

CHARACTERISATION AND CLUSTERING OF BRONZE AND IRON AGE GREY POTTERY FROM GOHAR TAPPE (4TH-2ND MILLENNIUM BC, IRAN)

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Introduction

As ceramics are often the main components of archaeological sites, they are one of the most important artefacts for researching cultural heritage. Mineralogical analysis of ancient ceramics can lead to a better understanding of specific technological aspects. The aim of this minero-petrographic study is the characterisation of common Bronze and Iron Age Grey Pottery from Gohar Tappe, to the south-east of the Caspian Sea.

Gohar Tappe is located in Mazandaran province, northern Iran, *c.* 5 kilometers west of Behshahr (36°40'42" N 53°24'07" E) (Figure 1). This site is located close to prehistoric sites, such as Komishan, Rostamkola, Kamarband and Huto Caves (Mahforuzi 2001). During the Middle Bronze Age, the settlement covered more than 10 hectares, but was later abandoned in the Late Bronze Age and was used again in the Iron Age II/III as a cemetery. Systematic excavation and comparative research have revealed that the settlement in this large ancient area had been occupied in different periods. Grey Pottery is the dominant cultural evidence of the Bronze and Iron Ages. The majority of pottery from this period is represented by black and grey colour types identified as domestic vessels (Majidzadeh 1989).

Methods and sampling

Twenty-five potsherds were provided for analyses by the archaeological authorities; the sherds came from the six layers of the Bronze and Iron Ages (Figure 2). The samples were classified based on their macroscopic and microscopic properties. Macroscopic observations provide us with preliminary information about colour, hardness, weight and fabric of the ceramic objects (De Bonis *et al.* 2010). In order to investigate production technologies and attest a possible classification of these ceramics, a multi-analytical approach was applied. Polarised light microscopy (PLM) analysis, using an "Olympus BX61", X-ray fluorescence analysis (XRF) with a "Philips PW1480" spectrometer, and X-ray powder diffraction (XRD) with a "Philips PW 1800" diffractometer including phase refining analysis by the Rietveld method, were carried out to determine the features of the fabrics, and textural typology within the samples from the archaeological layers.

All fragments were examined petrographically, whereas XRF and XRD analyses were performed only on six samples (EBA-2, MBA-1, LBA-1, IAI-2, IAI-3, and IAIII-1). These samples were considered to be the most representative on the basis of the petrographic observations, and were chosen on the basis of their weight and typology. Investigated samples needed to be large enough for multiple analyses using different analytical techniques.

The first group of samples contains four sherds from the Early Bronze Age (EBA), obtained from the AJ2XXI trench and context 15. Unfortunately no stratigraphical description from the trenches is available. Investigated samples were collected from the trenches during the excavation. Almost all these samples are thin-walled pots, light grey in colour and without any decorative motif on the surface. In this

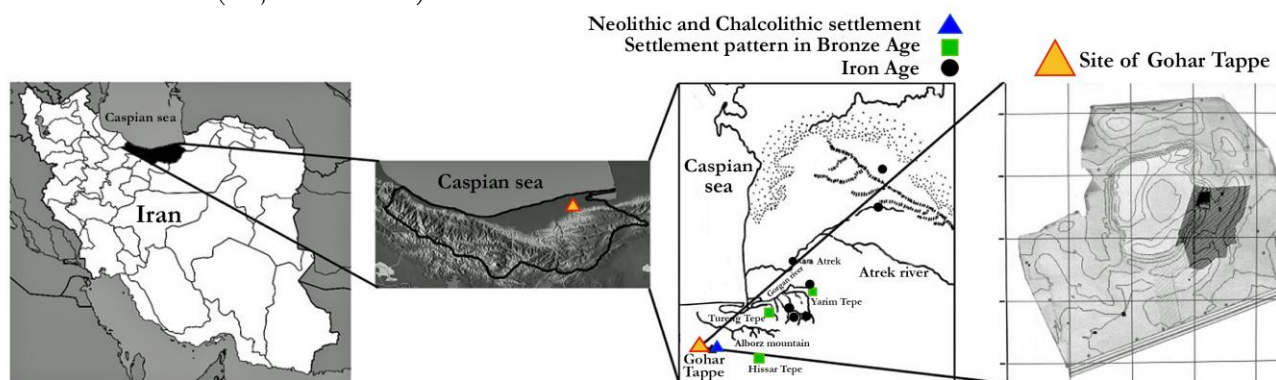


Figure 1. Geographical map of the eastern side of Mazandaran province, Iran, and location of archaeological sites.



Figure 2. Some investigated samples with variations in colour, shape, decoration and thickness.

group, only sample EBA-2 was selected for the XRD and XRF analyses due to its specific weight and the amount required.

Four samples were selected from the Middle Bronze Age (MBA; samples MBA-1, MBA-2, MBA-3, and MBA-4). Sample MBA-4 has decorative lines on the surface, whereas the others are thin-walled and light grey ceramics.

Four fragments were chosen from the Late Bronze Age (LBA) ST.S2XVI trench and context 64 (samples LBA-1, LBA-2, LBA-3, and LBA-4). Three of them have a dark grey external surface, and one is a light grey ceramic. Linear designs were the predominant decorative technique in this layer.

Five samples from Iron Age I (IAI) AJ2XXI trench and context 2 were also selected; three of them (samples IAI-1, IAI-2, and IAI-3) have quite thick and light grey walls. The other two samples (IAI-4 and IAI-5) have dark grey and very thin walls.

Four samples were selected from the Iron Age II (IAII) AJ2XXI trench and context 44. All samples in this layer have a dark grey external surface and a thick body. Finally, four samples were chosen from the Iron Age III layer (IAIII), ST.S2XVI trench and context 6. All samples have medium thick walls of a dark grey colour, without decorative features.

Results and discussion

Thin section analysis

All analysed samples show an isotropic matrix. Ceramics from these six archaeological layers do not show different textural characteristics. Almost all of them have fine pastes and low porosity which indicate sintering of the clay, with a uniform distribution of non-plastic inclusions constituted by fine sub-angular quartz, alkali feldspars, and plagioclase.

Macroscopically in terms of the frequency of calcareous fragments, the samples can be divided into two groups: calcareous-rich and siliceous-rich, which can be identified from fractured surfaces. An iron-magnesia rich rim surrounds the calcareous fragments (Figure 3). The porosity that can be observed in the potsherds is partly due to drying, shrinkage and degassing during firing, and partly due to breakdown of carbonates in highly-fired samples (Tschegg *et al.* 2009). The distribution of sub-angular quartz in all samples is similar and according to the presence of fine and semi-sharp angles, production of this mineral can be obtained by grinding the rocks (in the form of sand or sandstone fragments) and with appropriate screening (Riederer 2004). The absence of oxygen in the firing atmosphere and the resulting reducing conditions caused darkening of the inner part of the pots (Shepard 1956). In the centre of the thin sections in some samples there is a thin red line, which is likely due to the oxidation of iron oxide, which seems to be lacking in other zones. This apparent compositional distinction may represent distinct clays or zonal variation, which was not observed in all of them.



Figure 3. Sample no. IAIII-4 is a thin dark grey ceramic (left), and a dark red rim around a calcite grain illustrates the concentration of iron oxide (right).

In some cases, quartz inclusions are coarser and show a ferric concentration around the boundaries, which probably originated from argillaceous rocks that are more or less iron-rich (Emami and Trettin 2010). It is assumed that these highly-fired ceramics are tempered with quartz sand for heightened strength and toughness. The main minerals in these

samples are quartz, calcite, plagioclase and alkali-feldspar. Calcite grains are proven to be decomposed via decarbonisation process along external boundaries (Figure 4) and feldspars decompose into sericite-albite through weathering and alteration during burial, or as alkali-feldspar miscibility phases (mostly microcline-sanidine) (Emami *et al.* 2008).

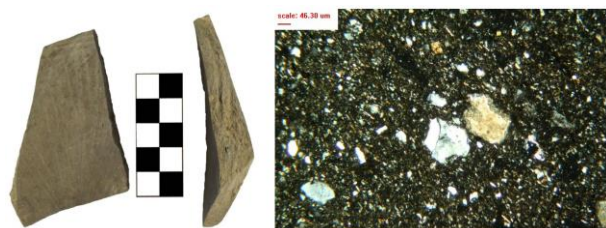


Figure 4. A thin light grey sample (left) with semi-coarse monocrystalline quartz, close to calcite grain which shows decarbonisation around boundaries (right).

There are some distinctive calcareous structures which could be seen in thin section images of sample EBA-4, it is likely that they are oyster shells (Martineau *et al.* 2007) (Figure 5). As these structures were not frequently identified in the majority of samples, it is probable that they occurred naturally in a few samples, such as EBA-4, IAI-3 and IAI-1. The texture in sample EBA-2 was completely changed

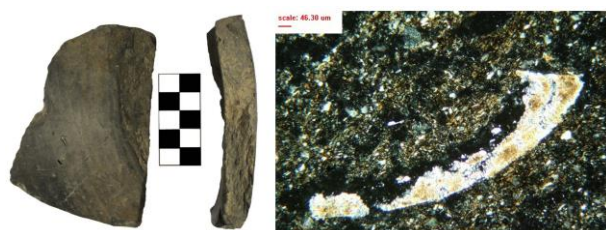


Figure 5. Oyster shells can be identified clearly with a curvy shape in the centre of thin section image (right) of the sample EBA-4 (left).

and transformed into a metamorphic texture, based on undulatory extinction (Figure 6).

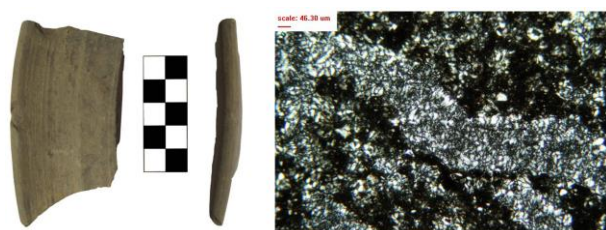


Figure 6. Quartz with undulatory extinction (right) in sample EBA-2 (left).

XRF analysis

In this study, quantitative XRF bulk analysis was conducted to enable discussion about the similarities

and differences between major, minor and trace elements of the ceramics and chemical composition of the minerals. The identification of elements such as calcium, sodium, potassium and magnesium can indicate presence of different clayey raw materials. This identification can be used to determine the nature of components as well as characterisation of production (Fazeli *et al.* 2010). These results give essential information about the chemistry and probably the provenance of the ceramic raw materials.

The XRF results (Table 1) show that the ceramic samples have different chemical compositions that are related to the variety of the raw materials. In particular, to distinguish between calcareous and silicate-rich samples, variation in the amount of SiO_2 and CaO are evident. The amounts of CaO in samples are varied, three being lower (1.5–2.5%) and three being higher (4–5%), while all of them show high levels of SiO_2 (61.15–64.71%). However, as the total amounts of CaO in the samples is less than \approx 5%, this means that all the studied samples are classified as silica-rich ceramics.

Overall it is well recognised that alkali oxides and alkali earth oxides may have a role as flux agents and cause formation of secondary minerals at low temperature sintering (Buxeda *et al.* 2003). Potassium oxides can be derived from muscovite or illite. The low ratio of calcareous fragments is similar in almost all samples, and this witnesses a well-controlled craftsmanship of Gohar Tappe in the technology of ceramic manufacturing (Maggetti 2001).

XRD analysis

Elemental analysis of the samples by XRF is not sufficient for crystalline phase determination in the ceramics. For instance, similar trace elemental compositions may arise from different workshops while the mineralogical phases may depend also on the firing temperature. Indeed, chemically similar pots may be differentiated by mineralogical phases, reflecting differences in firing temperature. Six pottery samples were analysed by XRD (Table 2 and Figure 7). The examined pots include quartz, phyllosilicates, plagioclase feldspars and calcite as were evidenced by PLM.

Quartz-feldspathic composition prevailed in all samples. Calcite appears in all samples as a trace phase or commonly in the shell structure. Quartz was observed as trigonal α -Quartz. This structure of quartz is stable at low temperature (< 573 °C), and the best crystallographic preferred orientation appeared at $2\theta=26.64^\circ$. The next important groups

Wt%	IAIII-1	IAII-3	IAI-2	LBA-1	MBA-1	EBA-2
SiO ₂	63.15	64.71	61.41	61.15	62.35	62.75
Al ₂ O ₃	17.21	16.41	15.32	15.07	15.57	14.93
Fe ₂ O ₃	9.14	6.09	7.01	7.96	6.83	7.76
CaO	1.46	1.48	4.08	4.93	5.01	2.46
Na ₂ O	0.74	0.88	1.08	1.12	0.73	1.09
K ₂ O	3.26	3.45	2.79	3.07	3.17	2.95
MgO	2.45	2.44	3.13	3.75	2.64	3.61
TiO ₂	0.927	0.741	0.721	0.735	0.851	0.759
MnO	0.114	0.104	0.120	0.122	0.116	0.121
P ₂ O ₅	0.170	0.193	0.300	0.277	0.144	0.246
S	0.002	0.001	0.003	0.001	0.002	0.003
L.O.I	1.02	3.22	3.74	1.54	2.35	3.04
Cl ppm	64	92	138	251	156	173
Ba	245	192	224	213	165	248
Sr	272	396	354	711	296	426
Cu	39	47	106	41	41	55
Zn	138	124	122	123	111	138
Pb	16	32	18	21	22	28
Ni	114	104	93	90	93	89
Cr	129	94	99	96	99	109

Table 1. XRF results: chemical composition of the samples analysed showing major, minor and trace elements.

	Quartz	Muscovite	Illite	Orthoclase	Anorthite	Calcite	Albite	Microcline	Diopside
IAIII-1	++ +	++	-	+	+	+	-	-	-
IAII-3	++ +	++	-	-	-	-	++	+	-
IAI-2	++ +	++	+	-	-	-	++	-	-
LBA-1	++ +	+	++	-	++	-	++	-	-
MBA-1	++ +	+	++	+	-	-	++	-	-
EBA-2	++	-	+	-	+++	-	+++	-	+++

Table 2. Mineralogical phases in samples identified by XRD.

are alkali feldspars and plagioclases such as albite, microcline, orthoclase and anorthite. With albite the best orientation appeared at $2\Theta=27.7^\circ$ and 36.7° . Overall, the highest intensity of these minerals is between $2\Theta=35-40^\circ$ and $2\Theta=27-30^\circ$. Diopside as one of the high temperature phases in sample EBA-2 at $2\Theta=21^\circ$ and 26.64° has been observed with albite and quartz. Furthermore, the lack of 7\AA lines of kaolinite in all samples indicates temperatures exceeded $600-650^\circ\text{C}$, when the crystalline structure collapses and metakaolinite forms (Ionescu *et al.* 2007). The presence of diopside in sample EBA-2 suggests firing temperature above 850°C .

Applying cluster-type analysis of the raw diffractograms (Figures 8 and 7) may allow grouping of samples based on the main characteristics

identified (Duminuco *et al.* 1998). Quantitative Rietveld analyses of the diffractograms were also carried out.

The quantitative Rietveld phase analysis reported in Table 2 allows understanding the cluster grouping observed in Figure 8.

As can be seen in cluster-type classification (Figure 8), samples IAII-3 and IAI-2, from the Iron Age II and I respectively, are most similar to each other among all samples. The similarity of these samples was also confirmed by the thin section analysis. Along with these two samples, sample MBA-1 (from the Middle Bronze Age) with slight differences, could be classified in this group. These fine differences could be due to a change in preparation of raw materials or kiln type, as they were made several

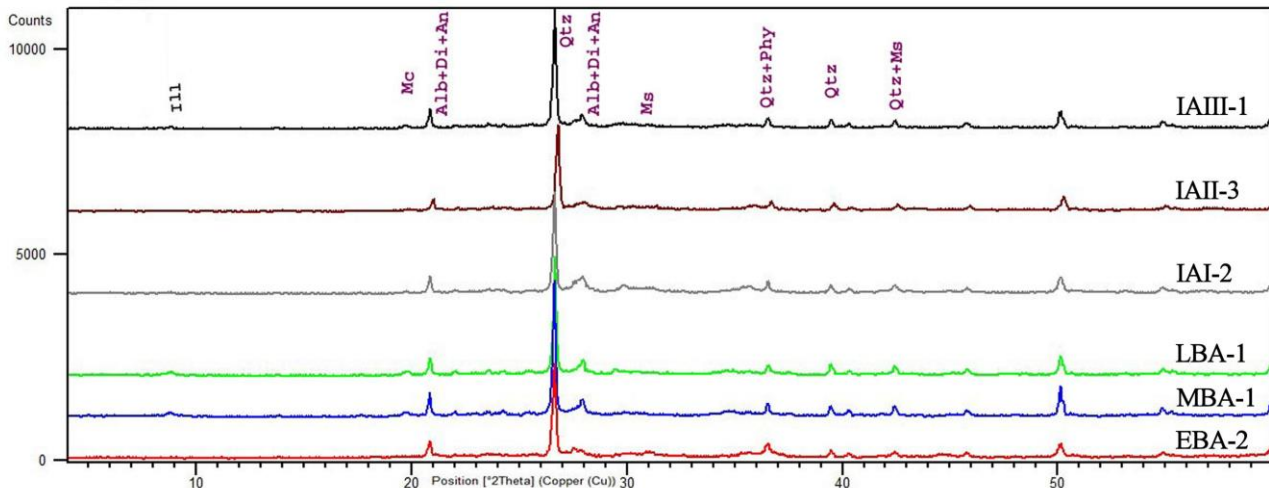


Figure 7. XRD diffractograms of Bronze and Iron Age Grey Pottery samples.

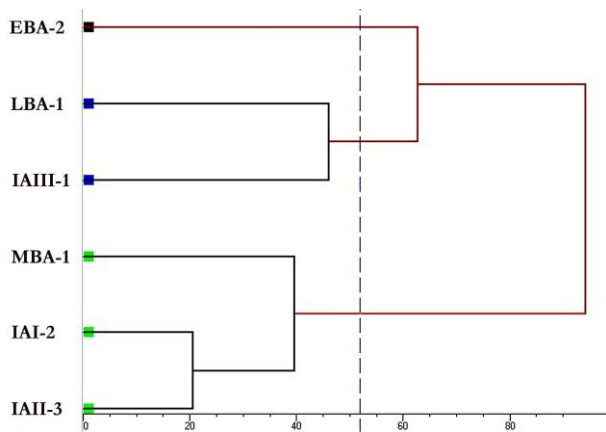


Figure 8. Cluster analysis of all samples, based on XRD analysis results.

hundred years apart. The similarity of XRD diffractograms in samples IAI-1 and LBA-1 (Iron Age I and Late Bronze Age respectively) classifies them in the second group. Meanwhile sample EBA-2 with relatively large difference is located in a separate branch (Figure 8).

Conclusion

The production of Grey Pottery types, which were attributed to the Bronze and Iron Age societies, gradually increased as this area of the Caspian Sea grew in importance, peaking at the end of the Iron Age.

Caspian oyster shells are detectable in the samples from the Iron Age I and in one sample of the Iron Age II. Oyster shells may have been added during ceramic manufacture or they might have been naturally present in the inclusions of the raw material.

Grey Pottery from Gohar Tappe was analysed with petrographic methods and mineralogical analysis (optical microscopy and XRD used with the Rietveld method). Petrological studies revealed that the texture of the matrices in all fragments is dense, with a low porosity, and the distribution of mineral grains is similar in almost all samples. Fineness and homogeneity of the inclusions suggest suitable screening; these properties were probably sought to increase the ceramics' strength. The pots were fired in kilns with reducing atmospheric conditions, which caused the greyish-black colour in all samples. Due to the high temperature phases detected by XRD, it is possible to suggest that the raw materials might have been originally calcareous (Cultrone *et al.* 2001).

Overall, the chemical composition of the potsherds show high silica (SiO₂ over 61% in each sample) and a relatively low amount of calcium oxide (less than 6% CaO), with an average of 8% iron oxide and about 15% aluminum oxide, which indicates that the ceramic materials can be classified as high-silica ceramics after Rankin diagram in system SiO₂ – Al₂O₃ – CaO+MgO (Noll 1991).

Based on the XRD analysis, quartz was identified as major phase, followed by muscovite, albite and illite, which were present in the exploited raw materials. Furthermore, cluster-type analysis obtained from the XRD results allows a classification of the samples based on their mineral content. Overall, Bronze and Iron Age samples are placed next to each other in one branch and this may imply that manufacturing techniques and origin of the raw materials did not change very much in these consecutive periods.

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