CODEN [USA]: IAJPBB **ISSN: 2349-7750**

INDO AMERICAN JOURNAL OF
PHARMACEUTICAL SCIENCES

http://doi.org/10.5281/zenodo.1048987

Available online at: http://www.iajps.com ***Research Article***

ELEMENTAL STUDY OF POTTERY SHARDS FROM AN ARCHAEOLOGICAL SITE IN DEDAN, SAUDI ARABIA, USING INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY AND MULTIVARIATE STATISTICAL ANALYSIS

Awad Nasser Albalwi[*1], Ahmad Hamed Alghamdi[1], Omer Abdurrahman Al-Dayel [2], Saud Abdulaziz Alghamdi[3], Hicham Al-Nachawati[4]

[1]Department of Chemistry, College of Science, King Saud University, Riyadh, Saudi Arabia
[2]Atomic Energy Research Institute, Abdulaziz City for Science & Technology, Riyadh, Saudi Arabia
[3]College of Tourism and Archaeology, King Saud University, Riyadh, Saudi Arabia
[4]Department ofStatistics and Operations Research, College of Science, King Saud University, Saudi Arabia.

Abstract:
This study uses a chemical analytical approach for the characterisation of 36 ancient pottery shards from an archaeological site in Dedan, Saudi Arabia. Dedan (Al-Ula) was one of the main towns in the northwestern area of the Arabian Peninsula during the first millennium BCE and was located along the ancient spice route connecting Arabia with Egypt, Syria and Mesopotamia. Inductively coupled plasma-mass spectrometry (ICP-MS) and multivariate statistical analysis were used to identify 29 elemental properties in the pottery fragments and to separate the studied samples into groups. The study findings support the existence of four major groups: Abbasid, Nabataea, Tayma and Dedan. Principal component and cluster analyses validated the existence of these four groups. The ICP-MS results demonstrated that concentration measurements of elements, such as Ti, Mn, Ga, Sc, Cs and Rb, can be used to discriminate the four groups of ancient potteries.

Keywords: *Dedan, Pottery, ICP-MS, Multivariate statistical analysis*

Corresponding author:
Awad Nasser Albalwi,
Department of Chemistry,
College of Science, King Saud University,
Riyadh, Saudi Arabia

QR code

Please cite this article in press as Awad Nasser Albalwi et al, ***Elemental Study of Pottery Shards from an Archaeological Site in Dedan, Saudi Arabia, Using Inductively Coupled Plasma-Mass Spectrometry and Multivariate Statistical Analysis****, Indo Am. J. P. Sci, 2017; 4(11).*

INTRODUCTION:

The geographical position of the Arabian Peninsula, situated between the ancient civilisations of India and Persia and states of the eastern Mediterranean and Egypt, contributed to the Peninsula becoming an important centre of trade and commerce and to the emergence of several Arab states along the peninsular trading routes. These routes ran from the south to the north and to the northeast. Ancient archaeological remains have also been found in Yemen, South Hadramawt and Oman, the Eastern Quarter, Tayma, North Dumat al-Jandal (al-Jawf), Qurayyah, al-Bad, Northwest al-Hijr and al-Ula (Dedan), and Qaryat al-Faw in the centre of the Peninsula. These are evidences of the important role played by this area in the commercial life of the ancient world [1].

Dedan (al-Khuraybah) is one of several famous archaeological sites in al-Ula, in northwestern Saudi Arabia. The town was one of the main settlements in the northwestern area of the Arabian Peninsula during the first millennium BCE. The town was located along the ancient spice route connecting Arabia with Egypt, Syria and Mesopotamia (Fig. 1).

Dedan was mentioned in the Old Testament, Assyrian records and old Arabic inscriptions. Archaeologists and historians believed that the town was the capital of the Dedan Kingdom during the first half of first millennium BCE [1]. According to Winnett and Reed, based on surface finds, the city flourished as early as the Iron Age and continued to be occupied at least intermittently until the mediaeval period when it was abandoned [2]. In addition, in the sixth century BCE, the oasis of Dedan was mentioned in Biblical sources, which speak of its “caravans” and merchandise of “saddlecloths” (Isaiah 21.13; Ezekiel 27.20) [3].

A team from the College of Archaeology at King Saud University, which has been conducting archaeological excavations at the Dedan site since January, 2004, identified different phases of occupation, as evidenced by architectural phenomena, such as temples, homes and tombs (Figs. 2 and 3). A number of Dedan inscriptions, pottery shards, coins, statues, altars, sculptures and alabaster objects have been uncovered [4,5]. Current and future excavations at the Dedan site could help establish a chronology, fundamental to any understanding of northern Arabia and its cultural development in archaic times.

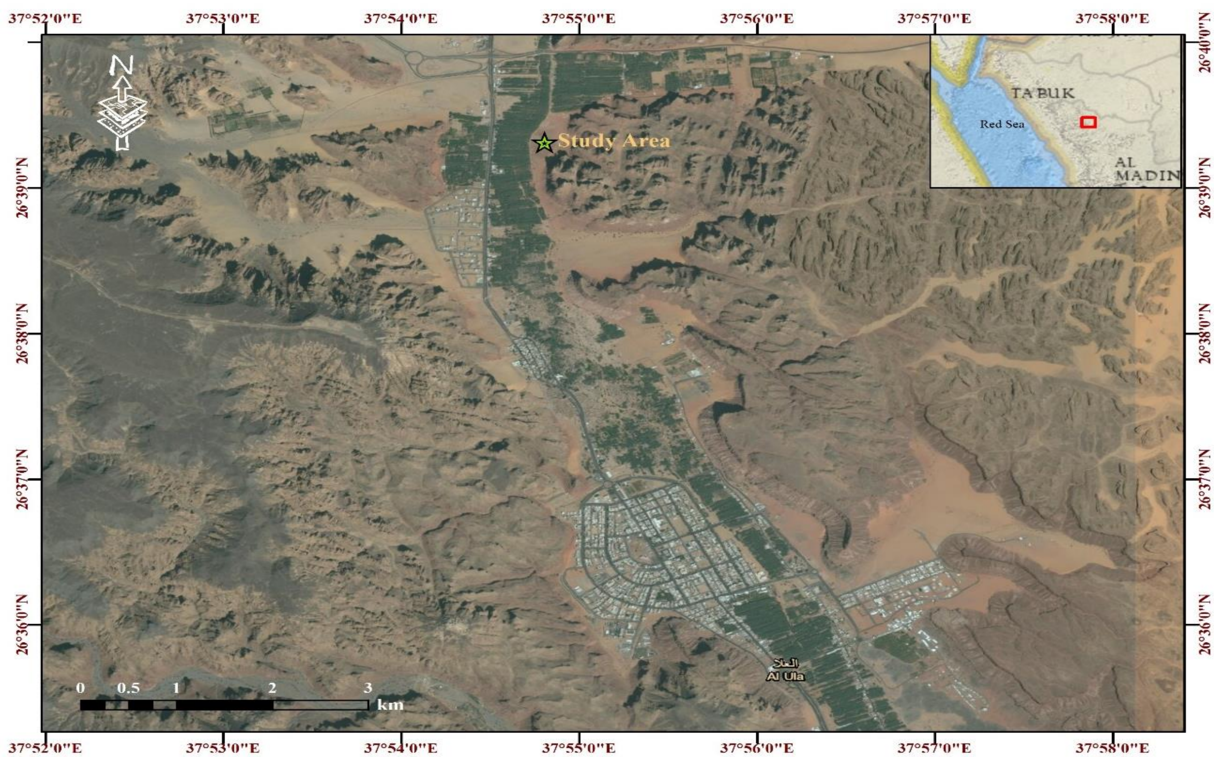

Fig.1. Location map of excavated pottery samples (Dedan)

Fig. 2: Photographs showing of ancient town of Dedan (July,2015)

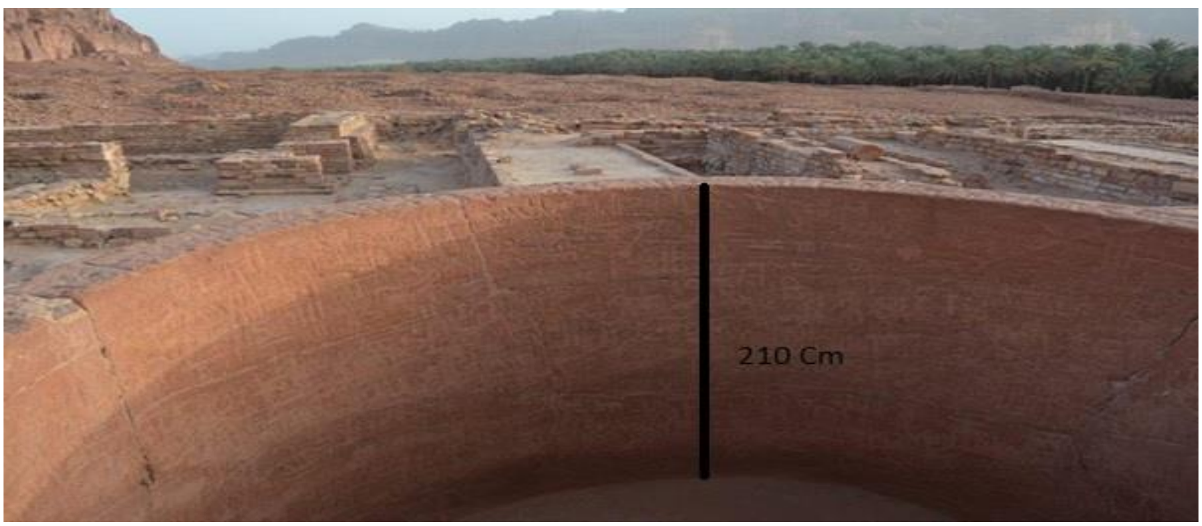

Fig. 3: Photograph showing of Dedan inscriptions on the wall of ancient pool (July, 2015)

Pottery fragments, often found at archaeological sites around the world, are one of the main categories of artefacts used by archaeologists. The study of pottery provides useful evidence for many aspects of the life of ancient societies (economic, societal, and ideological) [6]. Archaeologists have used pottery objects to trace trade routes and to determine the geographic extent of a given culture [7]. The physical and chemical study of ancient pottery objects can provide information on both provenance and the technology used to produce the artefacts [8].

A number of advanced techniques have been used to analyse ancient pottery and ceramic objects. These include instrumental neutron activation analysis (INAA) [9-12], atomic absorption spectroscopy (AAS) [13,14], portable X-ray fluorescence spectrometry [15,16], X-ray fluorescence spectrometry [17-20] inductively coupled plasma-optical emission spectroscopy (ICP-OES) [21-23], ICP-MS [24-27, laser ablation time-of-flight inductively coupled plasma-mass spectrometry (LA-ICP-TOFMS) [28], X-ray diffractometry (XRD) [29,30], scanning electron microscopy-energy dispersive spectrometry (SEM) and proton-induced X-ray emission analysis (PIXE) [31,32].

Currently, ICP-MS is the most frequently used inorganic mass spectrometric technique in many laboratories. The main advantages of the ICP-MS method for pottery analysis include the following: (1) high precision, accuracy and sensitivity for analytical data; (2) the ability to analyse small samples (100-200 mg), thus making it a less destructive technique for archaeological objects; (3) excellent detection limits (in parts per billion (ppb)); (4) multi-element capabilities; (5) the ability to measure the isotopic ratios of some elements; and (6) low cost per sample, particularly compared with other techniques, such as INAA [27,33,34]

A major objective of this research was to determine the elemental composition of ancient pottery fragments from the Dedan archaeological site, using multivariate statistical methods – cluster analysis (CA) and principal component analysis (PCA) – to identify data structures, to distinguish individual groups of samples and to verify whether the chemical differences reflect the archaeologists' classification of the archaeological objects.

EXPERIMENTAL DATA:

Chemicals and reagents

All chemicals and reagents used in this study were of analytical grade. We used MilliQ water (Millipore, Bedford, MA, USA), 69.5%nitric acid, 37% hydrochloric acid and 43%hydrofluoric acid. An ICP Multi-Element Standard Solution (Merck) (including Al, As, Ba, Be, Bi, Ca, Ce, Cr, Co, Cu, Ga, In, Ir, Pb, Li, Mg, Mn, Ni, K, Rb, Se, Ag, Na, Sr, Th, U, V and Zn) was used prepare a series of standard solutions (50, 100, 150, 200 and 250 ppb). Single-element standard solutions of Dy, Hf, La, Sc, Sm, Tb, Y, Zr, Lu, Ti, and Cs (1000 ppm, BDH, Poole, UK) were also used to prepare a series of standard solutions (10, 20, 30, 40 and 50 ppb). The accuracy was proven for use as a reference material (Basalt, Hawaiian Volcanic Observatory, BHVO-2, USGS, USA).

Sample preparation and chemical analysis

Thirty-six ancient pottery shards were obtained from the college of Archaeology at King Saud University. These objects dated from approximately the first half of the first millennium BCE to the ninth century CE. According to archaeological records, fifteen pottery fragments belong to the Dedan period (D1 to D15), ten to the Nabatean period in the first century CE (N-1 to N-10), seven to the Abbasid/Islami period around the ninth century CE (Ab-1 to Ab-8) and three are classified as Tayma/Madyan pottery (M1 to M3). Fig. 4 shows photos of some of ancient pottery fragments. All these pottery shards were excavated at the Dedan (al-Khuraybah) heritage site (26°39'18.3"N, 37°54'49.2"E), between 2008 and 2010, between the fifth and seventh excavation seasons in al-Ula, Saudi Arabia.

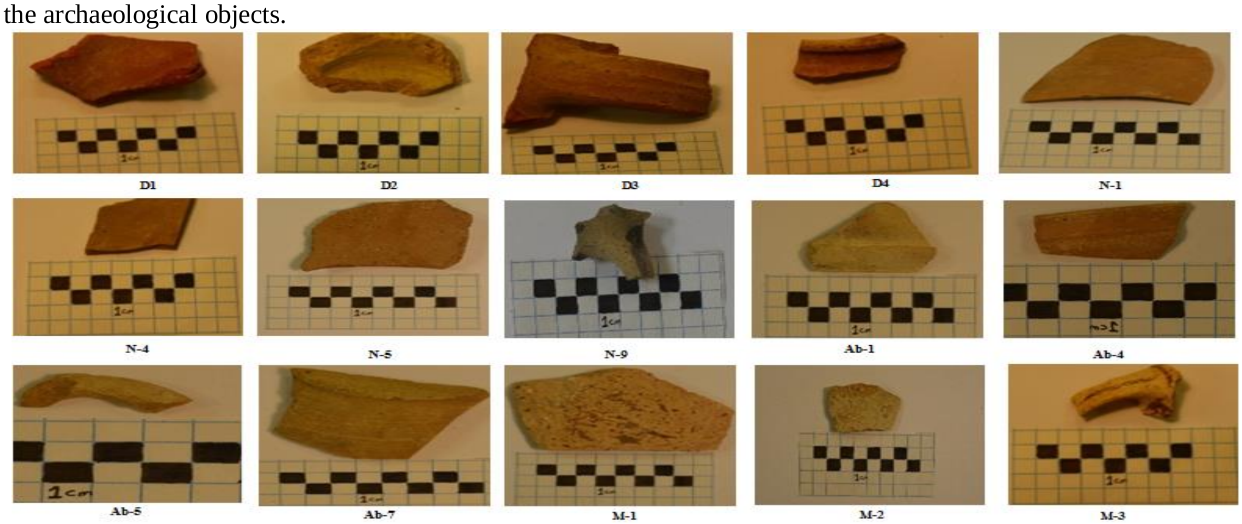

Fig. 4. Photograph showing of some ancient pottery shards from Dedan archeological site. Dedan, (D1-D4), Nabataean (N1-N, N4, N5 and N9), Abbasid (Ab-1, Ab-4, Ab-5 and Ab-7) and Tayma (M1-M3).

Sample digestion for inductively coupled plasma–mass spectrometry (ICP-MS) analysis

To avoid environmental contamination, the surfaces of the pottery fragments were removed. The shards were then drilled using a drill bit (HSS, solid carbide-tipped 5 mm jobber drill bit). Between three and five holes were drilled on the shard surface. The sample powder was then transferred into glass vials. All samples were then dehydrated in an electric oven at 105°C overnight.

Powder samples were digested with concentrated acids, as described below. Samples (0.1–0.15 g) were digested in 8 mL HNO_3 (69%), 2 mL HCl (34%) and 2 mL HF (43%) in a microwave digestion system (Topwave, Analytik Jena AG**,** Germany) using a 12-vessel (fluoropolymer) multi-prep router. For our experiments, vessels were used to digest archaeological samples, one was reserved as a blank sample, and the remaining vessel was used for a quality control sample (BHOV-2). The samples were cold-digested for 20 min prior to microwave digestion. The heating programme consisted of a 50-min ramp to 200°C, where the temperature was held for 30 min at 50 bars. After that, the cooling programme consisted of a 10 min ramp to 50°C, where the temperature was held for 10 min. The vessels were then left to cool to room temperature (approximately 40 min) to avoid foaming and splashing. The cooled samples were diluted to 50 mL in conical graduated tubes with deionised water (18.2 million ohm-cm). Next, approximately 5 mL of the sample was filtered through a nylon syringe filter with a 0.45-µm pore size to protect the nebulisation system and to improve the accuracy of the test results by removing unwanted particles. This was followed by a second, 10-fold dilution, making the final acid concentration less than 2%. A diluent containing 10 ppb Rhas an internal standard was used to make the second dilution.

Instrumentation

The analytical method used throughout this study is inductively coupled plasma-mass spectrometry (ICP-MS). ICP-MS identifies the chemical composition of targeted areas of the paste. The ICP-MS instrument used in this investigation was a NexION 300D ICP-MS (PerkinElmer, USA). Table 1 highlights the operating conditions used in this study.

Table 1: ICP-MS Operating conditions

Operations	Conditions
RF power	1600 W
Auxiliary Gas Flow RB	1.205 L/min
Nebulizer Back Pressure RB	35.355psi
Nebulizer Gas Flow RB	0.983 L/min
Plasma Gas Flow RB	18.013 L/min
Lens Voltage	9.25 V
Analog Stage Voltage	-1913 V
Pulse Stage Voltage	1099 FV
Number of Replicate	3
Reading / Replicate	20
Scan Mode	Peak Hopping
Dwell Time	40 ms
Integration	1200 ms

Statistical analysis of data

Two main types of multivariate statistical treatments were applied to the elemental data: a clustering technique aimed at partitioning the ancient pottery shards into groups of similar composition and PCA (part of a factorial technique), which used mainly as a data reduction and interpretative tool [35]. This statistical method is powerful way to justify and explain archaeological hypotheses, presenting an additional tool to simple visual inspection and stylistic classification [36]. The elemental concentrations obtained from ICP-MS were used as variables in the statistical treatment. In this study, Statistical Package for the Social Sciences (SPSS, version 22) was used for CA. Initially, the data were normalised using "z-scores", a transformation that generated new variables with an average of zero and a standard deviation of one. In CA, the square Euclidean distance was used as a measure in *n*-dimensional space along with hierarchical CA (HCA) using Ward's method [37]. In addition, Statistical Analysis System (SAS, released 8.02, Cary, NC, USA) software was used for PCA. The following 29 elements (or variables) were statistically analysed using both SSPS and SAS:Li, Be, Sc, Ti, V, Cr, Mn, Co, Ni, Zn, Ga, Rb, Sr, Y, Zr, Cs, Ba, La, Ce, Sm, Tb, Dy, Yb, Lu, Hf, Tl, Pb, Th and U.

RESULTS AND DISCUSSION:

Results of the ICP-MS analysis of the samples of 36 shards are displayed in Tables 2, 3(a) and 3(b), where the compositional data are expressed in µg/g of the 29 elements. Reference material (USGS, Basalt, Hawaiian Volcanic Observatory, BHVO-2) was used to gauge the accuracy of the elemental concentration data (Table 2).

Principal components analysis (PCA)and factor loadings

The chemical data were statistically analysed using the PCA method in SAS. The first principal component accounts for 37.88% of the total sample variance. The first two principal components collectively explain 57.21% of the total sample variance. As a result, we can say that sample variation is summarized well by the two principal components. A reduction in the data from 36 observations on 29 variables to 36 observations on 2 principal components is therefore reasonable (Table 4).

Fig. 5 demonstrates a scatter plot of the four groups of pottery shards (Abbasid, Nabataean, Tayma and Dedan) in a two-dimensional perspective, with each dimension being represented by the principal components, PC1 and PC2, with PC1 along the y-axis and PC2 along the x-axis. It should be noticed that the four groups are clearly separated. Groups 1 and 2 are close to each other, despite being visually separated. Cluster 2 was characterised by negative values of PC1 and PC2, taking into account a more relevant contribution of Rb, Tl and Sc in the PC plot. Cluster 1 has higher concentrations of Ni, Mn, Zr and Hf than cluster 2, whereas cluster 2 has higher concentrations V and Tl than cluster 1. For example, the average concentration of vanadium (V) is approximately 155±21 µg/g in cluster 2, while it is 112±10.5 µg/g in cluster 1. Cluster 3 is separated from the other groups and is associated with high concentrations of Rb, Cs and U. In general, cluster 4 was characterized by positive values of PC1 and PC2, taking into consideration a more relevant contribution from high concentrations of elements, such Zr, Zn, Cr, Co, Ti, Tb and Sm, in the PC plot. All the shards included in cluster 4 came from the Dedan period. As seen in cluster 4, the distribution between the pottery samples shows some variation, which is probably due to the different periods in which the pottery objects were manufactured. The presence of four associations in the data may be related either to the exploitation of four different sources of raw materials or to the presence of different production units. The projection of the cases on the PCA plane clearly differentiates four distinct sample groups. The factor loadings are the correlation coefficients of the original variables to the principal component (PC). These loadings range from -1 to +1, ranging from an absolute negative correlation to an absolute positive correlation. A value near zero indicates that there is no relationship between the variable and the principal component [38]. These factor loadings are summarised in Table 5 for three factors. In Table 5, the values that can be considered large are in boldface, using approximately 0.5 as the cutoff. Based on this criterion the following statements can be made. Factor 1 is correlated most strongly with Sm, Yb, Dy, Tb, Th, La, Ce, Y, Pb, Lu, Be, Ti, Ga, Co, and Ba and toa lesser extent Tl, Li, Ni and Mn. Therefore, in this case, it can be said that the first factor is primarily a measure of most of the variables with large factor loadings. Factor 2 is primarily related to Ni, Zr, Hf and Mn. Here, as these variables increase, elements such Rb, Li and Cs decrease. Factor 3 is correlated most strongly with Ba, Sr, Ga, Sc and Ti. Moreover, it can be noted that the variables Ba, Ga, Sc and Ti are negatively related to Sr.

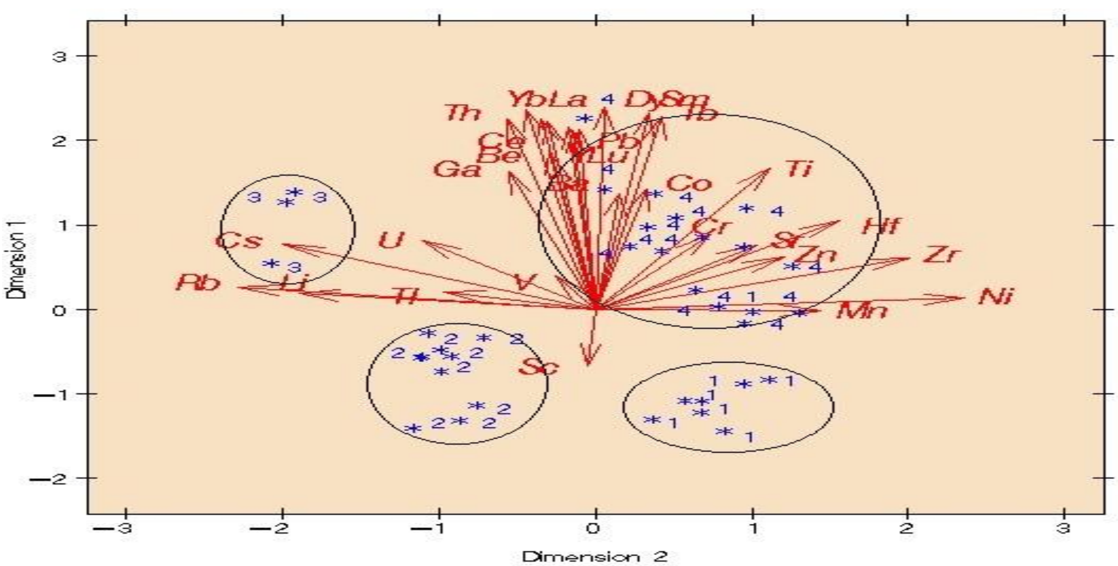

Fig. 5: Multivariate analysis PCA. The first two principal components account for 57.21% of cumulative variance in the ICP-MS data for Dedan site pottery shards shown with the element coordinates. The analysis reveals four distinct source groups: (1) Abbasid, (2) Nabataean, (3) Tayma and (4) Dedan.

Table 2 Chemical results of the pottery shards (in ug/g) from Dedan execration site, and certified Reference material BHVO-2*, and experimental BHVO-2**

Id	BHVO-2*	BHVO-2** (n=7)	D-1	D-2	D-3	D-4	D-5	D-6	D-7	D-8	D-9	D-10	D-11	D-12	D-13	D-14	D-15
Li	5	3.80±0.77	14.91	14.63	25.03	10.24	13.36	12.28	12.71	11.92	14.73	18.32	10.61	14.17	20.84	11.98	12.61
Be	NA	NA	1.3	1.84	2.82	1.98	1.4	1.4	1.6	1.87	1.75	1.92	2.02	2.3	2.38	1.34	1.55
Sc	32±1	36±1.5	5.44	7.67	6.17	32.12	50.59	44.4	67.09	57.16	56.17	79.77	80.88	85.23	109.08	76.79	61.32
Ti	16300±200	15634±540	6090.91	5282.83	4934.29	6097.24	5523.25	5106.67	6243.13	5423.57	4627.38	7089.55	6122.69	5094.63	7800.99	6122.19	5143.82
V	317±11	320±16	154.2	107.88	146.53	140.06	172.69	113.03	176.64	127.45	100.61	147.03	186.25	146.25	217.86	208.21	116.38
Cr	280±19	283±17	194.61	106.93	117.39	156.87	172.45	81.53	196.02	105.6	85.04	134.89	211.42	92.2	165.48	194.11	81.76
Mn	1290±40	1305±26	316.48	491.16	1096.76	626.81	362.43	283.27	383.13	858.71	881.84	2182.91	439.13	534.27	1360.82	296.77	679.4
Co	45±3	47.30±2.01	30.8	19.54	28.22	87.85	22.36	18.02	40.37	42.22	19.51	44.95	50.98	111.51	83.6	53.64	14.2
Ni	119 ±7	122±5.76	79.87	67.1	76.72	90.82	58.79	47.86	83.3	74.38	55.58	65.45	83.22	49.04	64.23	77.82	51.19
Zn	103±6	97.96±6	44.86	48.87	84.84	61.62	45.6	54.09	56.68	85.61	52.93	129.3	46.16	76.52	141.47	49.17	68.98
Ga	21.7±0.9	22.50±1.27	24.14	26.16	31.92	28.96	25.12	34.24	27.42	33.71	28.73	46.3	26.31	39.19	44.03	26.35	34.43
Rb	9.8±1	9.47±0.58	34.7	34.47	33.76	17.07	21.76	23.14	23.34	26.13	23.63	14.17	7	59.39	41.38	6	9.78
Sr	389±23	391±30	446.94	964.38	308.76	580.31	650.49	923.63	639.62	763.7	923.53	287.33	680.14	938.8	646	444.26	829.74
Y	26±2	22±3.46	13.28	24.8	20.95	15.13	12.92	29.31	19.12	25.09	27.22	9.69	9.15	36.08	24.51	7.89	20.18
Zr	172±11	178±10	124.68	120.05	105.57	132.36	126.33	85.28	126.74	128.43	97.85	89.39	127.01	121.79	86.82	126.03	86.98
Cs	NA	NA	2.52	1.59	2.62	1.1	1.11	1.4	1.26	1.14	1.15	3.11	0.6	2.94	4.36	0.55	0.69
Ba	130±13	125±12	197.29	275.55	465.09	321.55	270.15	311.63	253.59	379.72	323.18	958.44	227.83	455.41	583.48	208.01	319.84
La	15±1	15.74±1.77	22.73	49.63	26.88	24.88	27.45	55.17	34.48	45.68	48.26	7.3	13.17	63.53	27.5	10.92	34.73
Ce	38±2	37.48±3.80	57.46	116.99	74.24	77.24	72.11	138.33	93.16	115.32	115.03	19.8	34.41	133.41	69.88	30.48	89.92
Sm	6.2±0.4	6.06±0.69	5.39	8.47	6.1	5.82	5.09	10.89	7.24	8.71	8.78	3.05	3.61	11.5	7.78	3.15	8.2
Tb	0.9	0.88±0.1	1.49	1.4	0.95	0.97	0.83	1.54	1.12	1.27	1.22	0.41	0.57	1.61	1.19	0.49	1.18
Dy	NA	NA	4.54	6.62	5.04	4.82	4.12	7.44	5.94	6.54	6.62	2.4	3.31	8.54	6.3	2.86	5.98
Yb	2±0.2	1.7±.03	1.75	1.97	2.24	1.47	1.58	2.41	1.57	2.13	2.13	1.1	1.08	2.88	2.08	1.09	1.76
Lu	0.28±0.01	0.26±.03	0.65	0.36	0.36	0.22	0.19	0.32	0.25	0.31	0.31	0.15	0.15	0.42	0.3	0.15	0.24
Hf	4.1±0.3	3.93±0.3	5.31	3.06	2.87	2.96	2.91	2.42	2.81	3.14	2.43	2.23	2.98	3.1	2.24	2.97	2.26
Tl	NA	NA	0.94	0.41	0.37	0.18	0.28	0.22	0.2	0.14	0.12	0.6	0.18	0.29	0.37	0.17	0.15
Pb	NA	NA	33.06	27.76	29.74	21.33	31.77	61.93	37.26	44.68	37.27	43.46	34.33	51.4	58.56	34.84	56.29
Th	1.2±0.3	1.06±0.19	10.25	12.63	8.42	8.48	8.83	17.48	10.4	12.82	13	3.46	6.6	18.62	8.97	6.94	12.11
U	NA	NA	4.28	3.91	3.37	3.47	3.75	3.8	3.6	3.85	4.16	3.03	3.08	5.52	3.55	4.23	3.81

Table 3 (a) Chemical results of the pottery shards (in ug/g) from Dedan execration site

Id	Ab-1	Ab-2	Ab-3	Ab-4	Ab-5	Ab-6	Ab-7	Ab-8	M-1	M-2	M-3
Li	7.02	8.03	8.05	8.61	7.97	7.84	6.06	5.71	20.61	19.17	22.7
Be	0.8	1.01	1.29	1.21	1.33	0.69	0.94	0.84	2.23	2.14	2.9
Sc	141.48	140.84	178.32	157.22	191.38	180.87	157.12	142.46	167.68	158.24	166.66
Ti	4070.09	3926.25	4456.61	4136.28	4819.64	4044.22	4140.6	3621.74	5379.65	5754.71	5702
V	109.85	111.9	123.37	112.12	125.24	110.03	110.65	90.54	150.91	130.87	131.99
Cr	82.14	94.58	124.93	105.88	123.58	111.2	91.13	88.5	160.48	143.23	145.14
Mn	879.08	789.29	840.64	786.86	1138.32	776.02	793.97	718.22	135.02	78.32	148.98
Co	21.92	22.63	24.83	23.45	25.38	23.34	22.91	18.5	13.16	101.82	37.65
Ni	75.21	69.97	78.08	69.71	88.19	69.59	74.78	61.14	25.33	17.32	25.69
Zn	42.78	57.66	71.26	49.92	76.35	109.08	57.93	61.34	49.5	22.24	42.36
Ga	22.77	24.06	28.02	26.76	30.1	34.08	22.34	21.7	56.41	62.68	60.21
Rb	22.79	34.73	35.07	41.28	29.75	44.16	10.37	26.29	117.43	133.43	116.28
Sr	535.21	502.91	496.12	553.73	649.9	550.08	523.34	476.42	143.21	339.14	203.28
Y	8.08	2.25	6.96	3.64	5.47	19.05	1.27	5	12.17	17.26	17.58
Zr	88.22	111.27	119.95	110.73	113.74	130.13	100.42	91.32	62.91	76.94	71.61
Cs	0.5	0.89	1.41	1.37	0.78	1.7	0.19	0.44	5.69	5.82	4.34
Ba	263.35	243.39	292.66	284.28	334.55	505.63	239.25	217.67	601.78	698.32	649.61
La	10.16	3.44	8.69	4.75	6.59	24.55	1.17	5.52	26.23	54.64	38.49
Ce	26.4	25.18	44.62	32.91	37	51.22	7.31	26.6	64.47	136.7	121.06
Sm	1.91	0.61	1.71	0.99	1.35	4.7	0.29	1.01	3.48	7.23	8.23
Tb	0.28	0.14	0.23	0.12	0.18	0.68	0.02	0.13	0.44	0.69	0.82
Dy	1.6	0.36	1.26	0.72	1	3.87	0.12	0.82	2.61	3.77	4.2
Yb	0.69	0.26	0.65	0.37	0.39	1.59	0.05	0.35	1.64	2.23	2.48
Lu	0.1	0.07	0.08	0.05	0.06	0.22	0	0.05	0.24	0.29	0.36
Hf	1.96	2.43	2.52	2.51	2.58	2.95	2.27	2.12	1.71	1.85	1.9
Tl	0.1	0.36	0.06	0.24	0.28	0.31	0.06	1.24	0.94	0.63	0.68
Pb	3.73	13.4	4.62	11.76	24.24	30.53	4.12	5.65	56.11	46.89	64.31
Th	2.66	1.12	2.27	1.27	2.01	6.11	0.28	1.78	18.95	11.6	18.17
U	3.35	3.61	3.22	3.95	3.87	2.49	4.77	3.19	4.59	4.57	4.98

Table 3 (b) Chemical results of the pottery shards (in ug/g) from Dedan execration site

Id	N-1	N-2	N-3	N-4	N-5	N-6	N-7	N-8	N-9	N-10
Li	28.03	19.99	21.37	27.59	24.5	17.19	19.51	25.77	24.38	26.14
Be	1.25	0.76	1.44	1.16	0.97	0.79	1	1.28	1.2	1.38
Sc	84.22	41.68	57.58	58.69	71.84	62.31	53	65.56	48.4	67.31
Ti	3374.86	2358.88	2902.33	2748.88	3352.56	2125.7	3013.22	2860.9	2703.63	2909.78
V	182.72	149.1	136.66	132.39	183.36	144.28	180.55	148.71	158.22	130.93
Cr	99.11	76.75	94.11	84.52	104.44	66.33	96.31	84.93	90.89	94.48
Mn	339.51	282.81	329.26	276.7	380.93	299.19	302.55	294.23	239.32	216.02
Co	19.05	21.57	15.86	13.96	22.01	13.94	14.12	14.96	16.17	14.13
Ni	30.27	29.33	31.28	26.58	31.61	28.85	27.26	27.98	30.31	32.59
Zn	44.99	38.51	28.42	29.89	46.54	36.27	37.63	70.87	36.06	40.94
Ga	22.02	17.07	19.57	17.93	22.3	15.04	20.73	18.41	19.53	21.3
Rb	79.74	66.42	75.46	64.04	65.04	40.25	77.49	67.44	64.53	75.39
Sr	483.27	584.71	605.09	467.45	484.62	557.53	510.38	488.56	551.72	506.53
Y	17.86	13.93	14.05	3.07	16.75	9.5	17.41	2.77	15.66	14.67
Zr	92.4	65.69	80.45	67.55	98.65	56.31	82.2	76.63	79.42	84.18
Cs	3.95	2.73	3.48	2.77	2.68	1.66	3.44	3.06	2.4	2.8
Ba	114.24	97.05	101.88	70.38	108.79	70.7	88.81	80.41	112.48	85.48
La	22.91	18.53	14.63	2.65	22.89	14.45	21.1	2.45	19.59	15.28
Ce	60.48	50.28	32.98	7.38	65.33	40.48	55.15	10.15	53.29	31.99
Sm	3.94	2.87	3.13	0.53	3.74	2.16	3.54	0.51	3.23	3.14
Tb	0.55	0.41	0.49	0.08	0.56	0.3	0.49	0.06	0.5	0.46
Dy	3.04	2.27	2.57	0.48	2.90	1.78	2.8	0.41	2.69	2.68
Yb	1.45	1.11	1.29	0.32	1.43	0.79	1.43	0.28	1.26	1.31
Lu	0.22	0.15	0.17	0.04	0.22	0.1	0.19	0.04	0.18	0.19
Hf	2.08	1.44	1.8	1.61	2.22	1.17	1.82	1.79	1.72	1.85
Tl	0.28	0.32	0.5	0.34	0.29	0.16	0.44	0.32	0.31	0.5
Pb	9.67	23.01	11.1	8.18	9.29	9.26	11.01	16.89	13.94	12.32
Th	6.56	4.95	4.61	1.62	5.86	4.05	6.17	1.39	5.24	5.67
U	3.78	3.58	4.6	4.22	3.89	3.57	3.36	3.68	3.6	4.26

Table 4: Eigenvalues and the percent of explained variance

PC	Eigenvalue	Difference	Proportion	Cumulative
1	10.9864232	5.3825539	0.3788	0.3788
2	5.6038693	1.6835609	0.1932	0.5721
3	3.9203085	1.6985576	0.1352	0.7073

Table 5: Factor Loadings–Correlation coefficients between original variables and components.

Variable	Factor 1	Factor 2	Factor 3
Li	0.07743	**-0.75766**	-0.05307
Be	**0.74241**	-0.11709	0.38546
Sc	-0.26758	-0.01924	**0.60342**
Ti	**0.66711**	0.44349	**0.50270**
V	0.15850	-0.09865	0.14035
Cr	0.35584	0.29195	0.46504
Mn	-0.00621	**0.57464**	0.44714
Co	**0.57228**	0.13287	0.32446
Ni	0.05289	**0.94607**	0.15093
Zn	0.24725	**0.48143**	0.45803
Ga	**0.65029**	-0.22224	**0.64654**
Rb	0.10358	**-0.91124**	0.18590
Sr	0.30568	0.41165	**-0.69524**
Y	**0.86134**	-0.06977	-0.35458
Zr	0.24152	**0.80522**	-0.04357
Cs	0.30885	**-0.79775**	0.36061
Ba	**0.54893**	0.06294	**0.72838**
La	**0.90230**	-0.13785	-0.28942
Ce	**0.88787**	-0.12093	-0.23177
Sm	**0.95447**	0.02243	-0.23917
Tb	**0.91049**	0.17227	-0.32110
Dy	**0.92736**	0.13949	-0.30039
Yb	**0.94810**	-0.17783	-0.13043
Lu	**0.84582**	-0.05706	-0.13973
Hf	0.41987	**0.62241**	-0.03860
Tl	0.08167	-0.38765	0.38783
Pb	**0.84940**	-0.03962	0.25794
Th	**0.90410**	-0.22584	-0.08359
U	0.32682	-0.44521	-0.06504

Hierarchical cluster analysis HCA

Cluster analysis (CA) is a convenient method for identifying homogenous groups of objects. The CA here used Ward's method of the squared Euclidean distance matrix using 29 variables (Li, Be, Sc, Ti, V, Cr, Mn, Co, Ni, Zn, Ga, Rb, Sr, Y, Zr, Cs, Ba, La, Ce, Sm, Tb, Dy, Yb, Lu, Hf, Tl, Pb, Th and U) (Fig. 6). The resulting dendrogram shows that the data set of 36 fragments has two main parts. One of them is made up of the Abbasid and Nabataean groups, and the other is made up of the Dedan and Tayma groups. Cluster 1 contains 8 samples (Ab-1 to Ab-8) of pottery shards from the Abbasid period with a distance level of 5. Cluster 2 is an example of

Nabataean pottery (N-1 to N-10) at a distance level of 5. Another15 pottery shards (D1 to D15) are grouped in cluster 4 with a distance level of 10, which are related to Dedan pottery. In addition, cluster 3, which is smaller, contains samples M1, M2 and M3, which are classified as Tayma pottery. These four groups or clusters were also identified in both the PCA diagram and 3D scatter plots.

From the above plots and cluster, it could be concluded that the chemical compositions of the Dedan wares from different periods (from different excavation levels (depths) in the site) differ slightly. Although the distinctions are not big, they can be effectively grouped using multivariate statistical analysis. The slight difference between Dedan shards could be interpreted similarly to the results of Bagnasco et al. (2001), who suggested that differences between groups in HCA may not indicate separate provenances but may be due to the use of clays withdrawn from various beds (or from the same bed in successive periods), to the adoption of different technological procedures or to the occurrence of post-depositional phenomena.

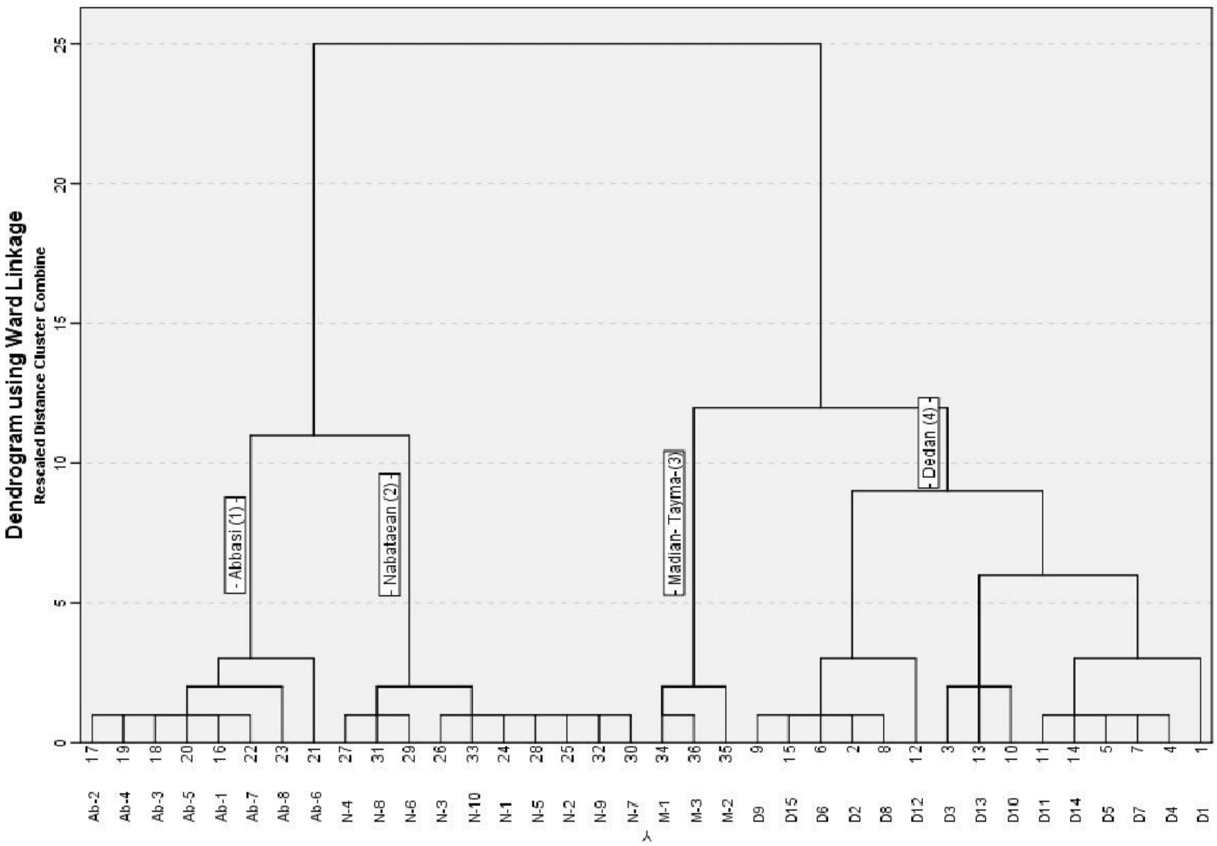

Fig. 6. Dendrogram using words methods and mean square Euclidean distance for 36 pottery samples:1-Abbasid; 2-Nabataean; 3-Tayma and 4-Dedan

3D- Scatter plots

A 3D-scatter plot was employed, using SPSS, to visualise the data, including the ability to examine the relationship between the three variables. For some selected elements, four groups can be visualised within 3-diminsional space (x, y, and z). Fig. 7(a, b, and c) illustrates that the Tayma group had the highest Rb concentration with an average of 122 µg/g and the lowest Ni and Mn concentrations with averages of 23 and 121 µg/g, respectively, among the rest of groups. In general, the Abbasid group has higher Sc and Mn concentrations, with averages of 61 and 840 µg/g, respectively, than the Dedan and Nabatean groups (Fig. 7(a, c)). The Nabataean group contains lower Ti concentrations, with an average of 2835 µg/g, than the Dedan group (5780 µg/g) (Fig. 7(d)). The 3D-scatter plots expressed clear differences between the four groups of ancient potteries. Effectively, these pottery fragments can be clustering using only three variables. These variables (elements) were selected from the PCA loading plot, with high loadings on the extracted factors, and mostly were orthogonal to each other (Fig. 5 and Table 5).

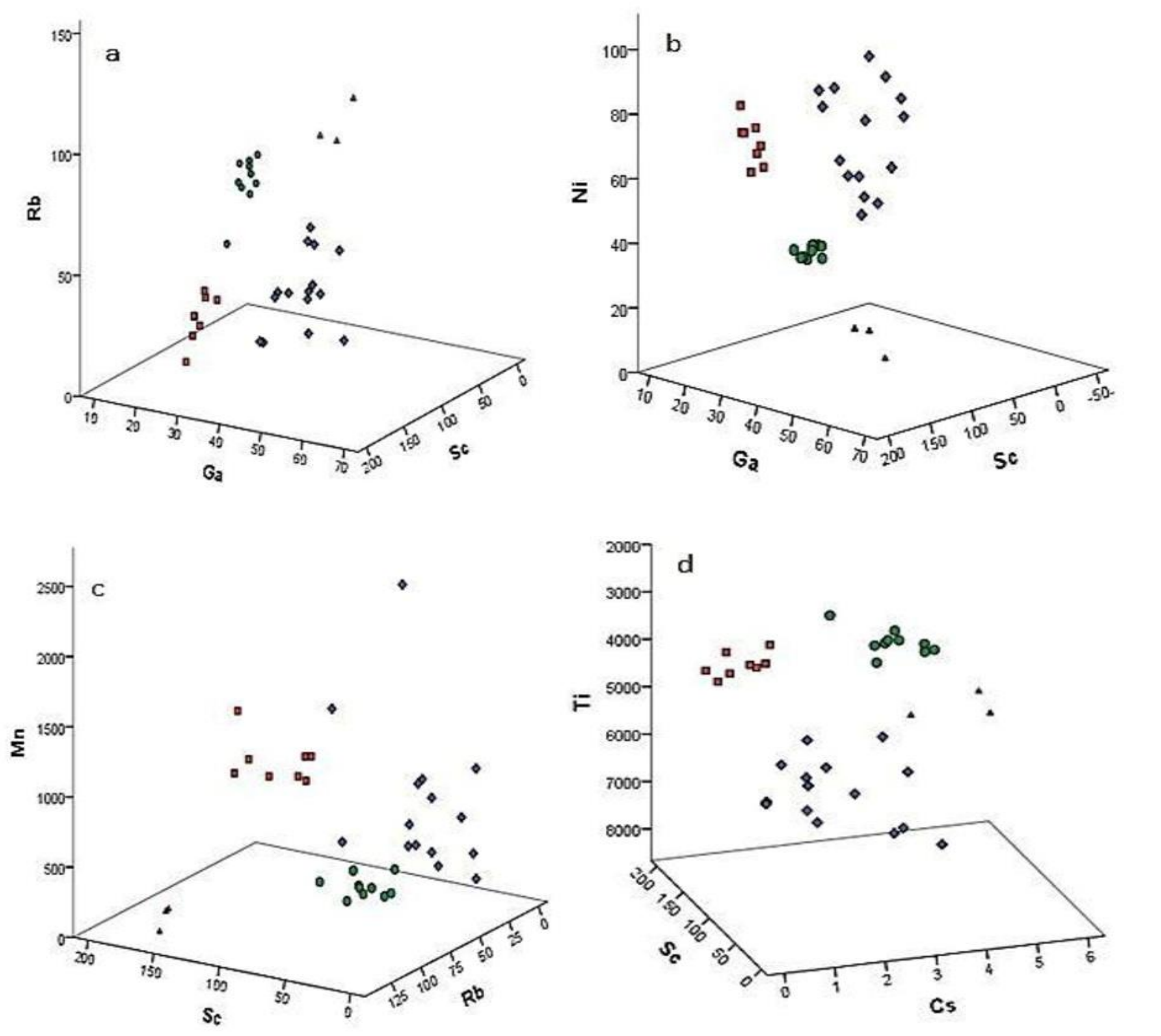

Fig.7. 3D Scatter plot of 36 pottery shards from Dedan site, Triangular symbols, Tayma; circles, Nabataean; Diamond, Dedan; squire, Abbasid. All quantities reported in (ug/g).

CONCLUSIONS:

This study has looked at the characterisation of pottery shards from an archaeological site in Dedan in northwestern Saudi Arabia. The ancient pottery shards differ in their chemical composition, reflecting variations in manufacturing technology and the possibility of different types of clay material. The analysis of 36 fragments of ancient pottery from the Dedan heritage site indicates the existence four different types of pottery shards (Abbasid, Nabataean, Tayma and Dedan). Multivariate analysis using principle components and clustering confirmed the existence of these different pottery groups, which are interpreted via plots and a dendrogram. In addition, the study demonstrates that high-precision ICP-MS elemental analysis is a powerful tool for the characterisation of archaeological pottery shards.

Finally, this work, based on elemental analysis using ICP-MS and statistical analysis to study ancient pottery shards from the old Arabian Peninsula, would be helpful for archaeologists, as it would contribute to the establishment of an elemental composition database regarding ancient Arabian pottery in Saudi Arabia.

ACKNOWLEDGEMENTS

This work was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

REFERENCES:

1. Nasif, A., 1988. Al-Ula an Historical and Archaeological Survey with Special Reference to its Irrigation. King Saud University, Riyadh.

2. Winnett, F.V., Reed, W.L., 1960. Ancient Records from North Arabia, Toronto, University of Toronto Press, 177.

3. Hoyland, Robert G., 2001. Arabia and the Arabs: from the Bronze Age to the coming of Islam, Routledge, London, New York, 66.

4. Al-Said, S., Sahlah, S., Elhassan, A., Omar, G., al-Amer,F., Mishaby, I., Excavations at Dedan (First Season 1425/2004): Results of Department of Archaeology (King Saud University), ATLAL: J. Saudi Arab. Arch.2010; 20: 76-99.

5.Al-Said, S.F., Al-Ghazzi, A.S., 2013. Archaeological Treasures from Dadan, Results of Seven Seasons of Field work, Saudi Society for Archaeological Studies, Riyadh, 128-450.

6.Arnold, D.E., Neff, H., Bishop, R.L., 1991. Compositional analysis and ‘‘sources’’ of pottery: archaeological approach. American Anthropologist 93, 70–90.

7.Bower, N.W., Bromund, R.H., Smith, R.H., Atomic Absorption for the Archaeologist: An Application to Pottery from Pella of the Decapolis. J. Field 1975;Archaeol. 2 (4):389-398.

8.Bernardini, F., Vecchiet, A., De Min, A., Lenaz, D., Mendoza Cuevas, A., Gianoncelli, A., Dreossi, D., Tuniz, C., Montagnari Kokelj, M., Neolithic pottery from the Trieste Karst (northeastern Italy): A multi-analytical study. Microchem J. 2016; 124: 600-607.

9. Descantes, C., Neff, H., Glascock, M.D., Dickinson, W.R., 2001. Chemical Characterization of Micronesian Ceramics Through Instrumental Neutron Activation Analysis: A Preliminary Provenance

10.Mommsen, H., The importance of a reliable grouping – Neutron activation analysis (NAA) data of Mycenaean pottery sherds re-evaluated with the Bonn filter method. J. Archaeol. Sci.2012;39 (3):704-707.

11. Mommsen, H., Beier, T., Diehl, U., Podzuweit, C.,Provenance determination of Mycenaean sherds found in Tell el Amarna by Neutron Activation Analysis. J. Archaeol. Sci.1992;19 (3): 295-302.

12. Day, P.M., Kiriatzi, E., Tsolakidou, A., Kilikoglou, V.,Group Therapy in Crete: A Comparison Between Analyses by NAA and Thin Section Petrography of Early Minoan Pottery. J. Archaeol. Sci. 1999;26 (8): 1025-1036.

13. Shingleton, K.L., Odell, G.H., Harris, T.M., Atomic Absorption Spectrophotometry Analysis of Ceramic Artefacts from a Protohistoric Site in Oklahoma. J. Archaeol. Sci. 1994;21 (3): 343-358.

14.Bower, N.W., Snow, D.H., 1984.A comparative study of early historic “Tewa” pottery. In New Mexico Geological Society Sourcebook, 35th Field Conference, New Mexico Geological Society, Albuquerque, 291-295.

15.Nazaroff, A.J., Prufer, K.M., Drake, B.L., Assessing the applicability of portable X-ray fluorescence spectrometry for obsidian provenance research in the Maya lowlands. J. Archaeol. Sci. 2010;37 (4): 885-895.

16.Goodale, N., Bailey, D.G., Jones, G.T., Prescott, C., Scholz, E., Stagliano, N., Lewis, C., pXRF: a study of inter-instrument performance. J. Archaeol. Sci. 2012;39 (4):875-883.

17. Leung, P.L., Luo, H., A study of provenance and dating of ancient Chinese porcelain by x-ray fluorescence spectrometry. X-Ray Spectrom. 2000;29 (1): 34-38.

18.Adan-bayewitz, d., Asaro, F., Giauque, R.D., Determining pottery provenance: application of a new high-precision x-ray fluorescence method and comparison with instrumental neutron activation analysis. Archaeometry,1999; 41 (1):1-24.

19.Ichikawa, S., Nakayama, K.,Nakamura, T., Loose-powder technique for X-ray fluorescence analysis of ancient pottery using a small (100 mg) powdered sample. X-Ray Spectrom. 2012;41 (5): 288-297.

20.Klein, M., Jesse, F., Kasper, H.U., Gölden, A., Chemical characterization of ancient pottery from sudan by x-ray fluorescence spectrometry (xrf), electron microprobe analyses (empa) and inductively coupled plasma mass spectrometry (ICP-MS). Archaeometry,2004; 46 (3): 339-356.

21. Cecil, L.G., Inductively coupled plasma emission spectroscopy and Postclassic Petén slipped pottery: an examination of pottery wares, social identity and trade. Archaeometry,2004; 46 (3):385-404.

22.Bagnasco, M.B., Casoli, A., Chiari, G., Compagnoni, R., Davit, P., Mirti, P., Mineralogical and chemical composition of transport amphorae excavated at Locri Epizephiri (southern Italy). Journal of Cultural Heritage ,2001;2 (3): 229-239.

23.Damjanovi, L., Mio, U., Bajuk-Bogdanovi, D., Cerovi, N., Mari-Stojanovi, M., Andri, V., Holclajtner-Antunovi, I., Archaeometric Investigation of Medieval Pottery from Excavations at Novo Brdo, Serbia. Archaeometry ,2016;58 (3): 380-400.

24. Li, B., Greig, A., Zhao, J., Collerson, K.D., Quan, K., Meng, Y., Ma, Z., ICP-MS trace element analysis of Song dynasty porcelains from Ding, Jiexiu and Guantai kilns, north China. J. Archaeol. Sci.2005; 32 (2): 251-259.

25. Barone, G., Ioppolo, S., Majolino, D., Migliardo, P., Tigano, G., A multidisciplinary investigation on archaeological excavation in Messina (Sicily). Part I: a comparison of pottery findings in "the Strait of Messina area. J. Cult. Herit. 2002;3 (2): 145-153.

26. Little, N.C., Speakman, R.J., Glascock, M.D., Kosakowsky, L.J., Lohse, J.C., Characterization of Maya pottery by INAA and ICP-MS. J. Radioanal.Nucl. Chem. 2004;262 (1): 103-110.

27. Aldrabee, A., Wriekat, A., Archaeometric characterization of ancient glazed pottery sherds from Khirbet Faris, Jordan by inductively coupled plasma mass spectrometry (ICP-MS). Microchem J. 2011;99 (2): 289-295.

28. Walton, M.S., Shortland, A., Kirk, S., Degryse, P., Evidence for the trade of Mesopotamian and Egyptian glass to Mycenaean Greece. J. Archaeol. Sci. 2009;36 (7): 1496-1503.

29. Wu, J., Hou, T., Zhang, M., Li, Q., Wu, J., Li, J., Deng, Z., An analysis of the chemical composition, performance and structure of China Yixing Zisha pottery from 1573 A.D. to 1911 A.D. Ceram. Int. 2013;39 (3): 2589-2595.

30.Kramar, S., Lux, J., Mladenović, A., Pristacz, H., Mirtič, B., Sagadin, M., Rogan-Šmuc, N., Mineralogical and geochemical characteristics of Roman pottery from an archaeological site near Mošnje (Slovenia). Appl. Clay Sci. 2012;57: 39-48.

31.Kuisma-kursula, P., Räisänen, J., 1999. Scanning electron microscopy-energy dispersive spectrometry and proton induced x-ray emission analyses of medieval glass from koroinen (finland). Archaeometry,1999; 41 (1):71-79.

32.Kostov, R.I., Protochristov, C., Stoyanov, C., Csedreki, L., Simon, A., Szikszai, Z., Uzonyi, I., Gaydarska, B., Chapman, J., Micro-PIXE Geochemical Fingerprinting of Nephrite Neolithic Artifacts from Southwest Bulgaria. Geoarchaeology.2012; 27 (5): 457-469.

33.Tykot, R.H., Young, S.M., 1996. Archaeological applications of inductively coupled plasma-mass spectrometry. In (M. V. Orna, Ed.) Archaeological Chemistry: Organic, Inorganic, and Biochemical Analysis. ACS Symposium Series 625. Washington, D.C.: American Chemical Society, 116–130.

34.Uggerud, E., Inorganic Mass Spectrometry. Principles and Applications. Von Johanna Sabine Becker. Angewandte Chemie 2008;120 (23): 4328-4329.

35.Jonson, R.A., Wichern, D.W., 1992. Applied multivariate statistical analysis. Englewood Cliffs, N.J., Prentice Hall.

36.Naseerutheen, A., Chandrasekaran, A., Rajalakshmi, A., Ravisankar, R., Elemental analysis of ancient potteries of Vellore Dist, Tamil Nadu, India by ED-XRF technique with statistical approach.Beni-Seuf Univ. J. Appl. Sci.2014; 3 (1): 45-51.

37.Vinagre Filho, U.M., Latini, R.M., Bellido, A.V.B., Buarque, A., Borges, A.M., Ancient ceramic analysis by neutron activation in association with multivariate methods. Braz. J. Phys. 2005;35 (3b): 779-781.

38. Un-Habitat, 2003. THE CHALLENGE OF SLUMS: GLOBAL REPORT ON HUMAN SETTLEMENTS 2003. UN-Habitat, London.