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Thermal analysis of ancient ceramics using the microchemical and microstructural alterations of foraminifera

Maria Daghmehchi[a,*], Adriano Guido[b], Adelaide Mastandrea[b], Mir Amir Salahi[c], Mehdi Omrani[d], Jebrael Nokandeh[e,f]

[a] Department of Archaeology, University of Tehran, Tehran 6619-14155, Iran
[b] Department of Biology, Ecology and Earth Sciences, University of Calabria, Via Bucci, cubo 15b, 87036 Rende, Cosenza, Italy
[c] Department of Geology, Ferdowsi University of Mashhad, 9177948974 Mashhad, Iran
[d] Department of Geology, Karaj Branch, Islamic Azad University, Karaj, Iran
[e] National Museum of Iran, Tehran 113665-4364, Iran
[f] Research Institute of Cultural Heritage and Tourism (RICHT)

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ABSTRACT

Thermal degradation of planktonic and benthic foraminifera within the coarse wares of Qizlar Qaleh and clay from Khangiran Formation in Kopet Dagh basin, Iran, were examined at different temperature rates. Hyaline and agglutinated tests of foraminifera were investigated through Thermogravimetry (TG), Derivative thermogravimetry (DTG), Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscope coupled with Energy Dispersive Spectrometry (SEM-EDS) to identify their thermal stability and chemical transformation from 500 °C to 1000 °C. TG/DTG and FTIR analyses show significant weight loss in the range of 750–800 °C and a progressive decrease in the intensity of carbonate bands at 1424, 2514 and 875 cm^{-1} (from 700 °C, to 800 °C) which indicates the release of CO_2. In addition, the chemical characteristics of the agglutinated tests indicate high thermal stability due to their high silicate component. The complete decarbonization of hyaline tests occurred at around 800 °C, whereas the agglutinated tests are still preserved at 1000 °C. Finally, microstructural and microchemical analysis of foraminifera from the ancient ceramics and Khangiran clay indicated firing temperature of the ceramics at around 700–750 °C. The X-ray diffraction (XRD) and a comparative TGA and FTIR analysis of the ceramics and the fired clay samples from Khangiran Formation also show a high intensity of calcite bands, indicating a firing temperature < 750 °C. This approach provides a new tool for estimating the firing temperatures of ancient ceramics.

1. Introduction

Thermal decomposition of foraminifera in the clayey matrices of ancient ceramics provides the basis for estimating the firing temperature of ancient coarse wares such as cooking pots and storage jars [1–4]. TG/DTG and FTIR spectroscopy provide useful means for identifying the thermal decomposition stage and phase transitions necessary for determining the firing technology of ancient ceramics [5–10]. This study documents microstructural and chemical alteration (thermal decomposition and recrystallization) of foraminifera tests at different heating rates from 500 °C to 1000 °C. In this project, the thermal alteration of planktonic and benthic foraminifera from the coarse wares of Qizlar Qaleh including storage jars (1817 ± 84 BP, TL date) and cooking pots (2268 ± 111 BP, TL date) [11], were studied through TG/DTG, FTIR spectroscopy, and SEM-EDS. These data were compared to the thermal decomposition of foraminifera from the fired clay of Khangiran Formation, in Kopet Dagh basin, northeastern Iran (Fig. 1). The presence of *Acarinina* sp., dated from late Paleocene to late Eocene, indicates that the ceramic production can be attributed to the Khangiran Formation. Presence of epifaunal and infaunal morphotypes within the ancient ceramic matrices from Qizlar Qaleh and the raw clay sample from the archaeological site corroborates local production for the ancient ceramics [11].

FTIR spectroscopy has been previously used for documenting the chemical composition of fossil sporopollenin, CaO catalysts, polymeric structure of microfossils and macromolecular structure of palynomorph fossils [12–18]. Studies conducted by Yule et al. [19] and Fraser et al. [20] indicated significant chemical evolution of organic microfossils such as pollen and sporopollenin through FTIR analysis. TGA and FTIR analyses identify the structures of degradation products and thermal

* Corresponding author.
E-mail address: Maria.daghmehchi@yahoo.com (M. Daghmehchi).

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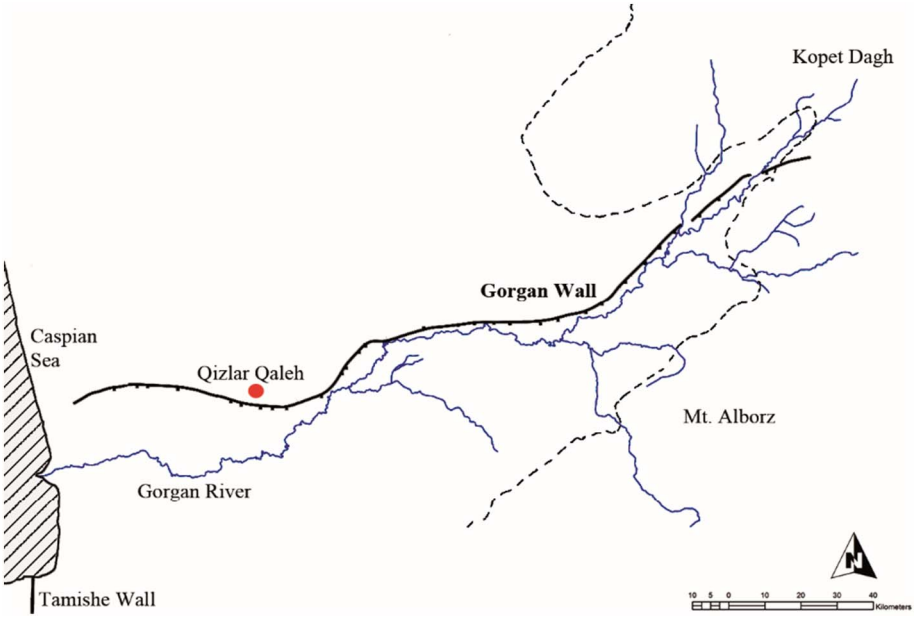

Fig. 1. Map showing the location of the archaeological site of Qizlar Qaleh and Khangiran Formation in Kopet Dagh basin, based on the map of Gorgan Wall project [26].

stability of sample at high temperatures [21,22]. Thermogravimetric analysis measures the continuous weight loss of a sample at different temperature rates in a controlled atmosphere [9,23,24]. Therefore, in this study, FTIR spectroscopy along with TGA was applied to identify the chemical alteration of planktonic and benthic foraminifera during heating. This paper presents a comparative study of thermal behavior of foraminifera occurring in the Khangiran Formation clay and the ancient ceramics in order to estimate the firing temperature of the coarse wares. Mineralogical characteristics of the ceramics were further investigated by XRD in order to determine the crystalline phase composition.

2. Qizlar Qaleh and Khangiran Formation

The archaeological site of Qizlar Qaleh, in the western part of the Gorgan Wall, was built as a military fort in the early Sassanian period, before the construction of the great Gorgan Wall [25]. It was then connected to the Gorgan Wall in the late Sassanian period (429–574 CE) ([26]; Fig. 1). The archaeological excavation of the fort provided a small collection of the coarse wares such as cooking pots and storage jars containing foraminifera (Fig. 2). A variety of planktonic, epifaunal and infaunal benthic foraminifera such as *Globobulimina* sp., *Hanzawia* sp., *Anomalinoides* sp., *Gyroidinoides* sp., and *Acarinina* sp. originated from Khangiran Formation, were identified in the ceramic matrix of the cooking pots and the storage jar (Figs. 3, 4, 5). Khangiran Formation is located in Kopet Dagh basin, northeastern Iran. The formation consists of sedimentary units of Late Paleocene to Early Oligocene age [27].

3. Materials and Methods

The coarse wares from the archaeological site of Qizlar Qaleh have the same mineralogical and chemical characteristics [11,25]. In this

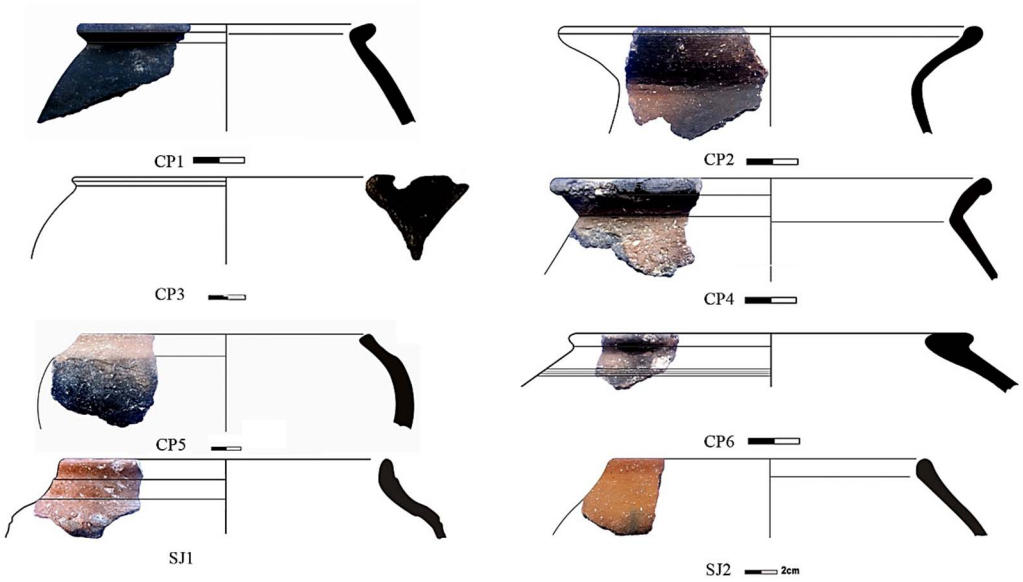

Fig. 2. Images of the cooking pots (CP) and storage jars (SJ) containing foraminifera from Qizlar Qaleh.