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Non-destructive characterization of minerals in ancient Greek ceramics using monochromatic neutrons

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Abstract

A collection of ancient Greek ceramic pieces originating from different excavations from Neos Scopos, Serres, in the North East of Greece has been studied at room temperature by means of non-destructive neutron diffraction using a monochromatic beam. Quantitative phase analyses revealed different compositions of the mineral fractions present, but a general similarity of the main materials is still recognizable. It is shown that the observed variations are partly due to the experimental set-up and they can be remedied by taking a sufficient number of measurements for different sample orientations while bathing the entire object in the beam. An additional reason for the observed anomaly in the mineral phase compositions may be the different heat treatments to which the mixtures of clays/pastes was subjected as well as the postproduction environmental conditions for the selected samples. The firing temperatures were estimated to be in the range of 850–1000 °C.

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

1. Introduction

The characterization of the mineral phases present in a historic object or classes of objects of cultural interest is an important step when gathering information about the use, the technical treatment and the provenance of material goods as well as the manufacturing methods and the trade patterns. Such information would lead to understanding of the level of technology or civilization that a particular culture had reached. Although the use of neutron spectroscopy is a well-known bulk sensitive technique in material science and engineering, it is only recently that this method has been employed as a tool in archeological science in identifying the mineral phase abundances, the microstructure or the texture of complete artifacts or 'intact' precious pieces of artwork, mainly through the work performed at the TOF-ROTAX/ GEM instrument at ISIS [1–7].

The neutron diffraction (ND) investigation presented in this work is the second stage of an evaluation study [8], which was proposed to the Serres Museum in North Greece, aiming

to show that the ND can be used as a non-destructive diagnostic tool for the identification of the various minerals present in archaic pottery. The current neutron diffraction experiments were performed with single-wavelength neutrons at a steady state reactor, in contrast to previous studies where the samples were exposed to pulsed white neutrons at a spallation source. It was our intention to determine the experimental conditions under which reliable data may be obtained from the scattering of monochromatic neutrons on bulk ceramics, which can be used to extract meaningful information on mineral weight fractions, so that this method can be used for non-destructive analysis. Furthermore these results will allow the identification, through fingerprinting, of similar ceramic fragments from broken pottery artifacts so that they may be reconstructed.

2. Materials, experimental conditions and method of analysis

The selected ceramic samples shown in figure 1, were considered to be representative of the various potshards and



Figure 1. Ceramic samples N1–N6. Rulers are used to show the relative sizes of the samples.

Table 1. Pottery fragments from Neos Scopos, Serres, Greece. Dating is based on stylistic grounds. The ceramics were kindly provided by the Greek Ministry of Culture and the Serres Museum.

A/A	Description	Date	Size (cm ²)	Accession No
N1	Cell from a hand made vase with graphite coating	Archaic period	14	Π1, σ23
N2	Cell from the rim of a vase	Archaic period	12	Π1, σ23
N3	Cell from a vase	Archaic period	12	Π1, σ23
N4	Cell from an archaic vase	Archaic period	9	Π4, σ4
N5	Cell from the rim of black glazed kratira	Classic period	1.7 × 3.7	Δ, σ26
N6	Cell from the handle of red figured kratira	Classic period	1.3–1.6 × 3.8	Π4, σ1
N10	Cell from black glazed pinakio	Hellenistic period	9	Π4, σ7

ceramic objects found in different excavations at the Neos Scopos location in Northern Greece. Archeological criteria of style, fabric and layered deposition were used to provide the initial classification of the pottery shards, suggesting that the selected shards were produced in different archeological periods ranging from the Archaic to the Hellenistic era. Information on location where found, dating, size and archeological classification of the objects is listed in table 1.

The measurements were made on samples using the SV7a diffractometer [9] at the DIDO reactor in FZ-Jülich, Germany. In this arrangement samples N1, N2 and N3 were placed at a right angle to the incident beam so that the maximum possible area of the sample was exposed to the 20 × 40 mm² beam's cross section while the rest of the samples (e.g. N4–N10) because of their smaller size and shape were fully bathed in the beam. With the samples in this 'one-position' set-up, the diffraction patterns were recorded at room temperature for 11 h, at a fixed wavelength of 1.0959 Å.

Additional measurements were performed on sample N1 at the texture diffractometer SV7b with $\lambda = 2.332$ Å. The measurements were conducted only at certain ϕ -rotations from 135°–225°, with a step of 5°, in three successive χ -orientations: at 0°, 30°, 60°. From these measurements a sum data set was generated by adding up the individual diffraction patterns of all sample orientations. Because this data set

is characterized by very good statistics as it corresponds to the summation of the scattered intensities from the sample throughout the entire counting time, a mean diffraction profile can be produced which can be compared to the 'one-position' diffraction pattern of N1 collected at SV7a.

Structure refinements were carried out using the program AMPHOrAe (Archeometric Multi-Phase Ornament and Artifacts Analyses). This program is a new extended windows version of IC-POWLS [10, 11], written to serve the specific multiphase modeling requirements for the analysis of the data collected from neutron diffraction measurements on historical objects. The new program is based on the two-step method in profile fitting [12]. It contains various automated and/or manual routines for background evaluation and its subtraction from the original experimental profile. It allows the partition of the experimental pattern into suitable 2Θ or d -spacing segments and the selection of pre-defined shape functions (e.g. Gaussians, Lorentzians, pseudo-Voigt forms) which can be fitted to the observed peaks or groups of peaks. The fitting procedure utilizes a non-linear weighted least-square algorithm that minimizes the sum of the weighted squared differences between the experimental and theoretically generated intensities. The routine produces a record of values with the refined peak positions $2\Theta_p$ or d_p , the full width at half-maximum β , the heights H and the corresponding standard deviation estimates. By means

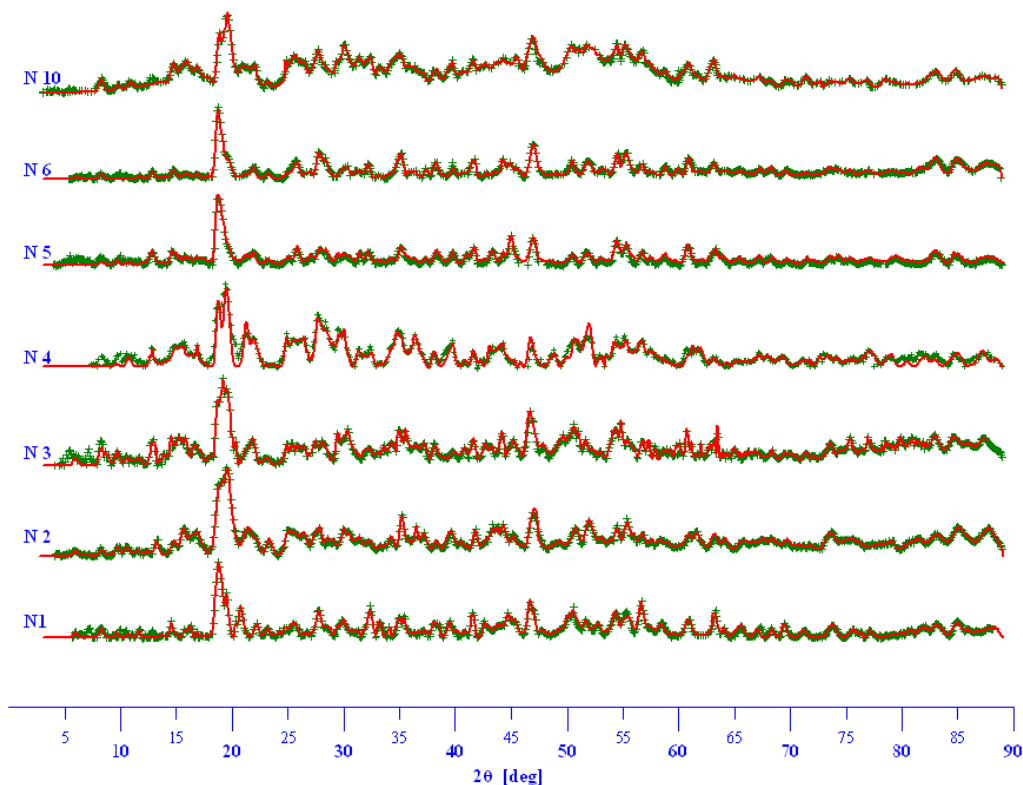


Figure 2. Experimental data (+) plotted against the calculated model fit (–) for each sample.

of a user friendly interface the parameters of the mineral to be modeled are entered in the database along with the instrumental parameters. The program generates and displays a theoretical diffraction profile of the mineral phase. Each phase can be individually refined with respect to lattice parameters, scale factors, zero shift displacement and site occupations when this is necessary, in order to map the mineral phase pattern to an appropriate cluster of theoretical peaks, which were produced from the fitting of the sum pattern in the first step. A final least-square intensity adjustment may also be employed to vary the theoretical peak height H of all phases contributing to the observed pattern, based on the known positions $2\Theta_p$ or d_p and β of the sum pattern. Peak shifts and peak broadening due to microscopic crystallite deformation or particle size can also be treated using the program. The software allows for the modeling and the refinement of magnetic structures so that minerals such as hematite can be easily fitted using the magnetic structure models prescribed in the bibliography. Similarly, by employing a quasi-crystal model and a Monte Carlo method the amorphous silica phase can also be simulated [13].

3. Results

The collected diffraction data set for all the samples at room temperature is plotted in figure 2, along with the corresponding calculated profiles derived from the theoretical analysis of the mineral fractions generated using the program. Measurements are represented by crosses (+), while the final calculated spectra correspond to solid lines (–). The starting model for the analyses of the observed data consists of a

quartz (Q), orthoclase (K-FS), plagioclase (P), hematite (H), calcite (C) and diopside (D) mineral composition, based upon earlier neutron diffraction measurements on comparable Greek pottery from the Athenian Agora, Neos Scopos, Serres [14], Krania [15] and Karabournaki [16]. The structural parameters of the starting phases were taken from the Inorganic Crystal Structure Database [17]. The structure model for muscovite was taken from [18] and used without further refinement in order to account for the muscovite/illite reflection in the diffraction profile. Pattern fitting procedures and mineral phase refinement have been described in section 2. The sum of the crystalline phases, apart from the illite/muscovite (I–M) phase, was normalized to 1.

Examination of the plotted diffraction data points to the following general similarities. All the patterns are characterized by pronounced very broad quartz and feldspar peaks indicating a small crystallite size. For the samples N2, N4 and N10, the plagioclase peaks are more intense, but comparable in magnitude to those of quartz, signifying a high feldspar content, while for samples N1, N5 and N6 the quartz reflections dominate. The feldspar profile was modeled as a plagioclase mixture of a bytonite/anorthite phase and an additional alkali–feldspar phase. In contrast, the pronounced peaks that appear in the N3 pattern exhibited a peculiar shape that required special attention during the analysis. In this case, the high temperature polymorphs of orthoclase, i.e. sanidine/anorthoclase, were used in modeling the mineral phase. The silica glass phase was synthesized from a sequence of broad Lorentzians peaks, produced by the program, based on a model that uses the crystallographic parameters of a

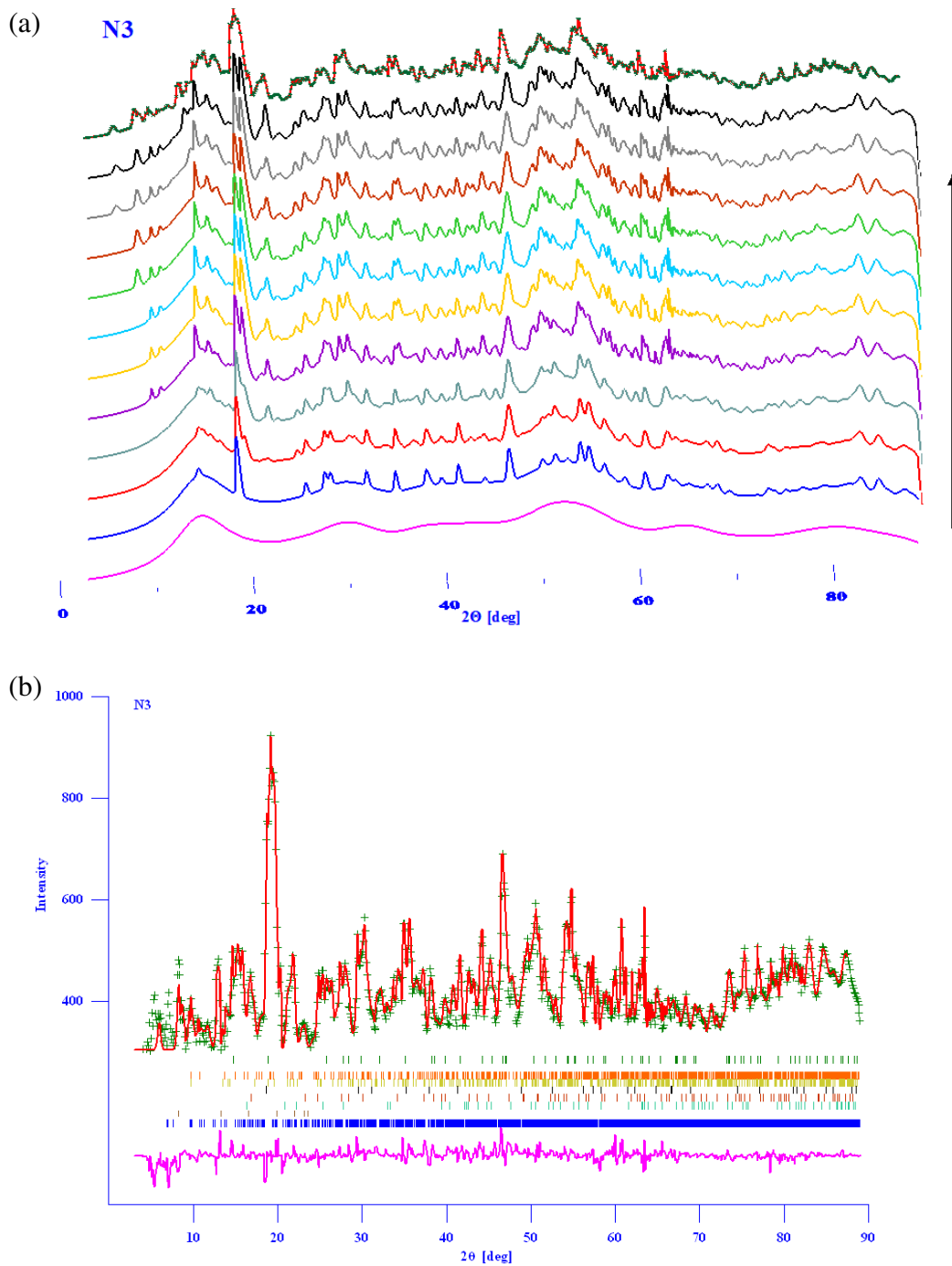


Figure 3. (a) A series of program generated diffraction patterns (not to scale) illustrating the successive modeling of the mineral phases and the building of the theoretical diffraction pattern; from bottom to top: silica glass, quartz, plagioclase, orthoclase, Na-rich orthoclase, albite, pyroxene, gypsum hematite, calcite, illite/muscovite, spinel/hercynite, the experimental (+) and final fitted (–) profiles. (b) Experimental (+) and final calculated spectra (–), resulting from the fitting process; residuals are shown at the bottom by a solid line (–). The bar code type markers (|) indicate the theoretical peak positions of the mineral phases.

carnegieite and cristobalite. Figure 3(a) shows a series of calculated diffraction patterns, illustrating the successive modeling of the mineral phases and the gradual construction of the theoretical diffraction pattern. In figure 3(b), the experimental data set for N3 is plotted with respect to the final theoretical pattern.

The presence of K feldspar and calcite points to an upper firing temperature of 850 °C and 920 °C respectively.

Additionally, Bragg reflections corresponding to pyroxenes, mainly diopside, and spinel (Sp)/hercynite (Hr) minerals, are clearly observed in all the patterns. These are typical mineral phases that undergo crystallization after the decomposition of the primary minerals has occurred during the firing process. Furthermore, the weak Bragg peaks observed at $2\theta = 13.8^\circ$ may be attributed to the (001) reflection of the (I–M) phase, which is known to decompose completely around

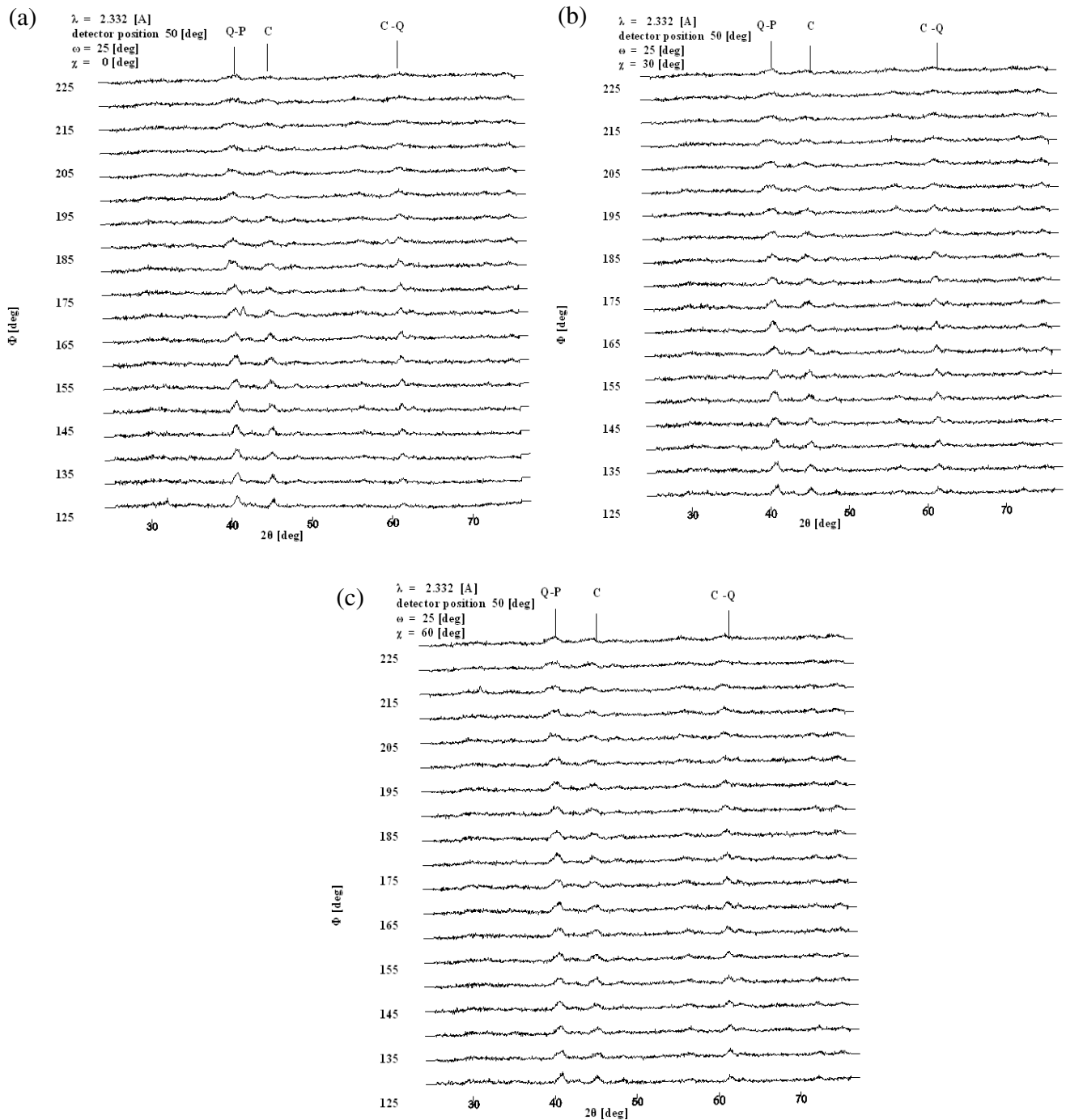


Figure 4. A sequence of neutron diffraction profiles of the sample N1 as a function of the rotation angle ϕ , for fixed χ orientations: (a) $\chi = 0^\circ$, (b) $\chi = 30^\circ$, (c) $\chi = 60^\circ$, showing intensity variations of the quartz (Q), plagioclase (P), and calcite (C) diffraction peaks.

950 °C [16, 19–23]. The extensive broad humps observed mainly in the diffraction spectra of N2, N3, N4 and to a lesser extent of N10 imply the growth of a vitreous phase, signifying that the firing of the clay was near 1000 °C. On the basis of the above observations the range of firing temperatures may be set at between 850 and 1000 °C as shown in table 2. The combination of spinel and diopside may imply that the MgO content of some primary phases during firing is fixed in either diopside or spinel depending upon the calcite content of the

pottery. Gypsum peaks of low intensity are also present; the constant weight fraction value indicates that it is a secondary phase that fused into the sample’s matrix during burial. The graphite content of N1 must have been lower than 1%, which is the limiting weight fraction for a phase to be identified.

A sequence of neutron diffraction profiles of N1 as a function of the rotation angle ϕ , in fixed χ orientations, is displayed in figures 4: (a) $\chi = 0^\circ$, (b) $\chi = 30^\circ$, and (c) $\chi = 60^\circ$. They show intensity variations mainly

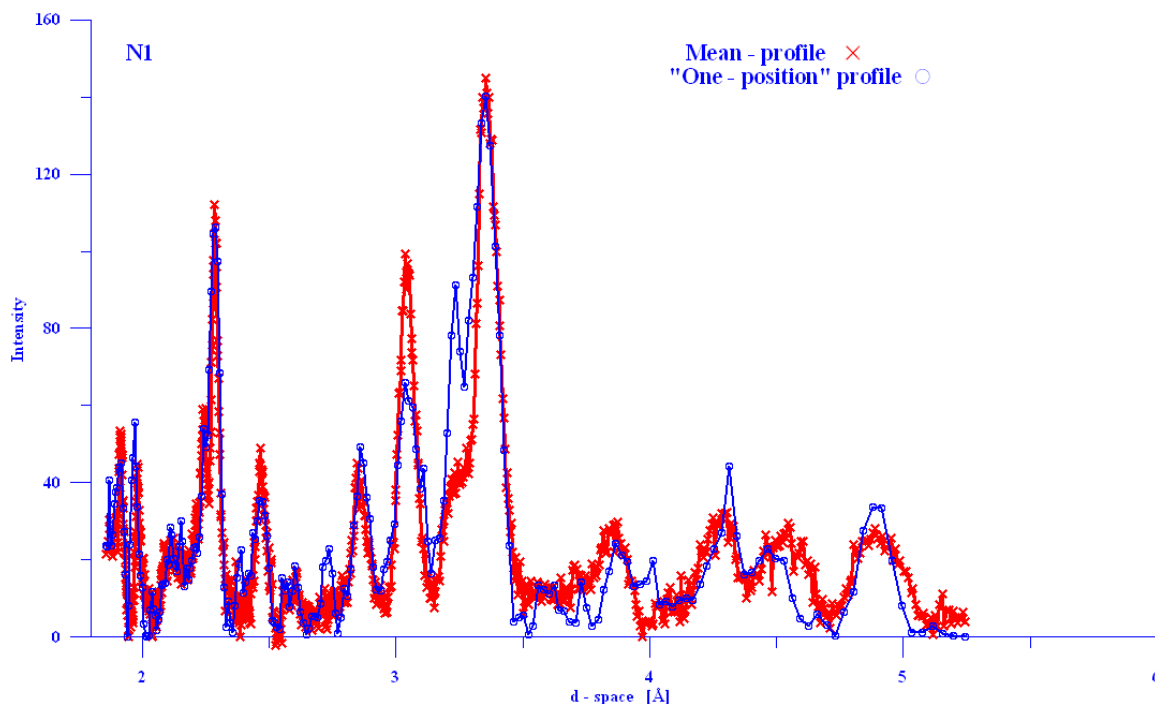


Figure 5. *d*-space plots of N1 showing (a) the mean profile generated by the sum data set (X) and the ‘one-position’ diffraction diagram (O) measured at SV7a.

Table 2. Estimated firing temperatures.

A/A	<i>T</i> in °C
N1	850–900
N2	850–900
N3	>950
N4	~1000
N5	850–900
N6	850–900
N10	~1000

of quartz, plagioclase and calcite diffraction peaks which can, apart from the geometrical instrumental texture, be attributed to a systematic preferred crystallographic orientation usually occurring/found in fired ceramics. It is evident that the diffraction patterns depend noticeably on the angle ϕ . Furthermore, the mean diffraction profile, although it matches the ‘one-position’ pattern (see figure 5), also shows localized differences which correspond to specific phases, namely plagioclase and calcite. The fitting procedure of the mean diffraction pattern yields an overall *R* value of ~7.5%, whereas the corresponding ‘one-position’ *R* value is 9.8%. For the two data sets, the weight phase fraction calculations of quartz, orthoclase and the iron containing minerals differ by approximately 1%, whereas for the plagioclase the divergence is 5.5% and for the calcite it is 7.7%. This result indicates that ‘one-position’ data set can be used for the mineral characterization and fingerprinting of ancient pottery, but it can only provide a rough estimate on mineral weight fractions. On the other hand, the items N5 and N6, which are of the same origin, comparable in size but dissimilar in shape, were

completely bathed in the beam; their diffraction characteristics are almost identical. Therefore from this analysis and for sample dimensions comparable to that of the beam’s cross section, one may conclude that in conducting non-destructive neutron diffraction experiments using a monochromatic beam it would require rotating the object at constant rate during the measurement so averaged statistics may be obtained, while the entire object is bathed in the beam.

The relative weight fractions (%) as well as Q/F = quartz/feldspar ratios calculated for the mean as well as the ‘one-position’ measurements are listed in table 3.

4. Discussion

In conducting mineral characterization experiments on archeological objects, sound conclusions on clays/pastes, preparation techniques and production methods can only be drawn when a sufficiently large number of items, in excess of 100, have been examined. However, this work is primarily concerned with the methodology used and the potential use of non-destructive neutron diffraction to archeological science. Nevertheless several observations can be made about the tested items. The firing temperatures determined from the analysis are in the range of 850–1000 °C. The experimental results show qualitative similarities in composition for all the samples, and several quantitative differences. Items N1–N4 are fragments of various vases, fabricated during the same archeological period and found at the same location (see table 1). Items N2 and N3 and to a lesser extent N4 present similarities in their diffraction patterns, whereas the diffraction profile of sample N1 significantly differs from the

Table 3. Relative weight fractions w (%) of quartz/trydimite (Q/Tr), alkali feldspar (A-FS), plagioclase (P), pyroxene (D), calcite (Ca), K spinel/hercynite (Sp/Hr), hematite (H) and gypsum (G). Strengths of reflection intensities at $2\theta = 13.8^\circ$ of the illite/muscovite (I-M) phase are indicated by (0), (+), (++) , (+++). R_{wp} is in (%).

A/A	Q/Tr	A-FS	P	D	Ca	Sp/Hr	H	G	Q/F	I-M	R_{wp}
N1/mean	41.2	8.9	18.1	0	20.6	5.8	5.4	0	1.53	+++	7.5
N1	42.2	9.7	23.6	0	13.0	5.7	5.8	0	1.27	+++	9.8
N2	14.8	10.4	53.8	12.6	2.8	2.7	1.9	1	0.23	+	8.2
N3	14.7	14.2	52.8	13.3	0.0	2.1	1.9	1	0.22	+	8.6
N4	16.4	5.6	60.7	10.3	0.0	4.6	1.4	1	0.25	+	10.8
N5	41.4	11.7	24.2	8.4	2.4	9.2	1.7	1	1.15	++	7.6
N6	38.7	12.8	23.3	8.6	1.3	9.3	1.9	1	1.07	++	7.6
N10	17.5	2.1	59.8	13.5	2.1	2.2	1.8	1	0.28	+	9.8

others. This difference may reflect the preparation method (clay and quality of construction) employed rather than the firing environment; it should be noted that item N1 is a hand made vase whereas the other three are wheel produced. On the other hand, although items N5 and N6 were found on different but near by locations, they were produced during the classical period and were parts of identical pottery; they present comparable profiles and mineral abundances from which one may hypothesize that the clay pastes and firing conditions were the same. The diffraction profile of item N10, which is dated at the Hellenistic period and found at a different location, shows similar characteristics to N4, so by analogy it may be assumed that comparable manufacturing techniques were utilized in the production of these items, even though the production dates differ by several centuries. Secondary phases were also identifiable with similar % compositions which imply that post burial deposition may have occurred.

5. Conclusions

The present mineralogical study, carried out on seven ancient Greek pottery shards, showed that the use of a monochromatic beam to perform non-destructive neutron diffraction can deliver quantitative phase fractions which are to be utilized for identifying characteristic signatures of the types of pottery as well as estimated temperatures of firing to which samples were exposed. However, this method is limited mainly by the following conditions: (a) during the measurement the sample has to be completely immersed in the beam, which puts a restriction on the size of the object to be analyzed and (b) it requires taking a sufficient number of measurements for different sample orientations, so an average sum spectrum can be obtained for quantitative phase analysis. Although the mineral phase compositions yield limited information about the origin of the pottery, when used in combination with results from other archeometric methods, they can provide useful information to the archeologist.

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