Journal of Molecular Structure 1122 (2016) 157–163

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Structural and compositional investigation of ancient ceramics from a fortified settlement in south-western Romania

O. Ponta [a], A. Vulpoi [a], V.V. Zirra [b], S. Simon [a, *]

[a] Babes-Bolyai University, Institute for Interdisciplinary Research in Bio-Nano-Sciences, Cluj-Napoca, Romania
[b] Vasile Pârvan Institute of Archaeology, Romanian Academy, Bucharest, Romania

ARTICLE INFO

Article history:
Received 1 March 2016
Received in revised form
27 May 2016
Accepted 30 May 2016
Available online 31 May 2016

Keywords:
Ancient ceramics
SEM/EDX
XRD
FTIR
EPR

ABSTRACT

We report on an interdisciplinary study focused on investigation of pottery fragments collected from the foundation of the wall of protohistoric site La Cetate, Bazdana village, Romania, close to the river Danube, dated towards the end of fourth century BC. The occurrence of pottery pieces under walls of that times is related to the foundation ritual. The samples were analysed by scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) spectroscopy, thermal analysis, X-ray diffraction (XRD) Fourier transform infrared (FTIR) and electron paramagnetic resonance (EPR) spectroscopies.

The characterization of the samples includes chemical composition and microstructural properties imposed by processing conditions. They are slightly calcareous ceramic matrices. The identified crystalline phases are preponderantly quartz, with plagioclase, mica, wollastonite and magnetite. The results indicate that the possible firing temperature in air could be above 1100 °C, or lower – if the artisans used reducing atmosphere, that is impressive for that times.

1. Introduction

Archaeological ceramic materials are made up of clay materials which consist of clay minerals, accessory minerals and amorphous materials [1]. Ancient ceramics are composites at the typical scale of 5–500 μm and their microstructure consists of sintered grains of different compositions [2]. The components of ceramic materials are the "fingerprint" of the solid phases formed during the firing, and the production processes of antique ceramics and pottery can be derived from their assemblage. The solid phases and their association depend on the properties of the used raw materials, maximum heating temperature, heating rate, duration of firing and kiln atmosphere.

The temperature at which ancient ceramics and pottery were fired varies over a wide range (600–1300 °C) depending on the type of clay used and the kiln available [3]. The characterization of archaeological ceramics and pottery can be certainly improved by differential thermal analysis (DTA) and thermogravimetric (TG) measurements.

Among the mineralogical and geochemical methods used in the analysis of ancient ceramics, beside optical microscopy and X-ray diffraction, the scanning electron microscopy coupled with energy dispersive X-ray spectrometry have created the potential to offer a seamless combination of textural and mineralogical data [4]. On the other hand, the infrared spectroscopy was applied on archaeological pottery shreds to identify the type of clay minerals used and to gather information regarding the firing temperatures [1,5,6], together with electron paramagnetic resonance (EPR) spectroscopy which also proved to be a useful tool in such investigations [7,8].

The present interdisciplinary study aims to characterize ancient pottery shreds collected from a Gethian fortified settlement in southwestern Romania (Dolj county), namely from the foundation of the wall of protohistoric site La Cetate, Bazdana village, close to the river Danube, dated towards the end of fourth century BC. Their microstructural properties, chemical composition and possible processing conditions were investigated using SEM/EDX, DTA/TG, XRD, FTIR and EPR methods.

2. Experimental

Five archaeological pottery shreds were collected from a foundation ritual wall of the protohistoric site La Cetate, Bazdana village, Dolj county, Romania. The settlement was dated towards the end of 4th century BC [9].

* Corresponding author.
E-mail address: simons@phys.ubbcluj.ro (S. Simon).

http://dx.doi.org/10.1016/j.molstruc.2016.05.100
0022-2860/

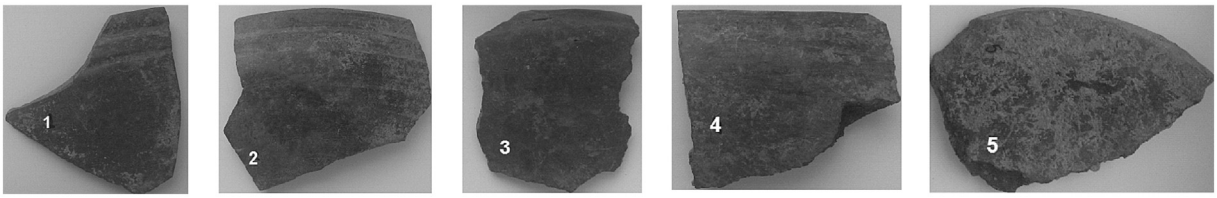


Fig. 1. Macroscopic images of the ceramic fragments.

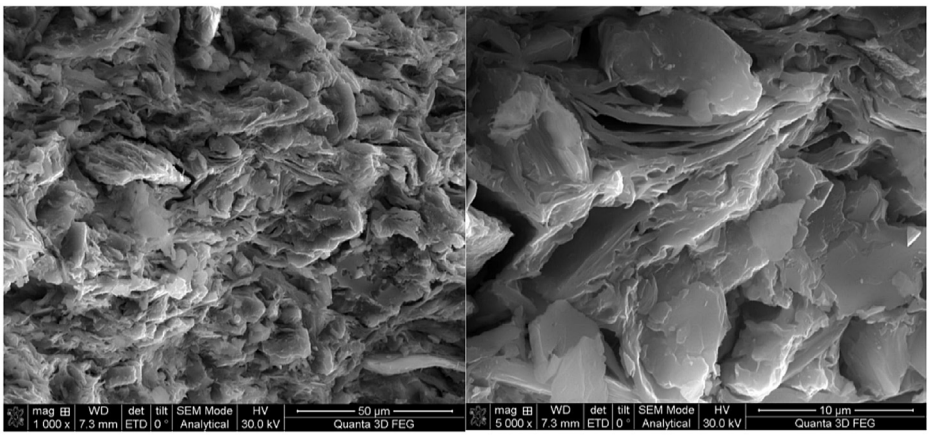


Fig. 2. SEM images from ceramic fragment (1).

Scanning electron microscopy (SEM) and chemical analysis of local area by energy dispersive X-ray spectroscopy (EDX) were carried out with a FEI Quanta 3D FEG dual beam microscope. Thermogravimetric analysis was performed with Shimatsu DTG-60H derivatograpf, with 10 °C/min heating rate. X-ray diffraction (XRD) analysis was carried out on a Shimadzu XRD-6000 diffractometer using Ni-filtered CuK_α radiation ($\lambda = 1.5418$ Å) at a scanning speed of 2°/min. FTIR spectra were recorded in the middle IR region (4000–400 cm^{-1}) with a spectral resolution of 2 cm^{-1}, in absorption mode, with a FT/IR-6200 Jasco Spectrometer by using the KBr pellet technique. The EPR spectra were recorded with an ADANI spectrometer at room temperature, in the X-band, using 4 G amplitude modulation.

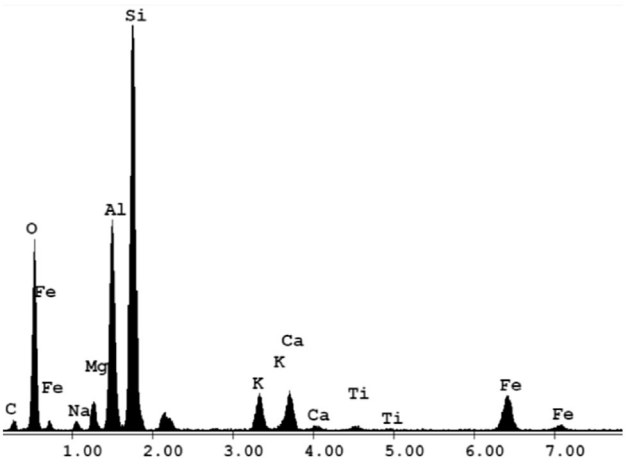
3. Results and discussion

The colour of the ceramic fragments was dark brownish with blackish insertions (Fig. 1). The SEM examination of all samples points out a grain morphology (Fig. 2, left image) which is slightly stratified, as can be observed at higher magnification (Fig. 2, right image). Vitrified components are also present.

The elemental analysis by EDX spectroscopy (Fig. 3) evidence the presence of C, O, Fe, Na, K, Mg, Si, Al, Ca and Ti. The atomic concentration of these elements is summarised in the adjacent table.

From the chemical mapping (Fig. 4) the elemental distribution of the major components does not occur homogeneously.

In the oxide composite one remarks several phases rich in Si, Al,



Element	at %
C	10.92
O	50.14
Na	0.88
Mg	1.94
Al	10.26
Si	21.31
K	1.26
Ca	1.34
Ti	0.17
Fe	1.76

Fig. 3. EDX spectrum recorded from a large area of ceramic fragment (1).