NEUTRON DIFFRACTION APPLIED TO THE CHARACTERIZATION OF ARCHAEOLOGICAL POTTERY

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Abstract
In the present paper, a recent analysis performed on ancient pottery samples is reported. The aim of the work is the mineralogical characterisation of two fragments, attributed to historical periods very far from each other, in order to reveal the compositional differences, that may support or disprove the dating of the findings. Neutron diffraction measurements allowed us to obtain a detailed qualitative and quantitative identification of the mineral phases present in the ceramic bulk in a totally non-destructive way.

Introduction

Objects of art and archaeology are of interest for cultural, historical and scientific reasons. Therefore, an accurate physical and chemical characterisations of these kinds of samples become important subjects for both scientific and humanistic field. A detailed characterization of the material of an artistic object is the first step to achieve a complete knowledge of the historical-geographical context in which it was produced. Cultural heritage research requires multitechnique and multidisciplinary approach and, above all, benefits from the development of non-destructive experimental techniques.

The present work is addressed to the characterization of the ceramic bulk of two pottery fragments, belonging to very different historical periods, by Time-Of-Flight (TOF) Neutron Diffraction measurements. The identification of the mineralogical phases is a fundamental part of the characterisation of pottery samples because the composition is related to the manufacturing materials and technique and can lead to geographical and historical attribution. The main purpose of this investigation is to put in evidence the differences between the two samples, that can be attributed to different manufacturing processes and hence to different period of production.

The samples

A series of ceramic samples was found during archaeological excavations performed in Caltagirone (Sicily, southern Italy) by the Cultural Heritage Department of Catania (Sicily). By a first inspection, the samples were distinguished into two groups, that archaeological and aesthetical considerations attributed to historical periods with a difference in time of almost three thousand year. Then, the Cultural Heritage Department suggested to carry out a scientific study in order to obtain detailed and undoubted information that could confirm or invalidate the time attribution. The samples are currently being investigated by different scientific methods such as Fourier Transform Infrared Absorbance, Raman Scattering, X-Ray Diffraction and Neutron Diffraction.

Here we report on the results from two samples, fragments of decorated pottery, representing the two periods. The first sample, namely CLT1, is dated back to 16th century A.D., has a light colour, a compact and fine grained mixture. The second one, labelled CLT8, was attributed to the 15th century B.C., its ceramic paste is brownish, coarse grained and friable.

Experimental set-up

The pottery samples were investigated by TOF neutron diffraction in order to identify the mineral phases present in the ceramic body. The measurements were performed on the ROTAX neutron diffractometer located at the ISIS Facility at the Rutherford Appleton Laboratory, UK.

The ROTAX set-up uses a “white” beam of neutrons, with wavelengths from 0.5 to 5 Å, which correspond to neutron velocities from about 8000 to 800 m/s. For a fixed flight path L of 15 m from the neutron source to the detector, and for a detector at a scattering angle 2 , the energy dispersion is obtained by distinguishing the velocity, which is achieved by measuring the time of flight t of the scattered neutrons, resulting in the crystallographic d-spacing d:

$$t \quad \frac{2m_n}{h} Ld \sin \quad ,$$

where h is Planck’s constant and m_n is the mass of the neutron. ROTAX has three linear position sensitive detectors that span an angular range from about 2 = 5° to 150°, allowing for a d-spacing coverage from 0.3 to 15 Å.

A particular advantage of the used technique is the possibility to investigate large fragments and even intact objects, so that the interior of an object can be analysed without breaking or damaging it. Details of the experimental set-up and examples of TOF neutron diffraction on ceramics [1] and metal objects [2] can be found elsewhere. The pottery fragments from Sicily were measured in a beam 20 20mm^2 cross section as received, i.e. without preparation, for about 2 hours. The radio-activation induced by the measuring procedure, disappeared after a few minutes. The data were subjected to a quantitative phase analysis based on the Rietveld method using the GSAS program [3].

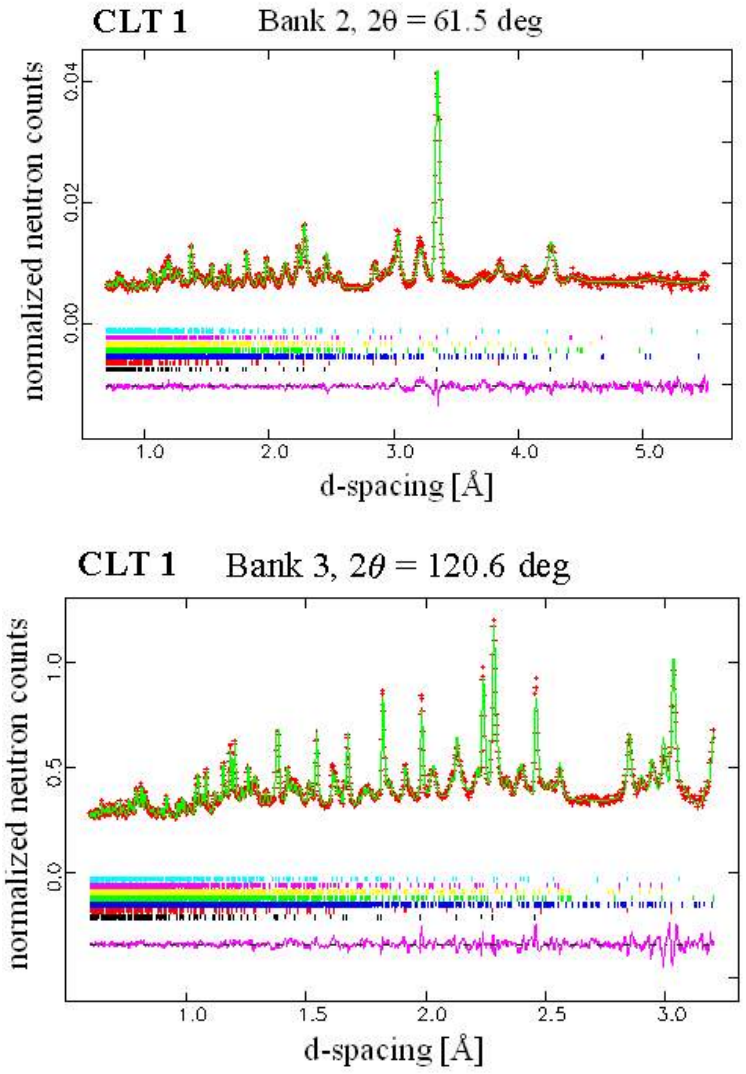

Fig. 1. Measured data (symbols), calculated pattern (solid line), and difference between the observed and calculated intensities (lower curve) of pottery sample CLT 1. The bar codes indicate the theoretical peak positions of the different phases (bottom to top): quartz, calcite, plagioclase, illite/muscovite, k-feldspar, diopside, gehlenite. The two patterns correspond to the foreward (top) and back-scattering detectors on ROTAX, respectively.

Results and discussion

The performed measurements and the ensuing Rietveld analysis allowed to obtain a good quantitative characterization of the main mineral components present in the investigated samples.

The measured diffraction patterns for the investigated pottery fragments CLT1 and CLT8 differ significantly. The experimental spectra collected by two of the three detectors in the range from 1 to 5 Å, as well as the fitted theoretical structure models of the mineral components for samples CLT1 and CLT8 are reported in Figures 1 and 2, respectively.

The identification of the mineral phases and the assessment of their relative weight fractions were obtained and are summarized in Table 1. Both samples contain mostly calcium-rich mineral phases, typical for Mediterranean paste. The ancient pottery (CLT8) consists mainly of quartz, illite, a calcium-rich plagioclase, calcite and K-feldspar. The more recent pottery sample (CLT1) additionally contains phases from the pyroxene group (most probably diopside) and from the melilite group (most probably gehlenite), while the amount of illite is much reduced. The structure model for illite/muscovite is not very reliable, so weight fractions for this mineral should be considered as approximate values, supported by the fact that its presence is clearly indicated by characteristic Bragg peaks. Diopside and gehlenite are new formation minerals that typically point to firing temperatures higher than 900° and 650°, respectively [4]. For the high amount of diopside in CLT1, we can deduce that the recent pottery was fired at a firing temperature much higher than the ancient one. In this last, diopside could come from raw materials, in fact sometimes diopside is present in rocks and clays that have not been fired, but not in high amount.

Conclusion

TOF neutron diffraction measurements were performed on pottery fragments, coming from Sicily (Italy), and allowed us to obtain the mineralogical composition of the samples. The quantitative determination of the mineral phases revealed compositional differences for the two samples. This result attests different recipes, materials and execution techniques for the pottery manufacture and hence these differences can be attributed to different periods of production.

A further advantage of the used method is that the result of the measurements is an average over a large sample volume of the intact object. The investigation is absolutely non destructive, which is a considerable advantage of neutron diffraction comparing with X-ray diffraction analysis.

References

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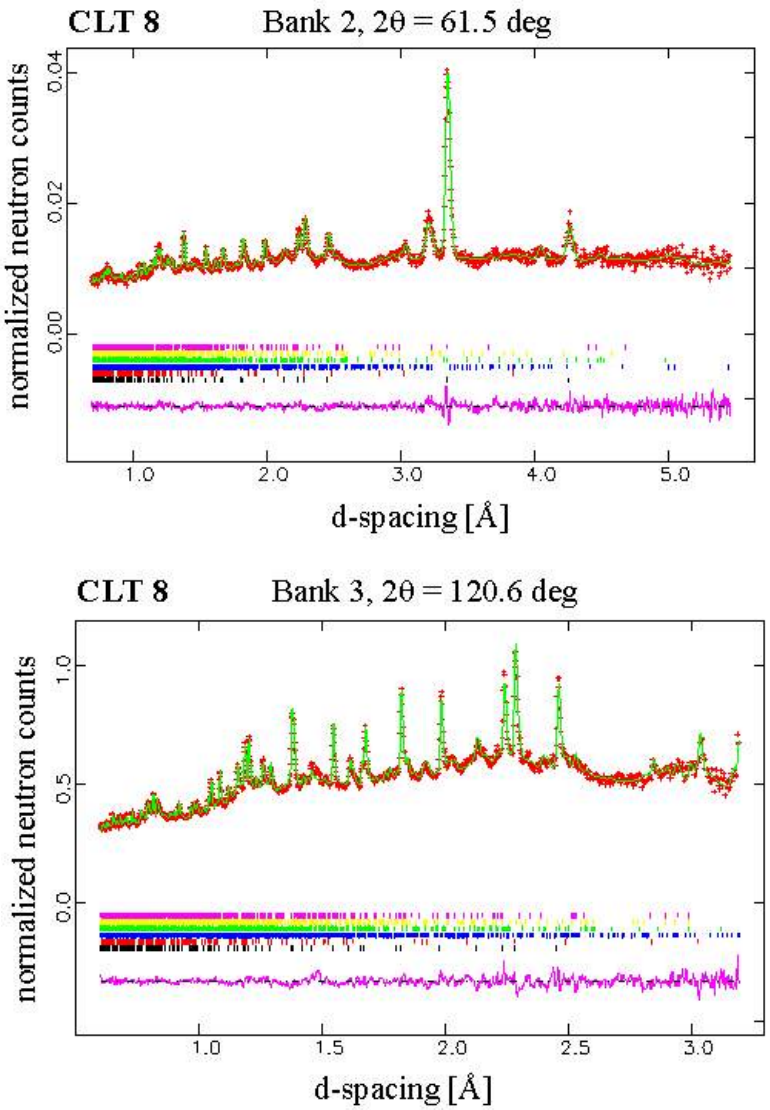

Fig. 2. Measured data (symbols), calculated pattern (solid line), and difference between the observed and calculated intensities (lower curve) of pottery sample CLT 8. The bar codes indicate the theoretical peak positions of the different phases (bottom to top): quartz, calcite, plagioclase, illite/muscovite, k-feldspar, diopside. The two patterns correspond to the foreward (top) and backscattering detectors on ROTAX, respectively.

Table 1. Mineral composition of samples CLT1 and CLT 8.

Mineral phase	Weight fraction (%)	
	CLT1	**CLT8**
Quartz	36.1	41.8
Illite/Muscovite	11.1	17.9
Plagioclase	18.9	25.8
Calcite	8.0	3.2
K-feldspar	2.3	4.5
Diopside	17.9	6.5
Gehlenite	5.5	not present