and alkaline feldspar) often altered by thermal action. Newly formed hematite is present. Groundmass is entirely covered by a dense intertwining of acicular crystals of tridymite (Fig. 14) and by spherical vacuoles whose diameter often exceeds 1 millimeter (Fig. 13). The massive presence of vacuoles and of tridymite indicates that the firing temperature overcame 1000 ° C. PXRD pattern confirmed the presence of diopside, quartz, labradorite and mullite (Fig. 15). The peaks corresponding to those of tridymite show 2θ angle shift of 0.3 degrees. The quantitative predominance of diopside and the presence of mullite are indication of unusually high temperatures reached during firing.

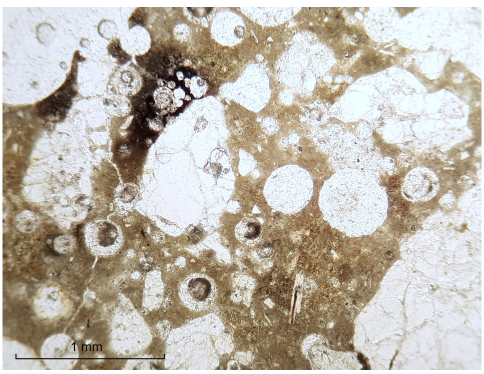

FIGURE 13. Sample TM4, micrograph, // nicols.

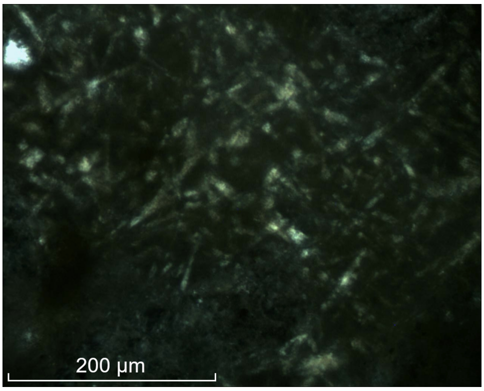

FIGURE 14. Sample TM4, micrograph, + nicols.

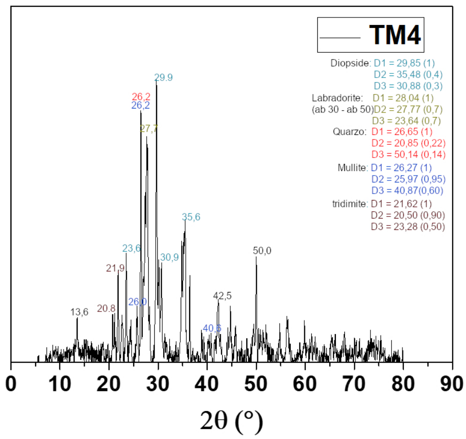

FIGURE 15. PXRD pattern of sample TM4. The three main peaks of the corresponding crystalline species are shown.

5. Discussion

The analysis of one sample from fragment MRC 7013 show a high amount of aplastic component, between 60 and 65%. The groundmass colour is due to the presence of green clay minerals (glauconite, celadonite, berthierine or chlorite), which are decomposed if subjected to temperatures above 400 °C (Haaland *et al.* 2017). PXRD analysis did not detect their peaks due to the prevalence of signals from the granular framework and a very pronounced background noise at the lowest values of 2θ. The absence of firing and the high quantity of the aplastic component constitutes an unexpected result in this archaeological context and it deserves further deepening. Indeed, the use of clayey mortars in Magno-Greek architecture it is not yet reported.

The granular framework of fragment MRC 7043 constitutes about 50% of the total volume. The groundmass of the three samples is strongly differentiated due to the different firing temperatures to which they were subjected. The yellow-green colour of the background mass of sample TM2 can be partly associated to the presence of glauconite, celadonite, berthierine or chlorite, an indication that the mixture didn't undergo firing at high temperatures. The groundmass colour of sample TM3 is orange-ochre, typical of a clay with a strong ferrous component fired up to 900 °C. The groundmass of sample TM4, which is greenish brown coloured, appears entirely covered by a dense intertwining of acicular crystals of tridymite under crossed nicols. The PXRD pattern (fig. 15) shows the quantitative prevalence of diopside, little present, instead, in the other two samples, and the appearance of the mullite's peaks. The peaks of tridymite show a 2θ angle shift of 0.3 degrees. The presence of these phases indicates that the firing temperature exceeded 1000 °C. The great maximum temperature's variability of the firing process could be due to uneven exposition to the heat source caused by incorrect stacking in the kiln.

6. Conclusions

The analysis of the sample from fragment MRC 7013 shows an unusual great amount of the aplastic component and the presence of green clay minerals (glauconite, celadonite, berthierine or chlorite), which are decomposed if subjected to temperatures above 400 °C. The absence of firing and the high quantity of the aplastic component constitutes an unexpected result in this archeologic context and it deserves further deepening. Indeed, Greek and Magno-Greek archaic temples revetments are always reported to be made of terracotta (Harbonneaux, Martin, and Villard 1978).

The groundmass colour of fragment MRC 7043 is strongly differentiated due to not homogeneous firing. The great temperature's variability of the firing process could be due to uneven exposition to the heat source caused by incorrect stacking in the kiln.

7. Authors contribution

V. Vecchio: conceptualization, investigation, writing – original draft, M. L. Saladino: investigation, F. Armetta: investigation, writing – review and editing, D. Costanzo: resources, writing – review and editing, B. Fazzari: supervision, C. Malacrino: resources, V. Mollica Nardo: investigation, R. C. Ponterio: supervision.

References

Aasly, K., Malvik, T., and Myrhaug, E. H. (2007). "Advanced methods to characterize thermal properties of quartz". In: New Delhi, India, pp. 381–392.

Dapiaggia, M., Pagliaria, L., Pavese, A., Sciascia, L., Merli, M., and Francescon, F. (2015). "The formation of silica high temperature polymorphs from quartz: influence of grain size and mineralising agents". *Journal of the European Ceramic Society* **35**(16), 4547–4555. DOI: 10.1016/j.jeurceramsoc.2015.08.015.

Dickinson, J. A. D. (1966). "Carbonate identification and genesis as revealed by staining". *Journal of Sedimentary Research* **36**(2). DOI: 10.1306/74D714F6-2B21-11D7-8648000102C1865D.

Franciscis, A. D. (1979). *Il Santuario di Marasà in Locri Epizefiri. I. Il tempio arcaico*. Monumenti antichi della Magna Grecia 3. Naples: Gaetano Macchiaroli Editore.

Grillo, E. (2011). *Locri Epizefiri: terrecotte architettoniche inedite dal santuario di Marasà*. Quaderni di Archeologia 1. Pisa: Fabrizio Serra Editore.

Haaland, M., Friesem, D., Miller, C., and Henshilwood, C. (2017). “Heat-induced alteration of glauconitic minerals in the Middle Stone Age levels of Blombos Cave, South Africa: Implications for evaluating site structure and burning events”. *Journal of Archaeological Science* **86**, 81–100. DOI: 10.1016/j.jas.2017.06.008.

Harbonneaux, J., Martin, R., and Villard, F. (1978). *La Grecia arcaica : (620-480 a.C.)* Milan: Rizzoli.

Heimann, R. B. and Maggetti, M. (2019). “The struggle between thermodynamics and kinetics: Phase evolution of ancient and historical ceramics”. EMU Notes in Mineralogy **20**, 233–281. DOI: 10.1180.

Heimann, R. (2019). *Classic and Advanced Ceramics: From Fundamentals to Applications*. New York: John Wiley & Sons.

Holmquist, S. B. (1961). “Conversion of quartz to tridymite”. *Journal of American Ceramic Society* **44**(2). DOI: 10.1111/j.1151-2916.1961.tb15355.x.

Orsi, P. (1924). *Caulonia II Memoria*. Vol. XXIX, col. 242. Milan: Hoepli.

Orsi, P. (2022). *I taccuini II*. Rome: Giorgio Bretschneider.

Ouahabi, M., Daoudi, L. E., Hatert, F., and Fagel, N. (2015). “Modified mineral phases during clay ceramic firing”. *Clays and Clay Minerals* **63**(5), 404–413. DOI: 10.1346/CCMN.2015.0630506.

Rubinich, M. (2007). “Resti di una forgia nell’area del santuario di Marasà”. In: *Caulonia tra Crotone e Locri, conference proceedings (Florence, May 30th - June 1st 2007)*. Florence: Firenze University Press, pp. 389–398. DOI: 10.36253/978-88-8453-931-1.

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