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A Method for Skeletal Arsenic Analysis, Applied to the Chalcolithic Copper Smelting Site of Shiqmim, Israel

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A method for analysis of skeletal remains for arsenic using inductively-coupled plasma mass spectrometry (ICP-MS) is presented. Skeletal arsenic analysis has the potential to identify individuals, groups and communities engaged in copper smelting. The analysis is applied to a preliminary study of Shiqmim, Israel, a Chalcolithic copper smelting community, to assess the usefulness of skeletal arsenic analysis in archaeological remains. The results from this pilot study suggest that it is possible to identify individuals who may have been involved in metal working activities in antiquity through the chemical analysis of human skeletal material. The results also point to the potential of using this method to identify metal workers in the archaeological record for other regions and temporal periods.

Keywords: BONES, ARSENIC, CHALCOLITHIC, COPPER SMELTING.

Introduction

Studies of archaeological skeletal remains have frequently focused on concentrations of lead. Most of these studies attempted to find the "natural" skeletal lead concentrations and have found only trace amounts of lead, less than 1·0 μg/g in premetallurgical populations in Peru, North America, Denmark and Nubia (Ericson *et al.*, 1979; Drasch, 1982; Patterson *et al.*, 1991). Waldron (1983) found high levels of skeletal lead in remains from Romano-British cemeteries. Aufderheide *et al.* (1988) used skeletal lead concentrations for anthropological purposes and found "a correlation between skeletal lead content and archaeological or historical information with respect to the extent of lead technology in those studied populations", as well as differences between societies and even groups within a society (Aufderheide *et al.*, 1988: 932). While lead has an exceptionally long half-life in bone compared to other elements (Aufderheide, 1989), it is not the only metal which can deposit in bone from respiratory exposure. Other metals which can accumulate in bone as a result of respiratory exposure include arsenic, cadmium, cobalt, antimony, selenium, vanadium, ytterbium, and zinc (Lindh *et al.*, 1980; Rhoads & Sanders, 1983; Tsiashala *et al.*, 1990). Arsenic is of particular interest with respect to copper smelting since it is commonly an impurity in copper ore and boils off at a lower temperature than the melting point of copper. Respiratory exposure to arsenic is associated with a high incidence of lung cancer in modern-day copper smelter workers as well as individuals living in towns adjacent to copper smelters (Axelson *et al.*, 1978; Owen, 1981; Dart, 1992).

Interest in the impact of arsenic and other metals on the body has led to the collection and analysis of tissue samples from deceased smelter workers employed at a smeltery/refinery in Sweden (Lindh *et al.*, 1980; Gerhardsson *et al.*, 1993). Lindh *et al.* (1980) analysed femur samples from workers employed at the smelter for more than 10 years and a control group with neutron activation analysis (NAA). Concentrations of arsenic in the femurs ranged from 6 to 210 ppb As for smelter workers and 5 to 7 ppb As for the control group. Similar analysis applied to archaeological

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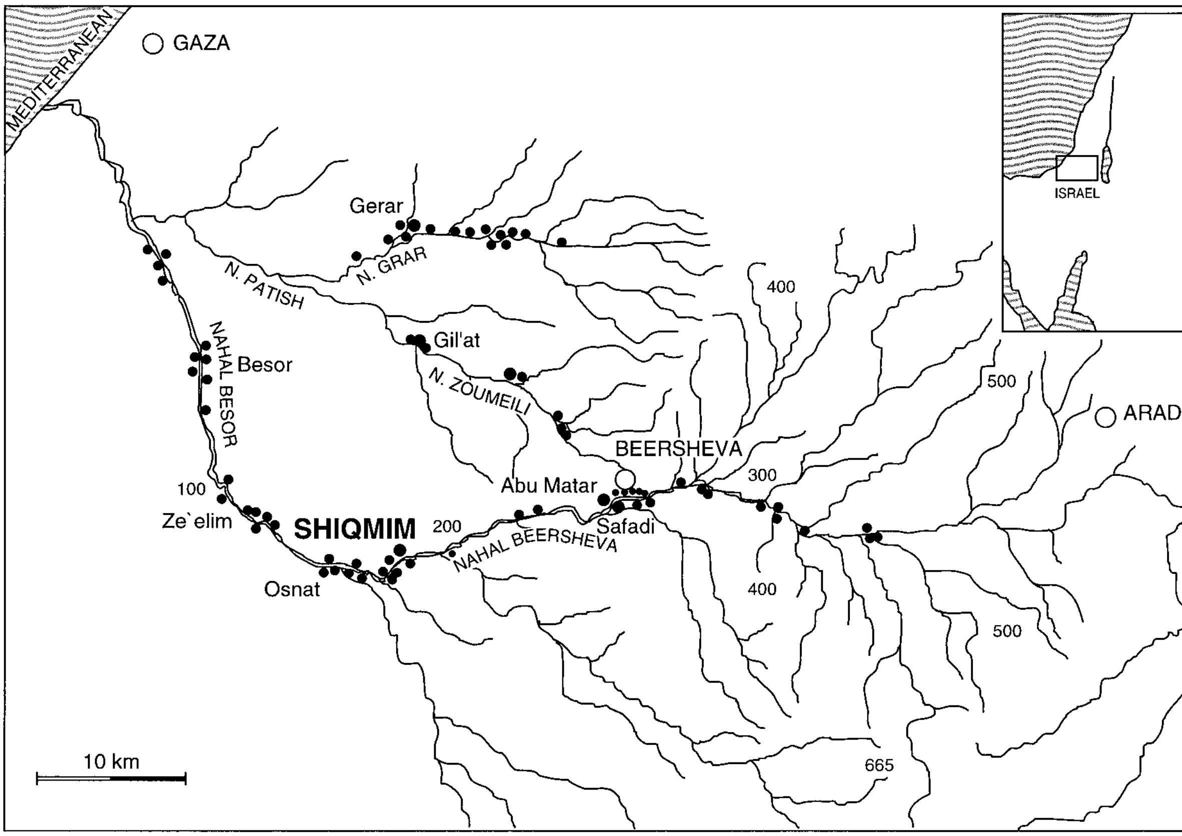

Figure 1. Map of northern Negev study area, Israel, with location of the Shiqmim village and mortuary complex.

skeletal remains has the potential to be useful in identifying individuals, groups, and communities that engaged in copper smelting.

Effects of Diagenesis

The difference between analysis of modern and archaeological bone is the introdution of a new variable—burial in the soil for thousands of years. Diagensis can have a substantial impact on the trace metal concentrations in bone. Metals may be removed or added by ionic substitution in the calcium phosphate lattice and incorporated by mineral replacement (Lambert *et al*., 1984; Pate *et al*., 1989). A variety of techniques have been used to reduce the effects of diagenesis and to determine whether diagenesis has made the analysis of a particular element unreliable. Techniques to reduce the effects of diagenesis include selecting samples from cortical bone of long bones which is least affected by post-mortem change (Lambert *et al*., 1984; Gilbert, 1985; Aufderheide, 1989) and washing samples with an acid solution to remove water-soluble contaminants (Pate *et al*., 1989; Patterson *et al*., 1991). The effect of ionic exchange of a particular element can be evaluated by analysis of soil collected from near the burial (Pate *et al*., 1989) and analysis to locate concentration differences between the exterior and interior bone of cortical bone in cross section (Lambert *et al*., 1984; Pate *et al*., 1989). The degree of mineral replacement in the bone sample can be measured by analysing the bone for crystallinity changes using X-ray diffraction (XRD), infra-red spectrometry (IR) or Fourier Transform infra-red spectrometry (FTIR) (Pate *et al*., 1989; Schoeninger *et al*., 1989; Weiner & Bar-Yosef, 1990).

Case Study: Shiqmim, Israel

The Chalcolithic site of Shiqmim, Israel, was chosen for a pilot study of skeletal arsenic analyses for several reasons. First, the site has abundant and well-documented evidence for copper smelting activity. Second, identification of individuals and groups involved in copper smelting is of great interest with regard to the close relationship between social structure and metallurgy. Finally, there is a large cemetery complex from which more than 250 burials have been excavated from a variety of burial structures representing different social status levels.

Shiqmim is an important site with regard to the study of copper production in the Chalcolithic. Copper working began in the Levant in the late 5th–early 4th millennium BC and was concentrated in the south, particularly in the Beersheva Basin (Figure 1). Metal working installations, crucibles, ores and slag were found at Abu Matar, Horvat Beter, Neve Noy, Miftan, Shiqmim and Gilat. Both ceremonial and utilitarian objects were produced, out of arsenical copper and pure copper, respectively (Ilan & Sebbane, 1989; Levy & Shalev, 1989). The excavations at Shiqmim have provided the most extensive detail of utilitarian object production in the Beersheva Basin (Levy & Shalev, 1989). Tools produced at Shiqmim contained a very small amount of arsenic (0·08%), but the concentration is much lower than that of prestige items (4·6–12%) which appear to have been made in Palestine but not on-site at Shiqmim (Levy & Shalev, 1989; Shalev *et al.*, 1992).

The nature of Chalcolithic copper smelting is based on recent "action archaeological" studies at Shiqmim by Levy & Hauptmann (in preparation) and metallurgical studies carried out at the site by Shalev & Northover (1987). The system is described as follows.

There was no Chalcolithic "smelting furnace" *per se*, but rather a system best described as "crucible based" smelting. A shallow hole, approximately 60 cm deep and eliptic in shape (maximum diameter *c.* 80 cm), was excavated in the ground. There was no furnace lining and no tapping arrangement. A bed of charcoal approximately 20 cm thick was laid over the bottom of the pit and ignited. Crushed ore, the size of coarse sand, was then placed in a clay crucible some 25 cm in diameter by 5 cm in depth on top of the charcoal. Once the crucible was in place, the entire pit was filled with more charcoal. This was then ignited until the coals reached a bright glow. As the top of the pit was open, ample ventilation was available. To achieve the needed temperature of *c.* 1083°C to melt copper, a series of two to three reed blow-pipes were used. To extract the copper meant taking the crucible out of the pit, letting it cool and then scraping the copper prills out. The slag–copper mixture found in the crucible was separated by breaking the slag on a stone block/anvil and then the metal was picked out in the form of metallic copper drops. Full details concerning these experiments is forthcoming (Levy, 1998).

While Chalcolithic metallurgy was not conducted on an industrial scale (Levy, 1998), as shown by recent experimental smelting work at Shiqmim by Andreas Hauptmann and one of the authors (T.E.L.),* primitive crucible-based smelting is labour-intensive. A single successful smelting takes approximately 45 min to 1 h and the yield is small—around 3 g of metal. Considering that one small Chalcolithic copper axe may weigh as little as 100 g, this represents over 30 h of work to smelt the metal necessary to manufacture a small axe. Archaeological evidence also indicates that smelting took place in secluded courtyards within the confines of the village. Thus, there is little doubt that these early metalworkers, using a blow-pipe based smelting system, would have been exposed to unusual levels of impurities associated with metal processing.

Copper metallurgy appears to have played an important role in the social hierarchy seen in the Chalcolithic. Gonen (1992: 40) explains the social nature of copper-working:

> metals, and in our case copper, cannot be found everywhere; they must be sought out in their natural beds and extracted from the bowels of the earth. The organization of search parties, the allocation of manpower for mining, the setting up of transportation and trade networks, all require an economic, transportation, and social infrastructure extending beyond the level of subsistence economies that characterize previous periods. The establishment of such networks and the know-how for transmuting raw metal into tools and objects required the allocation of manpower devoted exclusively to these pursuits. Thus there came into being strata or classes of miners, tradesmen, or artisans. We must therefore view Chalcolithic society as a complex and even stratified society, divided into professional fraternities and perhaps social classes.

Models have been proposed to explain how metal and metallurgy functioned amongst the earliest Levantine practitioners (Levy, 1995), but little is known about who within these societies may have participated in metalworking activities or what their social status may have been at the time. Application of trace element studies to human remains from Shiqmim may indicate some of the social divisions that existed between metal working and non-metal working members of the community.

While over 30 permanent villages have been recorded in the Beersheva valley, Shiqmim is the only settlement to have been discovered in association with a cemetery complex (Levy & Alon, 1982). The cemetery stretches for over 1 km along the Nahal Beersheva in close proximity to the Shiqmim settlement centre and its three satellite villages (Mesad Aluf, Shiqmim Darom and Shiqmim Mizrah). At present, it is not possible to determine how many settlements this huge mortuary complex serviced. However, the close proximity to Shiqmim of several cemetery hill tops crowned with Chalcolithic burial monuments point to their relationship specifically with Shiqmim. Many of the burials excavated were secondary burials within stone lined circles (Figure 4). Samples were collected from four of these grave circles: structure 51 in cemetery II, structure 101 in cemetery IV, and structures 101 and 200 in cemetery V.

Procedures

For this preliminary study only a small number of samples were chosen for analysis to test the feasibility

*In the spring of 1996, T. E. Levy led a National Geographic Society-sponsored international expedition to identify and retrace the ancient copper trail which existed between the main Levantine copper ore source in the Feinan district of southern Jordan and Israel's northern Negev desert where Shiqmim is located. Expedition members from Israel (David Alon, Dodik Shoshani, Avner Goren), Jordan (Dr Mohammad Najjar), United States (Prof. T. E. Levy, Dr Pierre Bikai), and Germany (Dr Andreas Hauptmann) participated with a team from the National Geographic Society (writer Katherine Ozment, photographer Kenneth Garrett, photographic editor Eli Rogers and artist Christopher Klein).

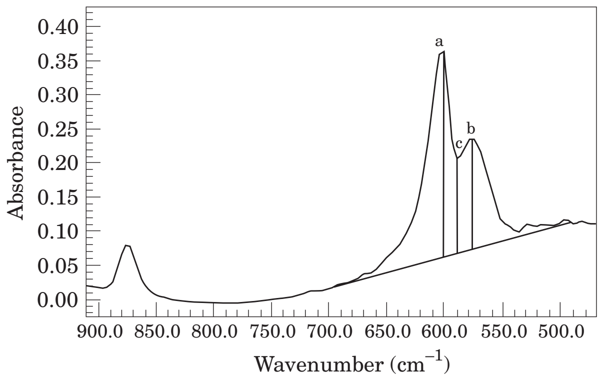

Figure 2. Fourier Transform infra-red spectra. Comparison of peaks used to calculate crystallinity index ((a+b)/c).

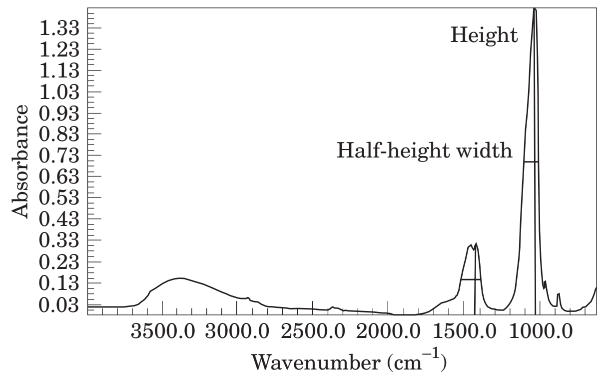

Figure 3. Fourier Transform infra-red spectra. Comparison of peaks used to calculate carbonate–phosphate peak ratios.

of skeletal arsenic analysis. Additionally, only long bones were selected for analysis due to diagenetic considerations. Some of the samples from structure 101 of cemetery V may be from the same individuals. The minimum number of individuals for the grave circle was 12: 5 adults and 7 children (Levy *et al.*, 1994). In addition, it is possible that the bone fragment from square 3 of structure 51 in cemetery II (2Sq3) may have come from the individual represented by H12. For each sample, soil and the outer surface of the bone were scraped off with a clean, rust-free knife blade. Soil was collected for analysis and the sample removed and put into a clean polypropylene vial. Sample sizes were approximately 20–30 mg.

The bone samples were cleaned ultrasonically in deionised, distilled water, rinsed with a 1% solution of HCl and rinsed again with deionised, distilled water. The samples were dried, weighed, and microwave acid digested with 1 ml concentrated trace-element grade nitric acid. Soil samples were leached in 70% nitric acid (HNO_3) for a week and diluted 1:100 with deionised, distilled water. The knife blade was also leached in HNO_3 for an hour and diluted 1:100.

A Perkin Elmer Sciex Elan® inductively-coupled mass spectrometer (ICP-MS) was used to measure the bone solutions for arsenic. Arsenic can be problematic with ICP-MS because formation of polyatomic ions with calcium and chloride in the bone matrix can mask the arsenic signal. However, a technique has been developed using 4% nitrogen in the plasma to provide a competing reaction for chloride. This technique routinely gives very good results for measurements of arsenic in toenail samples—a matrix very similar to bone (Chen *et al.*, 1999). Matrix effects were also minimised by preparing dilute solutions (Bourgoin *et al.*, 1992; Outridge *et al.*, 1996).

Approximately 0·1 mg bone powder was removed from the sample before cleaning procedures for analysis with Fourier Transform infra-red (FTIR) spectrometry. A Nicolet 510 Fourier Transform infra-red spectrometer equipped with a SpectroTech microscope attachment was used to obtain spectra for

Figure 4. Detail of grave structure 101, cemetery 5, Shiqmim, Israel (scale=20 cm). The stone-lined structure contains a number of secondary burials represented by piles of human bone.

measuring the crystallinity index (CI) and carbon-phosphate peak ratio for each sample of bone (Figures 2 & 3). Crystallinity index was calculated according to the method given by Weiner & Bar-Yosef (1990: 191): "a baseline is drawn from approximately 495–750 cm^{-1}. The heights of the 603 cm^{-1} and 656 cm^{-1} absorptions are summed, and then divided by the height of the valley between them (($a+b$)/c=crystallinity index or splitting factor)".

Results

Arsenic was detectable in all samples included in this study. Concentrations ranged from 1 to 8·41 ppb (Table 1). The mean value of arsenic for the Shiqmim samples was 5·3 ± 2·5 µg/g. Samples 5106-38 and 5107-3 have very similar cadmium and arsenic values and are likely to be from the same individual. There was no arsenic detected in the knife blade leachate, ruling out possible contamination from the metal knife. With only one exception, arsenic concentrations

Table 1. Information on all of the samples studied

Location	No.	Age	Sex	Bone	Bone As (µg/g)	Soil As (µg/g)	CI
Cemetery II, structure 51	H2	60 y	F	Long	1	2	2·34
	H5	48 y	M	Long	3·4	1	3·02
	H12	20 y	M	Long	5·63	1	3·31
	Sq3	Adult		Long	5·24	0·6	2·64
Cemetery IV, structure 101	331	Adult		Long	7·35	0·8	2·95
Cemetery V, structure 101	5106-38	Adult	M	Femur	7·85	0·7	5·38
	5106-76	Juvenile		Femur	7·59	0·4	3·44
	5107-3	Adult		Femur	7·91	0·6	
	5108-12	Juvenile		Tibia	4·1	0·3	4·06
	5108-18	Juvenile		Tibia	8·41	0·6	3·45
Cemetery V, structure 200	H1	Adult		Femur	4·2	0·5	
	H3	Adult		Long	5·8	0·8	3·23

were significantly higher in the bone than in the soil and there appeared to be no correlation between values of arsenic in the bone and corresponding soil samples (correlation coefficient $= -0{\cdot}38$). This suggests that the arsenic in the bone samples was not the result of ionic exchange with the soil. Crystallinity indices for the Shiqmim bones, ranging between 2·34 and 5·38 (Table 1), were comparable with the indices measured by Weiner & Bar Yosef (1990): 2·8 for modern bone, 3·0 for recently buried bone and 5·0 for a sample from Netiv Hagedud (9500 BP). There was no correlation of arsenic values with crystallinity indices (correlation coefficient=0·47). The subsamples 5107-3 (cemetery V, structure 101) and H1 (cemetery V, structure 200) showed an FTIR spectra characteristic of calcite, indicating that some mineral replacement had occurred. However, the degree to which mineral replacement had occurred in these bones cannot be determined since the subsample was so small. Corresponding samples analysed by ICP-MS did not show significantly different concentrations than the other samples. Both the lack of difference for these two samples and the lack of correlation between crystallinity indices and arsenic concentrations for the samples in general suggest that arsenic in the bones was not affected by mineral replacement.

In comparison to the results of Lindh *et al.* (1980), many of the values for skeletal arsenic at Shiqmim were the same as modern, non-exposed humans. However, there were a few samples—primarily those from structure 101 at cemetery V—which were somewhat higher than the control group of Lindh *et al.* (1980). The concentrations of skeletal arsenic from structure 101 in cemetery V (and cemetery IV) were significantly higher (ANOVA, $P<0{\cdot}05$) than the rest of the burials. This suggests that the group buried in structure 101 in cemetery V may have been exposed to arsenic to a greater degree than the other groups studied, possibly from copper smelting. Interestingly, two of the samples in this group are from juveniles. Although juveniles were most likely not involved directly in copper smelting, they could still have been exposed since copper smelting at Shiqmim was conducted within the confines of the village in secluded courtyards (Levy & Shalev, 1989). Although a high incidence of lung cancer is attributed to respiratory exposure to arsenic from copper smelters (Axelson *et al.*, 1978; Owen, 1981; Dart, 1992), there was no evidence for tumours in the Shiqmim sample. The only palaeopathology noted in the individuals sampled was arthritis in all individuals over 40 years old in structure 51 in cemetery II, including H2 and H5 (Levy *et al.*, 1990).

The two burial structures with the largest number of individuals sampled, structure 101 in cemetery V and structure 51 in cemetery II, were of different sizes. The size difference may indicate a difference in status of the individuals buried in those structures. A four-level ranking system used by Levy & Alon (1982) for cemetery I (with rank level 1 representing the highest status) was based on the amount of labour required to build the circle (e.g. diameter, type of stone). Using the same criteria, rank levels can be assigned to the two burial structures. Structure 51 in cemetery II measured 2·90 m × 2·36 m on the outside, 1·85 m × 1·6 m on the inside and had a depth of 51 cm. A number of grave goods were found including seven V-shaped bowls, four basins (one used as an ossuary), fragments of white-painted ceramics and a haematite macehead. Structure 101 (Figure 4) in cemetery V had "a maximum outside diameter of 1·70 m; an inside diameter of 1·40 m; and a maximum depth of 0·22 m" (Levy *et al.*, 1994: 100). Grave goods consisted only of a single bead; however, the circle had been disturbed. Based on the diameters of the two circles, structure 51 in cemetery II was assigned a rank level of two and structure 101 in cemetery V was assigned a rank level of one. Interestingly, the group from structure 101 in cemetery V, the lower status group, had significantly greater concentrations as compared to the group in structure 51 in cemetery II (ANOVA, $P<0{\cdot}05$). While a much larger sample size is required to make any definite conclusions, this result suggests that exposure to arsenic from copper smelting may correlate with a lower status in this context.

Conclusions

Clearly, more analyses are required in order to draw definite conclusions. However, the results of skeletal arsenic analysis at Shiqmim are promising enough to justify further investigation. A more thorough investigation of the status of metalworkers would be helpful in understanding some of the "processes that may have led to the emergence of complex societies during the late fifth and fourth millennia BC in the southern Levant" (Levy *et al.*, 1990: 29). Additionally, if skeletal arsenic concentrations are found to reflect respiratory exposure to copper smelting, they could be used not only to identify groups of metalworkers within a community, but also sites in which copper was worked. This would be especially useful in cases where copper artefacts have been identified with local ores, but smelting sites have not been identified in the absence of evidence such as slags, furnaces and crucibles.

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