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A non-invasive analysis of ‘proto-majolica’ pottery from southern Italy by TOF neutron diffraction

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Abstract

The employment of time-of-flight (TOF) neutron diffraction allowed for the quantitative determination of mineral phase contents of the ceramic bulk of several pottery fragments coming from Milazzo and Messina (Sicily, southern Italy). From an historical–artistic point of view, all the samples were dated back to the 12th to 13th centuries AD and classified as belonging to the ‘proto-majolica’ ceramic class. The adopted procedure is absolutely non-destructive, so that measurements were performed on the entire fragments without any sampling. The information derived, by applying the Rietveld analysis method, allowed us to formulate hypotheses concerning the fabrication processes of the artefacts.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Pottery is a precious testimony of the ancient world, maybe the richest provider of data and information. Pottery is of fundamental importance in archaeology because of its typological variety, abundance, spread and virtual indestructibility, together with the possibility of also obtaining information from fragments. For these reasons pottery is one of the most important historical sources, and it represents a dating instrument that cannot be easily superseded. In this context, the physical–chemical characterization of the composition of ceramic items is aimed basically at classifying them in the correct historical–geographical framework, and hence acquiring valuable knowledge about the technological and cultural evolution of the civilization that created them and the political and commercial relationships between populations.

During recent years neutron scattering has started to play a more and more important role in archaeometry [1–8]. Even if the neutron source fluxes and the scattering coefficients are low (compared to synchrotron radiation sources), the high penetration power of neutrons makes them an ideal probe for the investigation of the bulk of extended specimens. This fact, together with the availability of wide beams, provides properly averaged information about composition. In archaeometric research, then, the potential of neutron methods is clearly expressed by the possibility that they offer of investigating pottery artefacts non-invasively, i.e. without causing any damaging by the removal of material.

Neutron diffraction applied to archaeological ceramics allows the examination of the microscopic structure by the quantification of the predominant phases, by giving access to both the crystal and magnetic structure of the single phases.



Figure 1. Map of southern Italy.

The extracted information about phase composition allows the provenance of the artefact to be reconstructed, usually by comparison with an analysis of reference samples extracted from clay deposits. Furthermore, such information helps to elucidate the techniques used to manufacture the pottery: in fact changes in the phase contents are induced because of mineral transformations or phase transitions depending on the firing temperature and velocity.

We report the use of time-of-flight (TOF) neutron diffraction for the characterization of two classes of so-called 'proto-majolica' ceramics found in archaeological excavations in Milazzo and Messina (Sicily, southern Italy). Glassy coated pottery of the 'majolica' type appeared spread in a rather defined age, and can be dated back to the 12th to 13th centuries AD. Generally archaeologists have attributed materials with a beige-rose mixture, like the samples under analysis, to workshops from Puglia or Calabria, both in southern Italy, particularly in the area of the Strait of Messina (see figure 1). This is because many artefacts with these features have been found in the area of Vibo Valentia and Tropea (both in Calabria). Nevertheless, this provenance needs to be verified, since local production in the area of Messina or Sicily in general is not excluded. In particular, the samples coming from Messina were found in a furnace that was still closed and buried by lime materials; it was probably abandoned because of a flood and kept intact all the manufactured load, so we could expect all these artefacts to be local products. This study is therefore principally aimed at characterization of the findings, by gathering evidence of similarities and differences in the clay composition, in order to gain information concerning provenance and the firing process used.

2. Experimental details

2.1. Samples

The analysed samples were pottery fragments belonging to the 'proto-majolica' ceramic class, and dated back to the 12th to



Figure 2. Picture of sample MLZ1, from Milazzo.



Figure 3. Picture of sample ME11, from Messina.

13th centuries AD. The *Soprintendenza per i Beni Culturali ed Ambientali di Messina* (the local government office in charge of cultural heritage) requested, within an established collaboration with our university department, the mineralogical characterization and authentication of the fragments as a prerequisite for their cataloguing.

The samples were recovered during archaeological excavations at two different sites in Sicily. In particular, the samples labelled MLZ1 to MLZ10 come from Viale dei Cipressi in Milazzo, a little town 30 km away from Messina. Samples labelled ME11 to ME13 were found in the furnace of the Court of Messina.

A visual examination showed all the samples to have similar characteristics. The ceramic body is fine and friable and the surface is entirely decorated. As far as the dyes used are concerned, most of the fragments have an opaque beige layer with some differences in the decorations: some samples show brown and yellow entwined motifs of a type widespread in the insular region, others have green/blue geometrical decorations, typical of production from Puglia. As examples, photos of fragments MLZ1 and ME11 are shown in figures 2 and 3, respectively.

2.2. TOF neutron diffraction

A detailed description of the TOF neutron diffraction technique, together with the fundamental advantages of its use

Table 1. Instrumental characteristics for INES diffractometer.

Incident wavelength: 0.17–3.24 Å
Incident flight path: 22.804 m
Scattered flight path: 1 m
Angular range: 11.6°–170.6°
Q range: 0.4–60 Å ⁻¹
d range: 0.1–16 Å
Beam size: 40 × 40 mm ²

for archaeological objects, has been already reported elsewhere (the reader can refer to [1]), and we recall here the main principles.

As is well known, in a TOF diffraction experiment the scanning is performed at a fixed angle but with varying energy or wavelength of the incident neutrons. In particular, by using the de Broglie relationship, the energy dispersion is obtained by measuring the time-of-flight t that a neutron takes to cover the distance L from the source to the detector. Under the assumption that the neutrons do not suffer a change in energy during the scattering process, the time-of-flight values are directly related to the distance d between the crystallographic planes by:

$$d = \frac{h}{2m_n} \frac{t}{L \sin \vartheta}, \quad (1)$$

where 2ϑ is the scattering angle, h the Planck constant and m_n the neutron mass. This is the fundamental equation of TOF diffraction. The efficiency of TOF diffractometers is increased by using many detector tubes aligned in detector banks, so reducing the data collection time and focusing the superposing spectra afterwards.

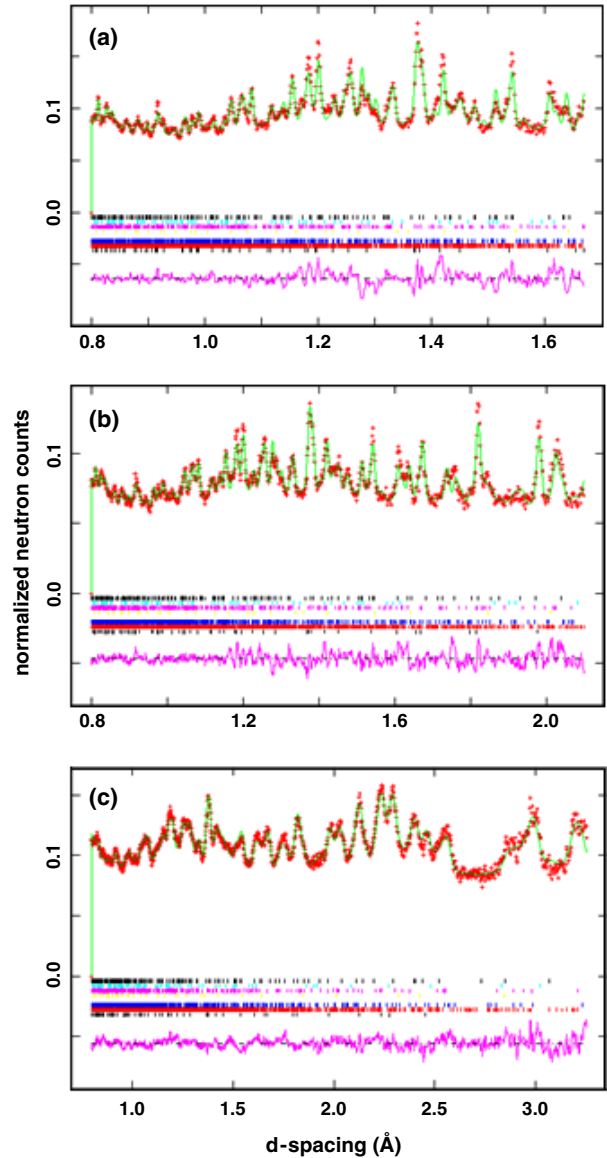
The measured neutron diffraction pattern will be available for quantitative phase analysis by assuming that each phase exhibits a unique set of diffraction peaks, whose intensity is proportional to the phase content in the mixture, and that the total diffraction pattern will contain the weighted sum of the single phase contributions.

The experiments were performed at the TOF diffractometer INES, installed at the ISIS spallation source at the Rutherford Appleton Laboratory (UK) and designed with an emphasis on archaeometric applications. The relevant parameters of the instruments are summarized in table 1.

Static measurement configurations and relatively long acquisition times (6–7 h) were used for measurements on large pottery fragments without any prior preparation. The activation induced by the measuring procedure was negligible and disappeared within a few minutes. The data treatment followed the well-established quantitative Rietveld analysis for phase identification and quantitative assessment of the material's composition, using the public-domain program suite GSAS [9]. This procedure is based on the assumption that the weight fraction W_i of the i th phase in a multiphase mixture is given by the normalized product

$$W_i = \frac{S_i Z_i M_i V_i}{\sum_n S_n Z_n M_n V_n}, \quad (2)$$

where S , Z , M and V are the refined Rietveld scale factor, the number of formula units per unit cell, the mass of the formula

**Figure 4.** TOF backscattering ((a), (b)) and forward (c) neutron diffraction pattern for sample MLZ3.

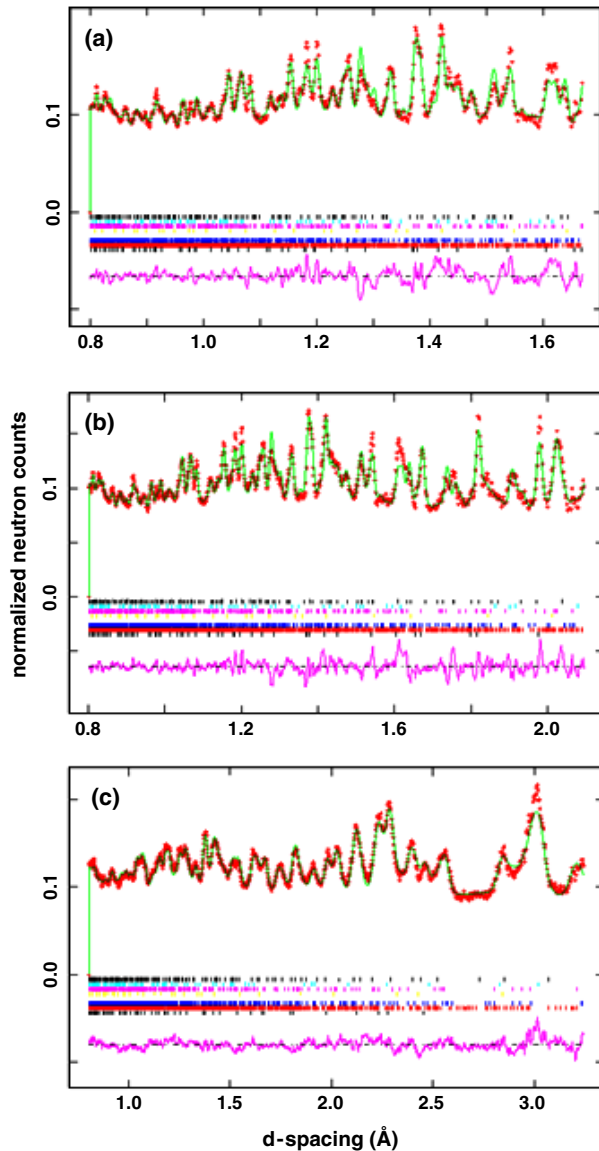
unit and the unit cell volume, respectively. The sum in the denominator accounts for all the crystalline phases revealed by the experimental diffraction pattern. The fitting procedure used is a least-squares minimization. The values of χ^2 and R_{wp} , indicating the quality of the pattern fittings, are shown for each sample in table 2.

3. Results and discussion

Figures 4 and 5 report the collected diffraction patterns for samples MLZ3 and ME13, as examples. In particular, the experimental data (symbols), calculated patterns (solid lines) and residuals (bottom curves) are plotted. For each sample, three selected diffraction patterns have been shown, among the forward and backscattering directions of the nine banks of detectors installed on the INES facility. In particular, we labelled with (a), (b) and (c) the detector banks centred at about

Table 2. Phase quantification as obtained by Rietveld analysis, together with goodness-of-fit parameters χ^2 and R_{wp} .

Sample	Quartz	Bytownite	Orthoclase	Spinel	Diopside	Calcite	Gehlenite	χ^2	R_{wp}
Milazzo									
MLZ1	0.299	0.149	0.094	0.011	0.305	0.006	0.134	4.471	3.28
MLZ2	0.298	0.099	0.089	0.013	0.361	0.007	0.133	2.216	2.82
MLZ3	0.275	0.138	0.090	0.003	0.355	0.008	0.131	2.386	3.69
MLZ4	0.313	0.143	0.092	0.005	0.268	0.041	0.138	2.215	3.26
MLZ5	0.277	0.137	0.080	0.009	0.354	0.030	0.113	2.682	3.27
MLZ7	0.258	0.125	0.060	0.025	0.390	0.009	0.137	2.998	3.19
MLZ8	0.326	0.158	0.101	0.020	0.295	0.006	0.094	2.878	3.23
MLZ9	0.323	0.165	0.049	0.010	0.355	0.006	0.090	2.392	2.70
MLZ10	0.300	0.166	0.025	0.004	0.405	0.007	0.091	1.749	3.70
Messina									
ME11	0.246	0.101	0.051	0.018	0.375	0.081	0.127	3.185	3.34
ME12	0.355	0.162	0.036	—	0.213	0.106	0.127	3.841	4.51
ME13	0.225	0.087	0.065	0.013	0.402	0.088	0.120	3.770	3.83

**Figure 5.** TOF backscattering ((a), (b)) and forward (c) neutron diffraction pattern for sample ME13.

$2\vartheta = 143.6^\circ$ ($d_{\min} = 0.11 \text{ \AA}$ and $d_{\max} = 1.76 \text{ \AA}$), $2\vartheta = 98.6^\circ$ ($d_{\min} = 0.13 \text{ \AA}$ and $d_{\max} = 2.14 \text{ \AA}$), and $2\vartheta = 62.6^\circ$ ($d_{\min} = 0.19 \text{ \AA}$ and $d_{\max} = 3.13 \text{ \AA}$), respectively. The Rietveld fit has been performed simultaneously on the nine banks. The bars at the bottom of the pictures indicate the theoretical peak position of the phases included in the model: (from bottom to top) quartz, bytownite, orthoclase, spinel, diopside, calcite and gehlenite for all the analysed samples. The fitting procedure is the following: first, each sample was individually fitted with a number of phases. Afterwards, a group of phases common to all samples within one class was identified, due to the high homogeneity of the set of findings, and the samples were fitted with this common set of phases, with phase fractions as free parameters. For each phase, the corresponding structural parameters were obtained from the Inorganic Crystal Structure Database [10]. The refined weight fractions are compiled in table 2. A graphical representation of the relative abundance is also shown in figures 6 and 7. For all the investigated pottery, the realistic estimates of the uncertainties are about 0.5%, that is, only minerals with phase fractions above this value are to be considered as present in the pottery.

From a general point of view, for the groups coming from both from Milazzo and Messina, quantitative phase analysis revealed a similarity in the composition of the mineral fractions present. All the samples revealed the presence of the newly formed minerals gehlenite and diopside that originate from the firing process of the ceramic body, and, in this sense, they can be considered to be distinctive parameters for the firing technology used during manufacture. In particular, gehlenite appears if the temperature reaches $\sim 650^\circ\text{C}$ and tends to vanish at $\sim 900^\circ\text{C}$, when diopside forms [11, 12]. For all the investigated samples, the simultaneous occurrence of both these mineral phases could indicate a firing temperature around 900°C , so suggesting a similar preparation technique. As far as calcite is concerned, its content in samples from Messina is relatively high compared to the Milazzo findings, despite their comparable amount of gehlenite. This result was not expected. In fact, on one hand it is well known that for temperatures higher than $750\text{--}800^\circ\text{C}$ the reaction of dissociation of calcium

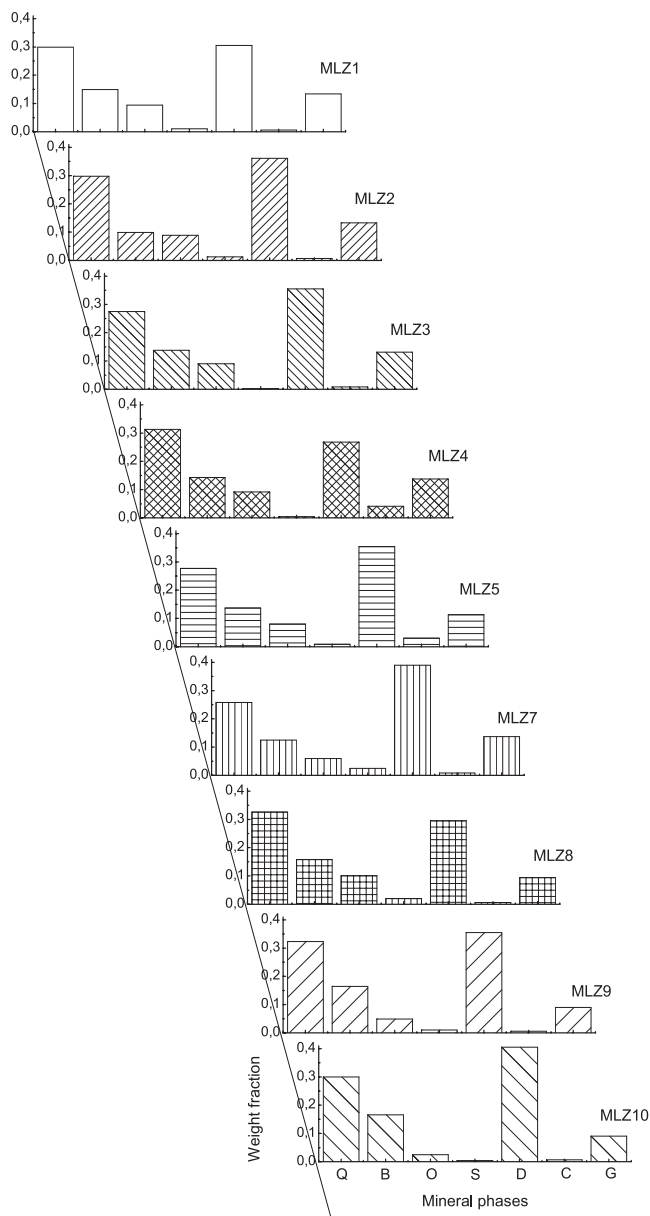


Figure 6. Histogram plot of phase fractions for samples from Milazzo: Q, quartz; B, bytownite; O, orthoclase; S, spinel; D, diopside; C, calcite; G, gehlenite.

carbonate in calcium oxide and carbon dioxide occurs and, on the other hand, above 650 °C the reaction of calcite with illite produces gehlenite.

The excess of calcite in samples from Messina leads to several hypotheses. At first sight, the presence of this mineral could suggest that the manufacturing process was incomplete or was performed at low temperature, around 650–750 °C, because for higher temperatures calcite should disappear. However, this hypothesis is not supported by the obtained phase fraction results. In fact, all the fragments show the presence of newly formed minerals and, in particular, a high percentage of diopside, from 20% to 40%. For this reason, we can deduce that the pottery was fired at a temperature ranging from 800 to 900 °C.

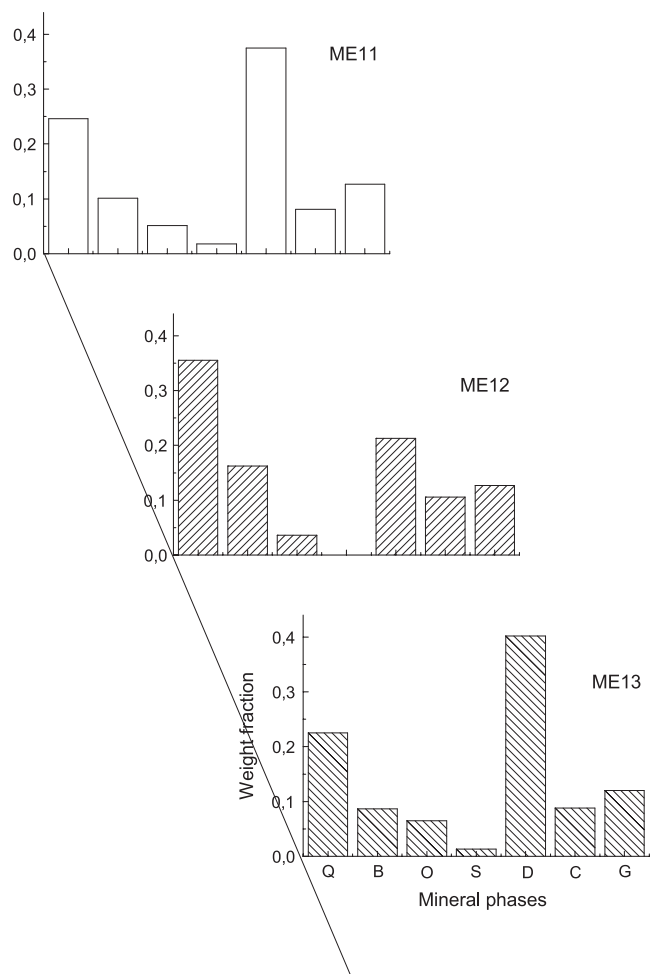


Figure 7. Histogram plot of phase fractions for samples from Messina: Q, quartz; B, bytownite; O, orthoclase; S, spinel; D, diopside; C, calcite; G, gehlenite.

Another hypothesis could attribute the presence of calcite to the conservation circumstances: samples from Messina were buried for a long period, so the calcite could be of secondary origin. Nevertheless, in this case, it seems really strange that other alteration minerals, such as montmorillonite, are not revealed. In any case, the validation of this hypothesis needs methods of investigation that are able to distinguish between primary calcite, coming from the raw materials, and secondary calcite, coming from a re-crystallization process occurring during the burial period. For this purpose, optical microscopy (OM) analyses are already in progress.

Starting from these considerations, we can assume, as the most reasonable hypothesis, that the excess calcite could be attributed to a different composition in the raw production materials for the two classes of findings.

In fact, the evidence of a similar quantity of gehlenite and diopside in all the samples, and the assumption that an equivalent amount of calcite for each sample underwent the aforementioned firing transformations, allowed us to deduce that a different amount of calcite was originally present in the Messina samples. This evidence is a really important result because it allowed us to point out a valid distinction

between the two groups of findings, based on scientific data, as requested by the *Soprintendenza per i Beni Culturali ed Ambientali di Messina*.

Even if a secure provenance attribution cannot be achieved, since most of the manufactured pottery consists of the same basic minerals, nevertheless, starting from the hypothesis of a local provenance for all the samples, some ideas about the origin of the findings can be put forward. In fact, assuming the reliability of the aforementioned archaeological consideration, i.e. that the samples were recovered in Sicilian sites and some of them show decorations typical of western Sicily, we start to form a hypothesis of provenance from the 'Strait of Messina' area for all samples. In this case, the calcite content could differentiate the production site. In fact, as reported in published [13] and unpublished [14] data, several studies have revealed that in the 'Strait of Messina' area the clay from Milazzo and neighbouring areas, such as Gioiosa, is typically non-calcareous and classified as 'argilla scagliosa' type, while clay from Messina and the Tyrrhenian coast is usually calcareous and classified as 'plio-pleistocene' type. Then, the origin of the samples from two different sites, Milazzo and Messina, could be hypothesized, even if to achieve a clearer scenario, a complementary analysis by other techniques, such as x-ray fluorescence (XRF) and optical microscopy (OM), is in progress, together with a comparison with data from control samples.

4. Conclusions

In this work, neutron diffraction has been applied to two groups of proto-majolica pottery finds from Milazzo and Messina, both in southern Italy. The aim of the present investigation was to refine the various mineral phases present in the samples, as well as to establish the firing conditions in which the ceramics were exposed.

Analysis of the diffraction patterns showed that the samples are composed of similar primary minerals, apart from a different amount of calcite that may suggest a different origin of the raw materials.

Again, the observation of newly formed materials allowed us to estimate, for both groups of samples, a firing temperature in the range from 800 to 900 °C.

We remark that the performed analysis offers great advantages linked to its non-invasive nature combined with the possibility of achieve a quantitative characterization of potteries of archaeological interest.

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