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Ceramics International 40 (2014) 16409–16419

CERAMICS INTERNATIONAL

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A combined use of optical microscopy, X-ray powder diffraction and micro-Raman spectroscopy for the characterization of ancient ceramic from Ebla (Syria)

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Received 17 July 2014; received in revised form 29 July 2014; accepted 29 July 2014
Available online 7 August 2014

Abstract

Ancient ceramics from the archaeological site of Ebla (Syria), dating back between 2250 and 1800 B.C., have been characterized by a combined use of optical microscopy (OM), X-ray powder diffraction (XRPD) and micro-Raman spectroscopy (micro-RS). Petrographic observations indicate that different fabrics are present, in terms of microstructure, groundmass and inclusions. XRPD allowed the identification and quantification of mineral phases of both unheated and heated samples at 950 °C, by means of Rietveld refinements. In particular, XRPD of heated samples highlights significant differences among the mineralogical assemblages of the analyzed samples, suggesting that the relative amount of carbonate and silicate minerals plays a key role, driving the reactions during the firing process. Furthermore, the mineralogical composition of unheated samples suggests a firing temperature in the 800–850 °C range, excluding a sample fired at lower temperatures (400–500 °C). Concerning the redox state of the firing atmosphere, the occurrence of hematite in some samples indicates that they were fired in oxidizing conditions, whereas other ceramic artifacts containing magnetite were fired in reducing conditions. Micro-RS results highlight that the mineralogical components of the decorated surfaces are hematite in the red areas and magnetite in the black ones.

Keywords: Bronze age; Pottery; Syria; OM; micro-RS; Rietveld analysis

1. Introduction

The common interest of scientists and archaeologists concerning analyses of ancient ceramics is mainly related to the identification of their mineralogical, petrographic and chemical features. The aim is to answer questions about the chemical composition of ceramic, as well as to explore the technological aspects (firing temperature and redox state of the firing atmosphere), and to define the nature and the provenance of raw materials [1–5].

Furthermore, the investigation of the micro-textural relationships between paste matrix and mineral inclusions, and their variations with increasing firing temperatures provide useful information to reconstruct the overall pottery production process.

The transformation process during firing depends on the grain size, mineralogy and chemistry of both clays and inclusions of the raw material and their relative abundances [1,6–10]. In particular, the chemical composition seems to drive the crystallization of new phases, such as gehlenite, wollastonite and anorthite.

For these reasons, in the investigation of archaeological pottery the main challenge is the choice of appropriate advanced analytical methods, in addition to those routinely used in the field of cultural heritage, to obtain qualitative

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http://dx.doi.org/10.1016/j.ceramint.2014.07.149
0272-8842/

and quantitative data for the complete characterization of the ceramic artifacts [11]. Indeed, while OM is essential in the definition of the ceramic fabric, XRPD and micro-RS provide information on structural parameters and molecular structures [12,13]. In particular, laboratory parallel-beam X-ray powder diffraction has been recently used for very accurate structural investigations also in the field of cultural heritage [14,15]. The experimental setup requires the preparation of the sample in a capillary, the data being collected in transmission mode. Such geometry allows an almost complete removal of the parasitic effect of preferred orientation.

In this study, a multi-analytical approach including OM, XRPD and micro-RS has been applied to Bronze Age Syrian potteries from the archaeological site of Ebla. The Rietveld refinement performed on XRPD data acquired in transmission mode allowed an accurate quantification of mineral phases. The nature of the pigments used for the decorations of the pottery has been investigated. Selected samples containing different amounts of carbonate minerals were re-fired at temperature well above the decarbonation temperature (800–850 °C for Ca-rich materials). These results allowed us to explore how the different mineralogical composition of the raw material drives the final mineralogical assemblage of the pottery.

Moreover, the results provide information about the firing process of the ceramics, from which the technological background of the ancient Syrian population can be inferred; in addition, these data can be very useful to trace the provenance of the raw materials.

2. Geological settings

The archaeological site of Ebla, located in the north-western Syria, is built on Paleogene limestone. Its name, meaning "white rock," seems to originate from the color of the sedimentary sequences outcropping in the area. A brief description of the geological framework of the Ebla area is reported in Fig. 1.

Syria is part of Levantine Basin, representing the southeastern-most sector of the Mediterranean Sea. It occurs in a complex geodynamic setting (i.e., a continental margin), between the Arabian and Levantine plates. These plates are separated by the Dead Sea transform fault. The Levantine basin, a thinned continental crust, originated during the opening of the Neo-Tethys [16]. Geological and geophysical data suggest that the Levantine basin is mainly composed by a Phanerozoic sedimentary succession overlying an igneous-metamorphic basement [16].

During the Cenozoic (mainly Neogene), an extensive igneous activity occurred in the Mashrek region, Middle East, producing alkaline mafic rocks and basalts [16,17].

In the area of the archaeological site of Ebla, limestones, marls, having intercalated lenses of clay materials, and cherts (Paleogene) are present. Moreover, in the western and eastern sectors of this area also ophiolites (Maastrichtian) and basaltic rocks (Neogene-Quaternary) are present in outcrops (Fig. 1).

3. Archaeological setting

Since 1964 "La Sapienza Expedition to Syria," directed by Prof. Paolo Matthiae, carried out a systematic exploration of the ancient site of Ebla [18].

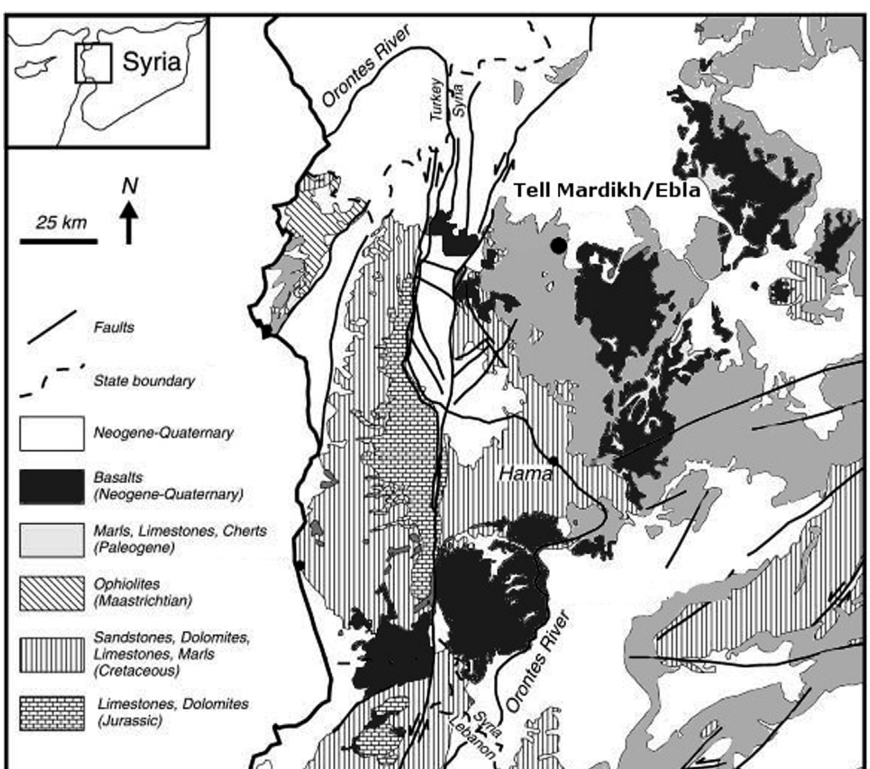

Fig. 1. A schematic geological map of central Syria reporting the location of Tell Mardikh-Ebla (modified from Maritan et al. [29]).