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View Journal

Investigation of tin, arsenic and lead concentrations in prehistoric arrowheads†

Cite this: DOI: 10.1039/c3ja50154j

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Received 29th April 2013
Accepted 13th June 2013

DOI: 10.1039/c3ja50154j

www.rsc.org/jaas

Copper arrowheads discovered inside burial sites at Jabal al-Buhais were analyzed using X-ray fluorescence spectrometry to reveal the elemental composition and to quantify the concentrations of tin, arsenic and lead. Archaeological analysis of the various artifacts found in the tombs reveals different chronological eras from the late stone-age (5000 BC) to the Hellenistic period (200 BC); thus determination of the arrowheads' copper alloys will improve the archaeological information pertaining to dating and provenance. Analysis of 39 arrowheads revealed that 19 are made of pure copper, whereas tin, arsenic and lead are present in trace amounts. The remaining 20 arrowheads are made of bronze (all, except two, were found in burial sites 51 and 64), with high concentrations of tin (min 1.79%, max 22.94% and average 8.9%). The elemental composition of the arrowheads strongly suggests that they were locally manufactured, most probably from raw copper smelted nearby at Wadi al-Hilo. Since there are no records of local tin mines, most probably it was imported from outside the region, from mines as far away as Afghanistan.

Introduction

Prehistoric artifacts serve as precursors to ancient civilizations. They are the keys that open the vaults of history and give us glimpses of how ordinary people lived thousands of years ago, and how societies interacted through commerce or war. Artifacts made of copper and copper alloys take the center stage in archaeology due to their durability and varied utilization,[1,2] with the earliest copper usage dating back to the 9th millennium BC.[3]

In general, excavated copper artifacts usually provide information pertaining to the historical period, provenance and technical know-how. Thus knowledge of the chemical composition provides information on their geographical origin, trade and cultural contacts.[4,5]

Interest in the composition of archaeological copper alloys started almost 200 years ago.[6] Nowadays different analytical techniques such as optical microscopy (OM), scanning electron microscopy (SEM), inductively coupled plasma mass spectrometry (ICP-MS), X-ray diffraction (XRD), Raman spectroscopy, neutron activation analysis (NAA) and X-ray fluorescence spectroscopy (XRF) are utilized in archaeological research.[7–10] The latter technique is the most preferred analytical method applied today, due to its non-destructive nature, cheap cost, small analysis time and the need for minimum sample preparation.[11]

This report investigates the elemental composition of a number of copper based arrowheads discovered in burial sites in Jabal al-Buhais, Emirate of Sharjah, United Arab Emirates (Fig. 1). Located in the center of the emirate, this Jabal (mountain) has been the focus of extensive archaeological research since 1995. Successive expeditions by local and foreign teams have led to interesting discoveries and chief among them is the 91 tombs at different elevations along the peaks of the Jabal. Analysis of the various artifacts found in the tombs reveals different chronological eras from the late stone-age (5000 BC) to the Hellenistic period (200 BC).[12] Thus the aim of our work is to advance the present knowledge about the history of Jabal al-Buhais in particular and the UAE in general through the XRF analysis of the arrowheads to determine the chemical composition and subsequently establish provenance.

Results and discussion

The nine major elements selected from the quantified spectra were copper (Cu), tin (Sn), arsenic (As), lead (Pb), iron (Fe), nickel (Ni), cobalt (Co), zinc (Zn) and manganese (Mn) (Table 1). Copper is the major element in all the arrowheads with an average concentration of 93.4% (min 74%, max 99.4%), while Mn, Zn and Co are present in detectable trace amounts only in a few samples. Iron is present in all the samples in concentrations less than 1% except for two samples 5 and 23 (Exs 381 and Bhs 1223) with concentrations of 1.8% and 1.79% respectively. However, its presence in low concentrations is most probably due to the corrosion process. Nickel is also present in the majority of the samples in concentrations that do not exceed 1%

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ja50154j

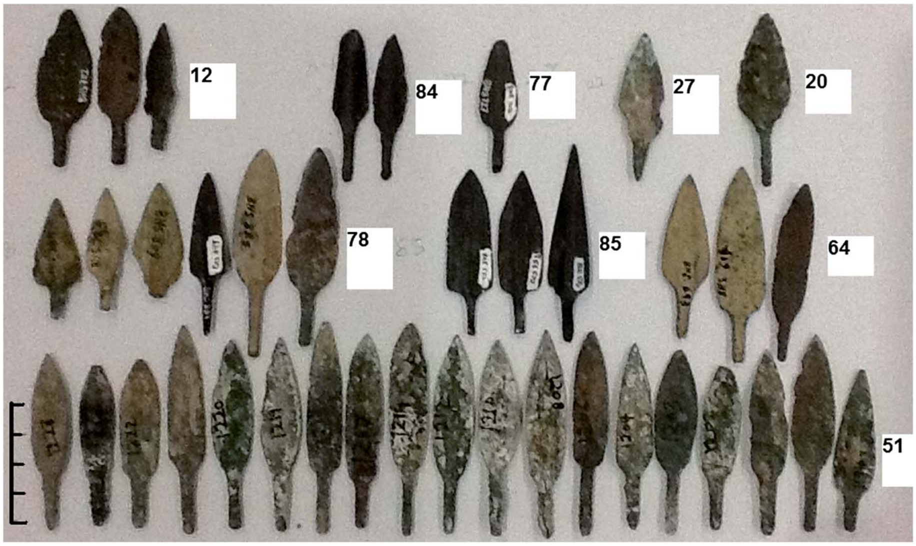

Fig. 1 Photograph of the 39 arrowheads arranged by burial sites (number shown to the right). Each division of the scale is 1 cm.

except for two samples 1 and 8 (Bhs 702 and Bhs 1201) with concentrations of 1.21% and 1.02% respectively.

Arsenic, lead and tin (Fig. 2) are discussed separately because of their importance in the production of the different types of copper alloys.[13] The three elements are usually added, individually or together, during the Cu smelting process, in various concentrations, to modify the properties of the alloy. Arsenic acts as an excellent deoxidant for the metal, reducing its porosity and noticeably hardening the alloy.[14] Arsenic, even at low levels, can change the colour of the metal giving a silvery appearance to the surface and adding 2–6% As in the alloy mixture is found to be most suitable for cold working of the alloy by increasing its ductility and hardness.[15] Arsenic has been discovered in archaeological artifacts belonging to the 5^{th} millennium BCE.[16] It is usually present in naturally occurring copper ores such as enargite (Cu_3AsS_4), olivenite ($Cu_2(AsO_4)OH$) and tennantite ($Cu_{12}As_4S_{13}$). It is generally accepted that copper alloys containing As in concentrations less than 1% are not considered as arsenical bronze.[17] According to this criterion only sample 8 (Bhs 1201) had As concentrations above that level; however a concentration of 1.32% could still be attributed to the copper ores or to re-smelting of the arrowhead.[18]

Lead is usually added to copper during the smelting process to lower the melting point resulting in a more malleable alloy.[19] However, the addition of Pb in high concentrations produces a copper alloy that is brittle and prone to cracking when hammered.[1,12] In the arrowheads analyzed here, Pb concentrations were between 0 and 1% for all the samples except sample 16 (Bhs 1214) that had a Pb concentration of 3.74%. Such a high level of Pb does not immediately mean it was deliberately added to the alloy, but most probably is a result of inhomogeneous distribution of Pb in the arrowhead due to its concentration in a particular zone during the smelting process. Another reason for such a high Pb concentration could be due to the use of scrap metal for the manufacture of this particular arrowhead.[20]

Bronze produced from the addition of tin to copper alloys, during the 4^{th} millennium BC, became an important discovery because of its hardness, durability and resistance to corrosion. Soon after its discovery various tools were manufactured for agriculture, weapons, armor *etc.*, hence the name "Bronze Age" was coined to refer to that period in history. Unlike arsenic, tin is not toxic and its alloy is stronger and easier to cast than Cu–As. Tin is deliberately added to copper during the smelting process because copper ores usually contain no tin.

It is clear from the quantitative results that the arrowheads are separated into two distinct groups. One group of unleaded bronze arrowheads with high Sn concentrations (min 1.79%, max 22.94% and average 8.9%), and another group of unalloyed copper arrowheads that have Sn concentrations very close to the detection limits ($C_i \leq 0.32\%$). The former group includes all the arrowheads discovered in burial sites 51 and 64 (samples 6 to 27) which represent more than half (22/39) the discovered arrowheads, except for two anomalies (samples 7 and 25) that have Sn concentrations of 0.26% and 0.24% respectively. At the moment we have no explanation for the two odd arrowheads, and further archaeological investigation is needed before a better conclusion could be reached. The latter group of unalloyed copper arrowheads includes the remaining 17 samples from the burial sites 12, 20, 27, 77, 78, 84 and 85. It is quite clear that the presence of the two distinct groups points to different historical scenarios. Either the burial sites 51 and 64 belong to a different period in history than the other burial sites, or the bronze arrowheads originated from another province and were introduced to the Jabal al-Buhais region through trade or war.

In another scenario, all the arrowheads could have been manufactured locally. It is well documented that the Land of Magan (Oman peninsula) was a source of copper as far back as the 3^{rd} millennium BC.[21] Kutterer and Jasim investigated the copper smelting site in Wadi Al-Hilo, Sharjah, and concluded that the site was occupied during the Early Bronze Age, and produced approximately 56 tons of pure copper. XRF analysis

Table 1 Summary of the elemental composition of the copper arrowheads. Elemental concentrations reported as mass%

Sample no.	Mn	Fe	Co	Ni	Cu	Zn	As	Sn	Pb
1	0	0.28	0.05	1.21	97.19	0	0.17	0.06	0.97
2	0	0.14	0	0.24	98.98	0	0.07	0.32	0.24
3	0	0.41	0.01	0.27	98.34	0.05	0.09	0.13	0.57
4	0	0.12	0	0.28	98.72	0	0.26	0.19	0.43
5	0	1.8	0	0.01	97.27	0	0.15	0.05	0.71
6	0	0.38	0.01	0.39	95.53	0.19	0.42	2.24	0.81
7	0	0.5	0	0.02	97.31	0	0.84	0.26	1.05
8	0	0.19	0.01	1.02	73.99	0	1.32	22.94	0.49
9	0	0.02	0	0.12	88.76	0.18	0.14	9.93	0.82
10	0	0.4	0	0.25	97.06	0.19	0	1.96	0.05
11	0.02	0.3	0.14	0.78	87.73	0	0.51	9.68	0.82
12	0	0.26	0	0	97.91	0	0	1.79	0
13	0	0.03	0	0.01	87.57	0	0	12.32	0.04
14	0	0.21	0	0	92.3	0	0	7.36	0.03
15	0	0.26	0	0.04	86.54	0	0.04	12.58	0.53
16	0.03	0.23	0	0.01	85.81	0	0.14	10.01	3.74
17	0	0.58	0	0.04	80.27	0	0.08	18.76	0.24
18	0	0.02	0	0.01	92.85	0	0	7.08	0.01
19	0	0.27	0	0.07	91.67	0	0.46	6.63	0.9
20	0	0.13	0	0.26	85.45	0.15	0.46	13.16	0.29
21	0	0.36	0	0.02	85.12	0	0.12	13.98	0.38
22	0	0.02	0	0	96.55	0	0	3.42	0
23	0.01	1.79	0	0.04	89.28	0	0.01	8.19	0.12
24	0	0.17	0	0.01	96.69	0	0	3.1	0.03
25	0.07	0.07	0	0	98.75	0	0.38	0.24	0.41
26	0.03	0.12	0	0.02	87.25	0	0.03	12.31	0.19
27	0	0.36	0	0.19	85.03	0	0.84	13.47	0.07
28	0.06	0.42	0.02	0.07	98.34	0	0.31	0.31	0.42
29	0.05	0.48	0	0.05	98.74	0	0.17	0.03	0.42
30	0.03	0.31	0	0.05	98.7	0	0.3	0.14	0.43
31	0	0.13	0.02	0.07	99.01	0	0.18	0.03	0.49
32	0	0.78	0	0.16	98.29	0	0.1	0.18	0.37
33	0	0.22	0	0.01	98.89	0	0.16	0.17	0.54
34	0	0.17	0	0	99.39	0	0.14	0.05	0.25
35	0.06	0.14	0	0	99.34	0	0.03	0.04	0.35
36	0.04	0.14	0	0	99.21	0	0.2	0.05	0.32
37	0	0.17	0.04	0.22	99.26	0	0.1	0.03	0.17
38	0	0.44	0	0.17	99.08	0	0.15	0.07	0.07
39	0	0.49	0	0.13	98.98	0	0.07	0.18	0.13

on one of the ingots discovered at the site revealed its composition to be pure copper (99.5%) with traces of Fe (0.2%), Ni (0.09%), As (0.5%), Se (0.02%) and Ag (0.02%),[22] which makes it a very good candidate as the source of copper used for the manufacture of Al-Buhais arrowheads. On the other hand tin must have been imported from outside the gulf region, since no tin deposits are found anywhere within the Oman peninsula, and according to Weeks, the most probable source at that time was Afghanistan.[23]

Experimental

The analyzed arrowheads are a sample representing a large hoard of arrowheads discovered at burial sites in Jabal al-Buhais. All the samples are corroded and as a result special care and attention was needed when cleaning small surface areas to expose the underlying shaft. Corrosion layers were removed from small areas on the surface of the arrowheads using a dentist drill, and the exposed copper layers were cleaned with acetic acid (CH_3COOH) at a concentration of 6 mol L^{-1} which was diluted further to 25% by volume.

EDXRF analysis was performed using a Horiba (7200) X-ray analytical microscope, operating at 50 kV and Auto current mode. Each sample was analyzed under vacuum, on three independent spots for 50 seconds each using a 1.2 mm diameter X-ray beam. Fluorescent characteristic X-rays were detected with a silicon drift detector (SDD) positioned at 45° to the X-ray beam and sample surface. It had a resolution of approximately 130 eV. The resulting spectra were quantified using the standard-less fundamental parameter method (FPM). Elemental concentrations based on the observed peak intensities were calculated using comprehensive software algorithms that consider the theoretical X-ray beam intensity, detector solid angle, matrix effects (element–element interactions), band overlap and spectral backgrounds. Mass concentrations were reported with 3-sigma error values that ranged between a minimum of 0.01%, a maximum of 0.25% and an average of 0.05%.

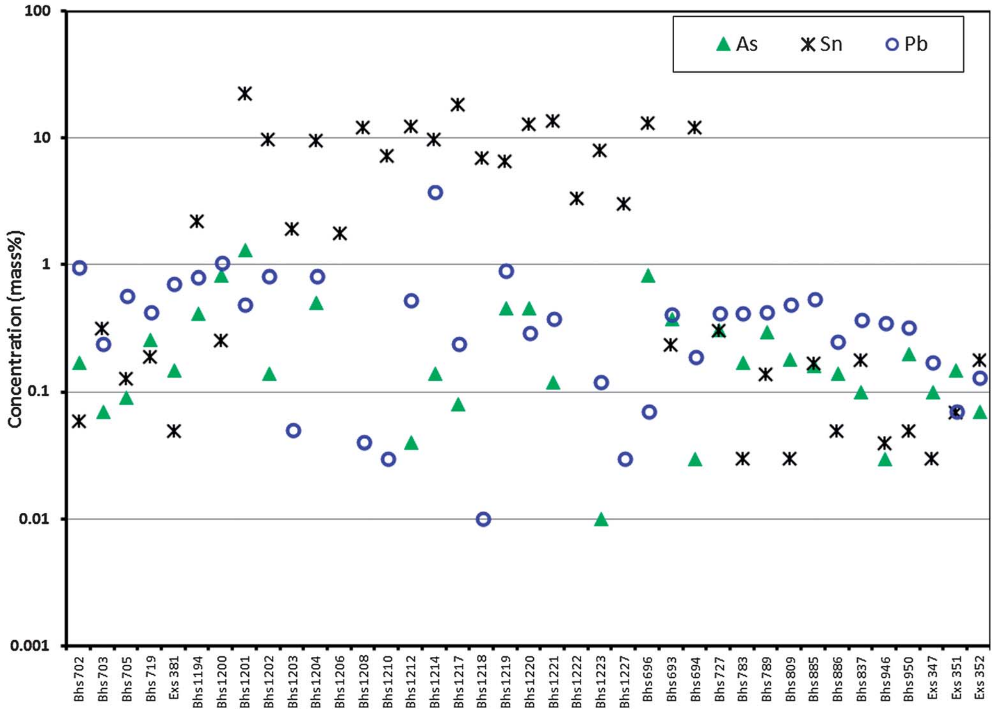

Fig. 2 Scatter plot of the concentrations of arsenic, tin and lead in the copper arrowheads.

Conclusions

Analysis of the 39 archaeological arrowheads discovered at Jabal al-Buhais clearly separates the samples into two groups. One group consists of unalloyed copper with Cu concentrations above 97% and traces of Ni, As, Sn and Pb that vary considerably but hardly rise above 1%. The other group comprises bronze (Cu + Sn) alloys in percentages ranging from 73.99% + 22.94% to 97.91% + 1.79%. Such erratic levels in trace elements are rather common in archaeological artifacts, and are usually attributed to a number of factors.[24–27] For example Key (1964) explained that the trace element variations in his samples were probably due to the fact that "the ornaments either are the products of one workshop or re-reflect the use of one rough formula. With one exception, the tools, by contrast, are of impure but unalloyed copper".[28]

The copper arrowheads reported here were most probably manufactured locally, from copper produced at Wadi al-Hilo. Chemical composition of the copper ingot coupled to the time period both sites were occupied lends great credibility to such thesis. Further investigation of Jabal al-Buhais and Wadi al-Hilo sites is planned for the near future in order to add to the body of knowledge about the rich history of the United Arab Emirates.

Acknowledgements

The authors would like to acknowledge the generous assistance of the Directorate of Antiquities, Sharjah, for providing us with information pertaining to archaeological finds in the emirate. The research was carried out at the National X-ray Fluorescence Laboratory (NXFL), United Arab Emirates. A national project (UAE-006) funded by IAEA.

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