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Constructing a Database for pXRF, XRD, ICP-MS and Petrographic Analyses of Bronze Age Ceramics and Raw Materials from Failaka Island (Kuwait)

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ABSTRACT

Ceramic artefacts from Failaka Island (Kuwait) as well as raw materials from the surrounding areas of the archaeological sites were analyzed by means of petrographic thin sections, non-destructive portable X-ray fluorescence (pXRF), and high precision powder X-ray diffractometry in an attempt to fingerprint production centres, raw material sources, as well as trade and exchange routes in the Bronze Age.

The study of the bi-phase composition of ceramics (matrix and clasts) is a powerful indicator of raw materials used in the manufacturing process (*e.g.* clays and tempering materials) and can be successfully deployed in understanding the physical parameters of the techniques of manufacturing. Mineralogical (*e.g.* the presence of the mineral gehlenite, partial decomposition of micas, advanced fissuring in quartz and melting of quartz rims) and textural changes (*e.g.* developments of secondary pores and contraction voids around large clasts, later filled by melt) observed within the same sample and throughout the sample set, especially in the composition of the matrix, argue for relatively high firing temperatures of at least 800-850°C and oxidizing conditions.

The quantitative and qualitative mineralogical composition of the analyzed clays (*e.g.* illitic-kaolinitic clays) considered as potential sources of raw materials yielded positive results. However, the lack, in the vicinity of the site, of tempering material similar to the one identified in the artefacts (*i.e.* intermediate-acidic (meta) igneous rocks - granitoids and gneisses) precludes any unequivocal interpretation as to the origin of the raw materials and later, to the origin of the ceramics and the location of the production centres.

KEYWORDS

Archaeometry, Bronze Age, Dilmun ceramics, Failaka Island, Provenance study.

Introduction: typology as chronology

In the past, work has been carried out on Dilmun Bronze Age ceramics from Kuwait and Bahrain in order to better describe and categorize ceramic types and also to develop a chronology. Attempts have been made to determine whether the ceramics from different sites have Mesopotamian, Indus, or Dilmun style, and also to address trade and exchange, and social complexity in the Bronze Age (Højlund 1987, 2007). The significance of this research resides in it being the first such scientific study on Bronze Age ceramics in the Persian/Arabian Gulf, particularly Kuwait and Bahrain. Our contribution represents the foundations of a database for archaeometric information (chemical compositions, petrological descriptions, etc.) of Failaka Island and Barbar ceramics. This research will also explore the ancient trade and exchange network by employing non-destructive portable X-ray fluorescence (pXRF), allowing for a better understanding of the sources of Failaka ceramics and regional interactions as well.

Archaeometry in the Gulf

Even though archaeometry is a crucial tool and method for provenance studies of ceramics, there are few studies that have employed archaeometric methods on ceramics in the Persian-Arabian Gulf (Blackman *et al.* 1989; Méry 1991, 1995, 2000; Mynors 1983). These works were focused on using petrographic thin sections to characterize ceramics and identify fabric types from the 4th and 3rd millennium BC sites in Oman and the United Arab Emirates (UAE). Comparing the Mesopotamian fabrics from Mesopotamia and the Gulf, the researchers were able to document a connection and confirm the presence of Mesopotamian vessels in Eastern Arabia, implying its participation in the larger trade network that included Iran and the Indus Valley.

Few studies so far have focused on the provenance of raw materials of ceramic types from the Persian-Arabian Gulf using instrumental neutron activation analysis (INAA). Along with petrographic thin sections, INAA was employed to examine the origin of foreign jars from the Oman Peninsula and to determine a zone of production in the Indus Valley (*i.e.* Harappa vs. Mohenjo-Daro) and Iran (Blackman *et al.* 1989; Méry and Blackman 1995, 1999).

Chemical analysis using X-ray fluorescence (XRF) has been successfully used to obtain quantitative data about Bronze Age ceramics from Oman, UAE, and Mesopotamia, as well as to provide suitable elements for discrimination (Méry and Schneider 1996, 2001). The results of the latter studies (high Ca vs. low Mn compositions) revealed that chemical outliers have different petrographic composition, indicating a possible Southern Mesopotamian origin. To date, XRF has been the only analytical method used in Kuwait (Pollard

1987) for the identification of chemical components of a small number of glass, faience, and glazed pottery artefacts. The results revealed that the glazed pottery has an exceptionally high alkali ratio in the Bronze Age material, which seems to be a particular feature of that time period on the site. Portable XRF application in the Gulf is considered new, however, a new study sheds light on the using pXRF non-destructively to establish a chemical database in Turkey. Goren and his colleagues (2011) have shown the potential power of the instrument in grouping Bronze Age clay cuneiform tablets from Hattuša, Turkey, and el Amarna, Egypt.

The realm of Dilmun

Contemporary with the Kingdom of Bahrain, Dilmun was favoured as the most active entity in the Persian-Arabian Gulf in the early 2nd millennium and shipped commodities to different regions, thus dramatically expanding its territory and wealth. Unlike during the 3rd millennium BC, Dilmun would dominate the Mesopotamian trade network during the 2nd millennium BC by expanding to the north, including Failaka Island (Fig. 1). Its centres and ports became attractive to traders looking for markets where the flow of commodities and a reliable supply of raw materials were secured.

This millennium witnessed intensive interregional interaction, trade and exchange, and a noticeable expansion of socio-political complexity in the Arabian Gulf and in neighbouring regions like Iraq, Iran, and India. Dilmun sites on Failaka Island speak to the role Kuwait had in the region as a participant in a larger network that had socio-economic cohesion with other entities in the region. Dilmun and Mesopotamian archaeological findings appear along the Arabian shores of the Gulf. Moreover, metal works originating from Maggan (Oman) and Harappa (Pakistan) validate the fluid nature of regional exchange, productivity and craft centres.

Failaka Island: Dilmun power in the north

Failaka Island is part of the State of Kuwait and it is the second largest island in Kuwait. It lies twenty kilometres east of the mainland of Kuwait, opposite Kuwait Bay (Fig. 1). Its area is approximately twenty-four square kilometres, which is roughly half the size of Manhattan, New York; its maximum length is fourteen kilometres, and is roughly six kilometres wide (Fig. 2). The island has a flat topography, apart from a 9m tall hill located in its western part. It is roughly rectangular in shape, is adjacent to *Meskan* Island to the northwest, while having the island of *O'ha* in its southeast vicinity.

Failaka Island is mostly sandy with some rocky coastlines. The "Shbija mound" is considered the highest point at about 9m above sea level (Salem 2006). The entire shoreline of Failaka is considered to be a natural port, where ships used to be protected during storms. The recent excavations of the Slovak expeditions (Benediková *et al*. 2008, 2009) have shown that the oldest port of the island, known to date, was located in the northern part, in an area known as Al-Khidr. Its position, facing Al-Basra in Iraq, makes it a suitable natural harbour and a convenient stop on the maritime route along the western coastline of the Persian Gulf (Benediková *et al*. 2008)

Fig. 1. The location of Dilmun (Bahrain) in the middle of the Gulf controlling the maritime trade and its presence on Failaka Island (Kuwait) in the early second millennium B.C. The State of Kuwait is shaded in green and a red star represents the geographical position of Failaka Island.

Numerous archaeological sites on Failaka Island pertain to a new culture that appeared at the beginning of 2nd millennium BC. This culture was associated with the Dilmun culture, located in the contemporary Kingdom of Bahrain. The most studied archaeological sites on the Island belong to the Dilmun period and date from 2000 to 1700 BC. The Temple (known as F3), the Palace (known as F6), and al-Khidr (known as "the port") have been the focus for many archaeological missions since 1958, when the Kuwait government invited the Danish archaeologists to carry out the first archaeological excavation in the history of the country.

The study site

The discovery of the Al-Khidr site (known as "the Port") on the NW coast of the island by the Kuwaiti-Slovak expedition during the 2004 to 2009 campaigns (Benediková 2010) revealed early Dilmun influence on the island (Fig. 2). This site appears to have served as a port in the early 2nd through mid-2nd millennium B.C. according to its geographical location and the numerous ceramic artefacts and metal objects found during excavations. The typological and spatial observations support the assumption that these ceramics belonged to the Dilmun tradition/style and were used to store and transport foods.

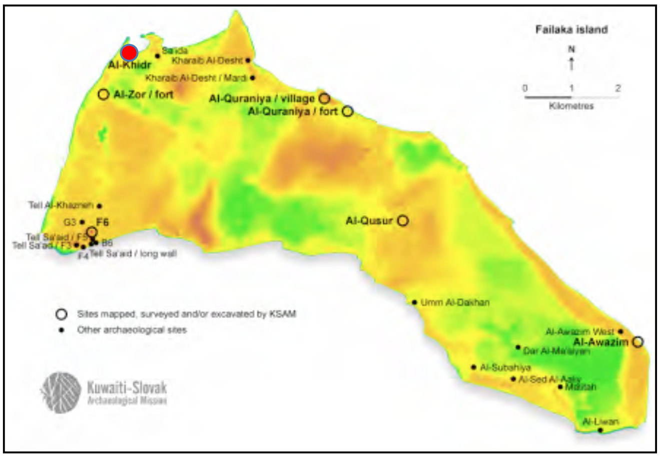

Fig. 2. The main Bronze Age sites (F3 and F6) on Failaka and the area of this study Al-Khidr site, known as the Port, (red dot) in the NW corner of the island (After KSAM 2012).

The site stretches along the NW shore of al-Khidr Bay, a natural port where ships were protected during storms. The recent excavations led by the Joint Kuwait-Slovak Archaeological Mission have shown that the oldest port of the island known to date was located in the al-Khidr area in the N part of the island. Its position, facing al-Basra in Iraq, makes it a natural harbour and a convenient stop on the maritime route along the western coastline of the Persian-Arabian Gulf (Benediková *et al*. 2008, 2010).

Barbar type pottery

Our preliminary study, aimed at establishing a chemical and mineralogical database of Bronze Age Dilmun ceramics from Kuwait, is focused on eight ceramic potsherds selected to fingerprint the production centres within the Dilmun territory or to track exchanges that took place between different cultural entities (*e.g*. Mesopotamia and the Indus Valley). Also, to trace the source of raw materials used in the manufacturing of Dilmun ceramics. The samples were chosen from the Slovak excavation site and identified as being Dilmun pottery, known as Barbar Type.

The large amount of ceramic artefacts found at al-Khidr comprises large red-ridged jars as well as smaller slipped reddish sherds. From the sample population selected for this study, seven samples have the ridged reddish slipped feature typical for the Barbar pottery type. This type of pottery can be further divided into groups based on colour, grain size, and hardness. Furthermore, the Barbar type ceramic artefacts are hand-made and the colours are homogenous and well fired (Fig. 3). The slip can be gray in colour, also known as C-ware type, for sample no. 13694, or can be coated with red slip, as seen on sample no. 13697 (see Højlund, 1987). Texturally speaking, the only distinctive type of sherd is represented by sample no. 13695 which is strongly tempered with coarse material. It has straw impressions (G-ware) and sand particles are seldom seen, while the colours range from pale brownish and pale greenish to light gray (Hojlund, 1987). It is assigned to the G-ware group which is wheel-made, except for the giant storage vessels, and belonging to the Mesopotamian tradition.

Since there is little available information on clay composition and overall geological data on Kuwait geology, clay samples from north Kuwait were also selected to characterize their texture and identify their mineralogical composition, and compare them with the data obtained by means of pXRF on ceramic artefacts.

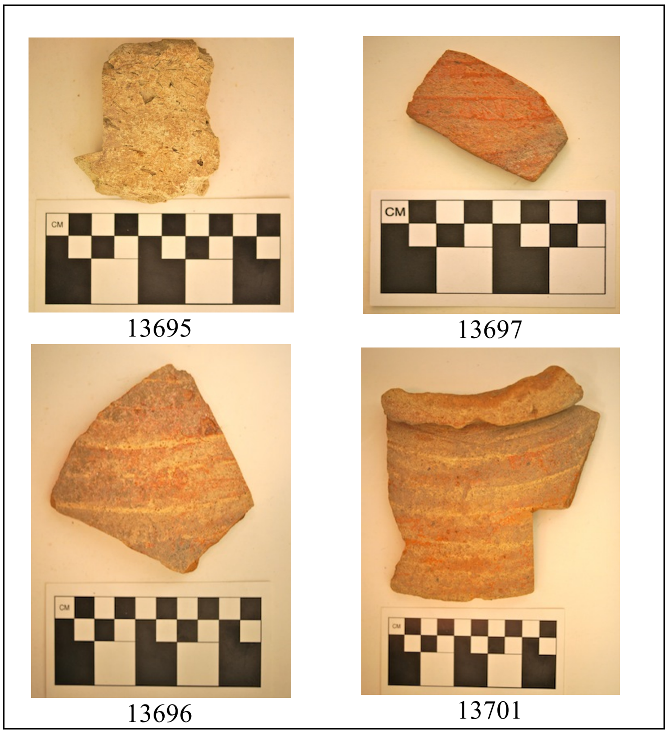

Fig. 3. Potsherds from the early second millennium B.C. from al-Khidr showing Barbar and Mesopotamian types.

Initial results of archaeometric analysis

Portable XRF sample preparation and analysis

One of our research aims was to examine the homogeneity of ceramic recipes on Failaka Island using non-destructive methods such as pXRF. This would allow us to determine the chemical composition of clay and ceramic samples, thus being able to further classify the artefacts into distinct ceramic groups. Glazed and painted ceramic potsherds were excluded from our analysis. Potsherds were thoroughly cleaned before the analyses to avoid any contamination with dust or soil residues. The elemental composition of the ceramic surface was analyzed non-destructively using a Bruker Tracer III-SD portable X-ray fluorescence spectrometer. The instrument was set up to provide quantitative results for trace elements including, but not restricted to, Ba, Rb, Sr, Y, Zr, and Nb. These elements were chosen because they were proven to be successful for determining sources and sub-sources for various ancient materials such as obsidian tools and ceramic sherds (Speakman *et al.* 2012; Tykot 2002). The inner and outer surfaces of the samples were analyzed in order to obtain an average elemental composition.

The results obtained using the Bruker pXRF clearly show the ability of this instrument to make distinctions between al-Khidr ceramics with homogeneous compositions. Using the trace elements Ba, Rb, Y, Sr, and Nb, the initial analysis shows the samples can be clustered into two groups, making sample no. 13695 an outlier (Fig. 4. A and B). Also, the results show the consistency within each potsherd and the outlier (sample no. 13695) is not just one part or surface.

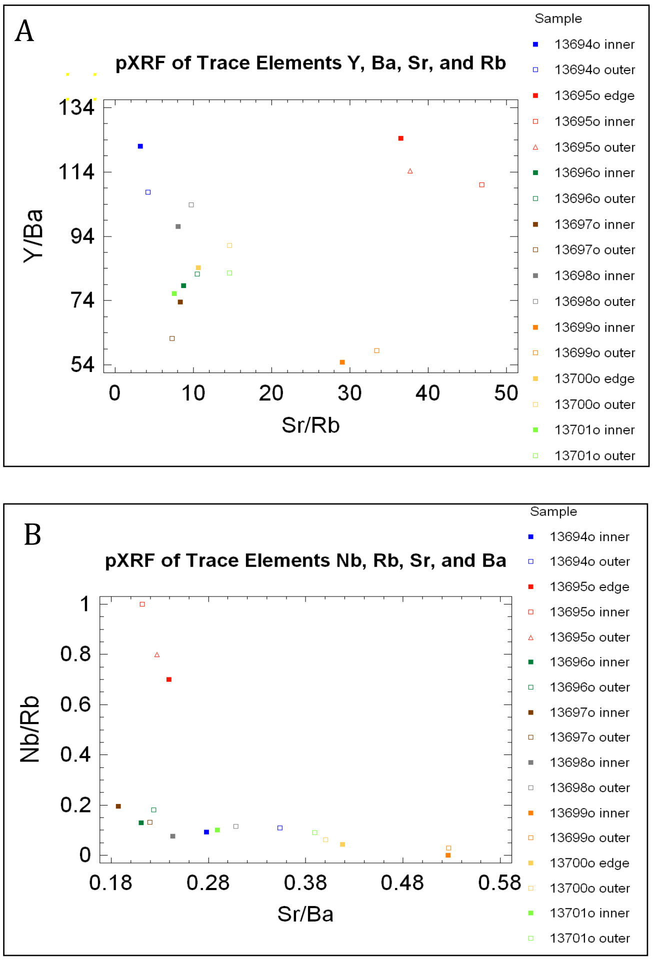

Fig. 4. Scatter plot showing the ceramics groups within a site and sample no. 13695 as an outlier. Both graphs A and B showing the best separation of samples analyzed by pXRF using Y, Ba, Sr, Rb, and Nb.

Petrographic analysis

Petrographic investigations of thin sections allowed us to better characterize the textural features of the samples, as well as to identify the major mineral phases that were used as temper material. Furthermore, our findings allow some inferences to be made on the techniques used by the manufacturers (*e.g.* firing temperature).

The petrographic characterization of ceramic artefacts deals with the description of the matrix (*i.e.* groundmass), clasts (*i.e.* crystalloclasts, lithoclasts, grog, fossil remains, etc.) and voids (*i.e.* primary and secondary pores).

The samples analyzed for this study exhibit two general types of matrix, both of which are firing temperature and clay composition dependent: amorphous and microcrystalline. Most of the samples have a well developed microcrystalline matrix, characterized by random orientation of needle-like micro-crystals and subordinate amounts of glass. The matrix tends to be birefringent to highly birefringent (Fig. 5), a feature related to high concentrations of illitic clays in the paste. The colour of the matrix, observed in plane polarized light, ranges from shades of reddish-brown to grey-brown, the latter being associated with sample 13695, shown to also be an outlier based on pXRF data. Sample 13701 has an almost isotropic matrix and thin films of glassy material are detectable around the micro-crystals in the groundmass. Ionescu *et al.* (2007) have shown that such features are due to the use of kaolinitic clays in the manufacturing process.

Sample 13695 has a very different matrix when compared to other samples used for this study. Aside from its unusual colour (gray-brown in plane polarized light and greenish-gray in cross polarized light), the matrix tends to be a combination of opaque amorphous and translucent microcrystalline phases with low birefringence. The clasts present in the analyzed samples are a combination of crystalloclasts, lithoclasts, and grog in various proportions.

The vast majority of the crystalloclasts are quartz grains. They range from sub-angular to rounded, with a direct correlation between the degree of roundness and grain size. Almost all quartz grains, irrespective of their size, have undulatory extinction and lack primary inclusions. Some of the small and intermediate-size quartz grains have fissures caused by abrupt cooling. In some cases, these fissures are filled with glassy material migrated from the matrix or have reaction rims at the contact with the matrix. Melting of a thin layer of quartz at the matrix-crystal interface is randomly visible in the samples.

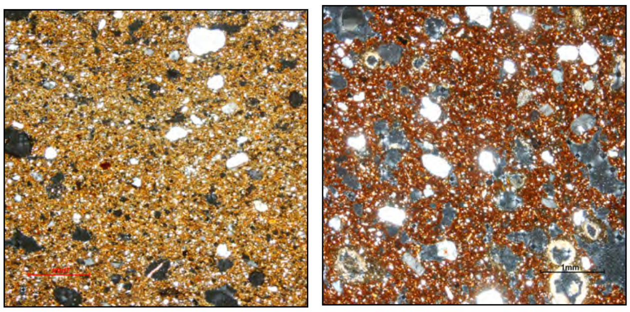

Fig. 5. Microphotographs of thin sections of the Failaka Bronze Age samples No. 13697 (left) and 13701 (right).

Feldspathic crystalloclasts are sparse in the studied samples and, when present, they are always small in size and sub-angular. Plagioclase feldspar usually shows compositional zoning and polysynthetic twinning, and is seldom fresh. Sericitization and calcitization are the ubiquitous secondary minerals developed on plagioclase grains. Alkali feldspar is rare and microcline (with specific tartan twinning) and orthoclase (with granophyric texture) are small in size and sub-angular to sub-rounded. Some grains have fissures filled with amorphous matrix. Less common crystalloclasts include micas (fine-grained muscovite lamellae partially destroyed during firing and small fragments of biotite), zircon (with different morphologies), and sparse epidote.

The most abundant lithoclasts have granitic composition (Fig. 6), while quartzitic lithoclasts are less common. No fossil remains have been identified in the samples chosen for this study. Grog was found in several samples and it is abundant, albeit the fragments are very small.

The porosity can be quite high in some samples and it is often composed of elongated voids, either primary (fluid pockets trapped inside the paste during the manufacturing process) or secondary (complete decomposition of mineral phases, thermal contraction – often visible around large quartz grains).

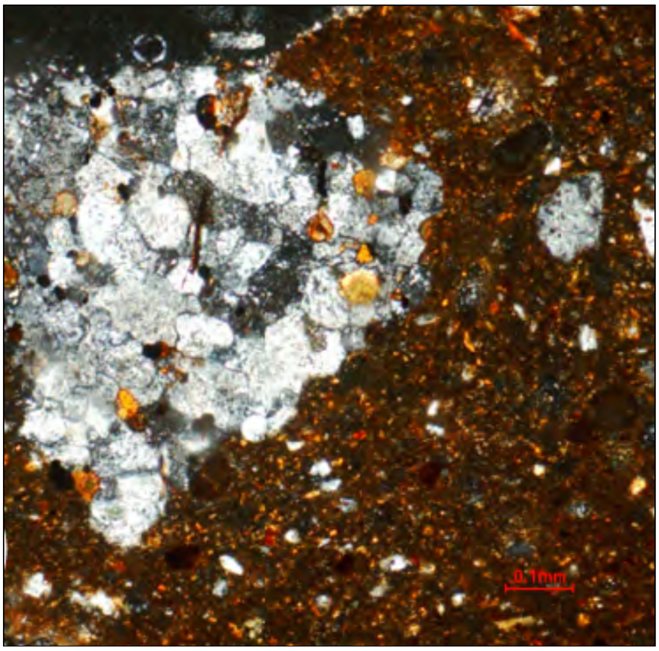

Fig. 6. Lithoclast (gratinoid) used as tempering material.

The fabric of the ceramics is generally isotropic, weekly oriented, with the exception of sample 13695, which shows a very good orientation of the clasts and elongated pores, parallel with the wall surfaces.

X-ray diffraction analysis

Powder X-ray diffraction was carried out on selected samples in order to identify the mineralogical composition of the mineral phases, both primary and secondary, present in the ceramic artefacts. Most of the major mineral constituents, identified by means of petrographic observations (*e.g.* quartz, plagioclase and alkali feldspars, muscovite, and biotite), were also found in the XRD patterns of the samples. Furthermore, newly-formed minerals were also identified. The most important mineral is gehlenite, a Ca-rich sorosilicate formed during the reaction of clay minerals and calcite, at temperatures in excess of 850°C (Traoré *et al*. 2003).

ICP-MS sample preparation and analysis

Inductively coupled mass-spectrometry (ICP-MS) analyses were carried out for comparison with the chemical composition results obtained from the pXRF technique. Samples were crushed in an agate mortar to under 200 mesh and then digested using the $LiBO_2$ flux-fusion technique, based on the method proposed by Kelley *et al.* (2003), with a flux-to-sample ratio of 4:1 to ensure complete dissolution of more resilient mineral phases (*i.e.* zircon) identified during petrographic investigation. Trace elemental concentrations were obtained using a quadrupole ICP-MS at the University of South Florida's Centre for Geochemical Research. The accuracy and precision of the measurements is generally better than 5%. The elements measured by means of ICP-MS comprise most of the REE (with the exception of Pm and Tm), large-ion lithophile elements (LILE), and high field strength elements (HFSE).

The dataset yielded by means of ICP-MS is in good agreement, albeit not completely overlapping, with the composition obtained using pXRF (Fig. 7). As shown in Figure 7, selected elements measured both by ICP-MS and pXRF correlate rather well, with the exception of Sr. Since Sr has partition coefficients larger than 1 in plagioclase and alkali feldspars from intermediate to acidic lithologies (*i.e.* granitoids), but smaller than 1 in most clay minerals, the results yielded by pXRF have to be carefully interpreted as representative for the bulk composition of the artefact, especially in samples showing large plagioclase and alkali feldspar crystalloclasts. Overall, the dataset shows that, when carefully utilized, pXRF can be a useful and non-destructive tool for characterizing the chemical composition of ceramic artefacts. Speakman *et al.* (2011) show also the great potential of pXRF for quantitative analyses of ceramic sherds from the American southwest. Moreover, their results obtained by means of pXRF are in good agreement with the instrumental neutron activation analysis (INAA) data even though the latter is considered to have greater analytical precision (Speakman *et al.* 2012). pXRF will be a significant method to measure trace elements and effectively identify compositional groups of heterogeneous material such as the Bronze Age ceramics from Kuwait and adjacent regions.

Conclusions

The results of this preliminary study of Bronze Age ceramic artefacts from Failaka Island (Kuwait) can be summarized as follows:

- pXRF was successfully applied to examine sample homogeneity in a non-destructive manner
- The method we present is suitable for distinguishing between samples from a site and supporting the consistency within each potsherd.
- Mineralogical, petrographic, and chemical data can be useful tools for identifying raw materials used for the manufacturing of ceramics as well as for grouping the artefacts into categories based on common features.
- The clays used for the paste were a heterogeneous mixture of illitic and kaolinitic clays.
- Material used for temper range from granitic compositions to grog, but completely lack fossils and carbonate-rich lithologies.
- Firing temperatures, based on newly-formed minerals and the morphological features of crystalloclasts, range from 600 to at least 850°C.

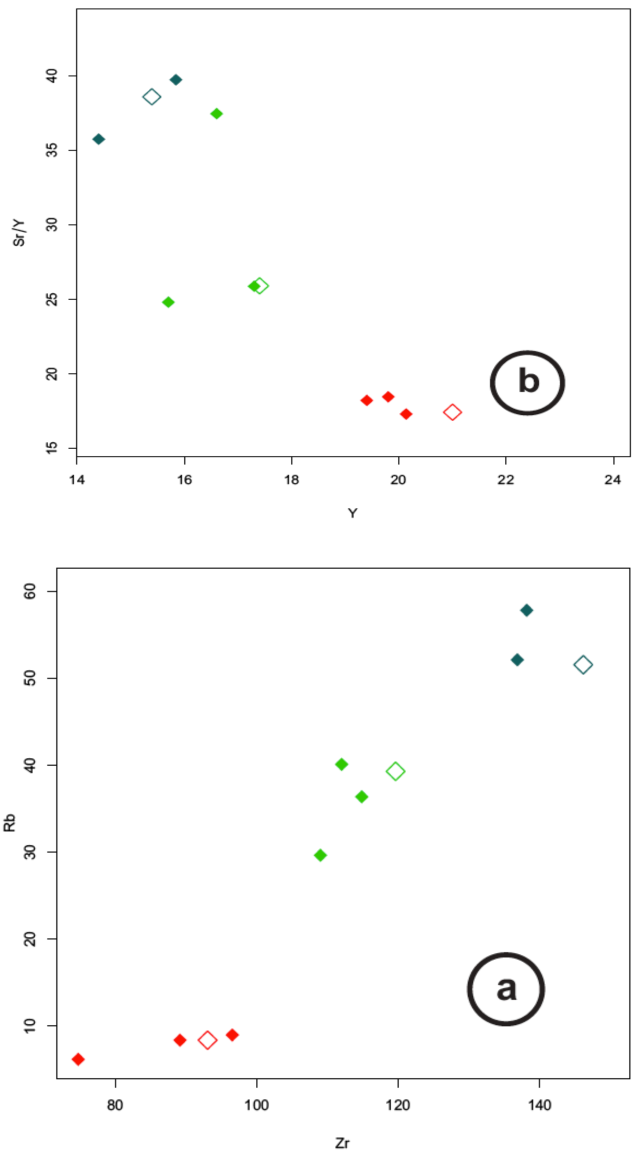

Fig. 7. Selected elemental plots for three Failaka Island samples. Open diamonds are samples analyzed using ICP-MS; samples were digested using "classic" $LiBO_2$ flux fusion. The compositions yielded by ICP-MS are in good agreement with those yielded by pXRF.

Acknowledgments

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