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Chemical and Isotopical Analyses on Weapons from the Middle Bronze Age in Sidon

Introduction

Metal weapons were found in Middle Bronze Age graves at the Sidon College site (British Museum excavations) (see p. 38). The weapon's metal and lead isotope chemistry was investigated at the Institute of Environmental Geochemistry, Heidelberg and at CEREGE, Aix-en-Provence, respectively. Chemical analysis provides important information on the composition of the object which is related to technological developments (Bourgarit and Mille, 2003; Philip, 1991). Despite some limitations (Budd *et al.*, 1995; Pollard and Heron, 1996), lead isotope-analyses are an additional advantage in constraining the provenance of metal ores (Gale and Stos-Gale, 1982; Hosler and MacFarlane, 1996; Lambert, 1997; Pollard and Heron, 1996).

Method

Due to the uniqueness of the weapons, only corroded layers around the artefacts were sampled. These are a mixture of altered metals but also include soil from the excavation site. Corrosion induces many problems in the analysis of metal artefacts (Giumlia-Mair *et al.*, 2002; Lambert, 1997), but in a first approach, it enables the saving of samples and to characterize the average composition of the objects. Metal compositions were measured on an ICP-OES (Varian Vista-MPX) after hot digestion of total samples (20 to 100mg) using concentrated HNO_3 acid. Because in the measured samples, not only metals but soil was also digested; table 1 represents the results of metal concentrations in % of the total measured metal content. Aluminium and Iron concentrations are especially influenced by soil composition and corrosion as demonstrated by the two replicates of sample S/1820 and thus also reflect the amount of soil incorporated in the sample.

A different approach was used for the measurement of lead isotopes. The samples were rinsed in diluted HCl acid and ultraclean water (MilliQ water). However some oxides could not be leached by this procedure. The metallic residues were then hot digested in Aqua-Regia (HNO_3+HCl) in Teflon bombs and after appropriate resin extraction, were measured by Thermal Ionisation Mass Spectrometry (Hamelin *et al.*, 1990) for stable lead isotopes composition (table 2).

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SAMPLE NAME	PERIOD	Type	Burial	Cu (%)	Ag (%)	As (%)	Au (%)	Fe (%)	Ni (%)	Pb (%)	Sn (%)	Zn (%)	Al (%)
S/1747	Sidon´s phase 1 (1st part of 19th Century B.C.)	Spearhead	5	97,16	ul	0,04	Ul	1,30	0,01	0,10	0,50	0,03	0,88
S/1744	" "	axehead	5	97,24	ul	0,03	Ul	0,23	0,00	2,28	0,11	0,01	0,11
S/1820	" "	Axehead	12	83,59	ul	0,02	Ul	10,88	0,01	0,73	0,56	0,03	4,18
Replicate of S/1820	" "	Axehead	12	93,66	ul	0,02	Ul	2,76	0,01	0,66	1,39	0,02	1,49
S/1821	" "	Spearhead	12	98,31	ul	0,03	Ul	0,35	0,00	0,03	1,16	0,00	0,11
S/3003	" "	Axehead	23	72,52	ul	0,14	Ul	0,52	0,00	26,23	0,42	0,02	0,16
S/1825	" "	Dagger	13	94,49	0,17	0,11	Ul	0,86	0,00	0,20	3,78	0,04	0,35
S/1854	Sidon´s phase 4 (Intermediate Early/Late Middle Bronze Age)	Arrowhead	14	96,34	0,10	0,28	Trace	0,71	0,01	0,26	2,12	0,03	0,15
S/1734	Sidon´s phase 5 (Late Middle Bronze Age)	Knife	4	97,15	ul	0,20	Ul	2,11	0,02	0,12	0,12	0,02	0,25

Table 1: Metal concentrations of corroded samples in % of total metal content. Bi and Sb were also measured but were always under the detection limit of the method (u.l means under the limit of detection).

Table 2: Corrected lead isotopes measured in the "metal fractions" of the corroded metals around the weapons (SD: standard deviation, 2s).

NAME SAMPLE	*206/204*	*SD*	*207/204*	*SD*	*208/204*	*SD*	*208/206*	*SD*	*206/207*	*SD*
S/1747	18,038	0.004	15.566	0.003	37.935	0.008	2,1031	0.0002	1,1588	0.0001
S/1744	17,402	0.004	15.455	0.004	36.926	0.008	2,122	0.0004	1,126	0.0001
S/1820	18,566	0.006	15.652	0.005	38.659	0.013	2,0822	0.0001	1,1863	0.0001
S/1821	18,463	0.009	15.791	0.011	39.019	0.033	2,1133	0.0008	1,1693	0.0002
S/1825	18,635	0.008	15.630	0.007	38.659	0.017	2,0746	0.0001	1,1923	0.0001
S/1734	18,383	0.035	15.643	0.029	38.531	0.075	2,0959	0.0004	1,1751	0.0003

Results and Discussion

All the weapons except S/3003 are copper objects. Since Zinc and arsenic concentrations are very low, these objects are not made of brass or arsenic-copper. Intentional addition of Arsenic is defined by a concentration between 0.5 and 2% (Giumlia-Mair *et al.*, 2002). It suggests therefore that Arsenic found in the artefacts is only impurity.

Since there is no mixed Tin-Copper ores normally in the surrounding nature, even the low contents of Tin (Sn) are interpreted as intentional additions. Employment of low tin alloy during the studied period and in this region is common (Philip, 1989) and discussed briefly in Giumlia-Mair (2002). Different reasons like malleability or a recycling of scrap bronze are possible explanations.

Lead and silver are commonly associated with copper in ores and therefore only S/3003 could be considered as a leaded copper weapon.

Lead isotopes are presented in table 2 and on $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{204}Pb$ diagrams associated with the signatures of possible used copper ores (figure 1). Contrary to the metals composition, the lead isotope ratios are maintained during the metallurgical processes because there is no fractionation of these four heavy isotopes ($^{204,206,207,208}Pb$). Consequently lead isotope ratios could be used as fingerprints of the ores used to make the object. However processes like recycling or mixing of different ores could result in an artificial signature (Pollard and Heron, 1996), which would not reflect the original ore. Moreover some mining regions have the same range of isotopic values.

Despite these limitations, two samples (S/1820 and S/1825) can be associated with Turkish or Cypriot or even closer Syrian ores. One artefact (S/1747) is associated to Feinan ores, another

(S/1734) perhaps with Turkish ores. Two objects (S/1821 and S/1744) have original signatures (Gulson, 1986), especially S/1744 ($^{206}Pb/^{204}Pb$=17,402, $^{207}Pb/^{204}Pb$=15,455). This sample also has the second highest concentration of lead (>2%) and could perhaps also be viewed as a lead and copper alloy. Further examination of the objects is needed to confirm these particular features.

Conclusions

Chemical and lead isotopic analyses on metal weapons found in Sidon dated from the Middle Bronze Age show different technological aspects of ancient metallurgy in the Levant, like tin alloying or the use of ores from different provenances. Tin and in one sample lead additions are evidenced by chemical analysis. Lead isotope-ratios provided evidence of a Metals trade between Eastern Mediterranean regions during the Middle Bronze Age.

Non-destructive chemical investigations like SEM (Scanning Electron Microscope) or micro-XRF (X-ray fluorescence Spectrometry) on the non-altered weapons would give a better appreciation of their chemical composition. The same instruments would also clarify the effects of the corrosion on the samples investigated in this study.
Finally, these archaeometallurgical investigations could be related to environmental factors like harbour sediments to better understand the impact of the ancient metallurgy on human beings and their environment (cf. articles of Le Roux *et al.* and Morhange *et al.*, this issue p.).

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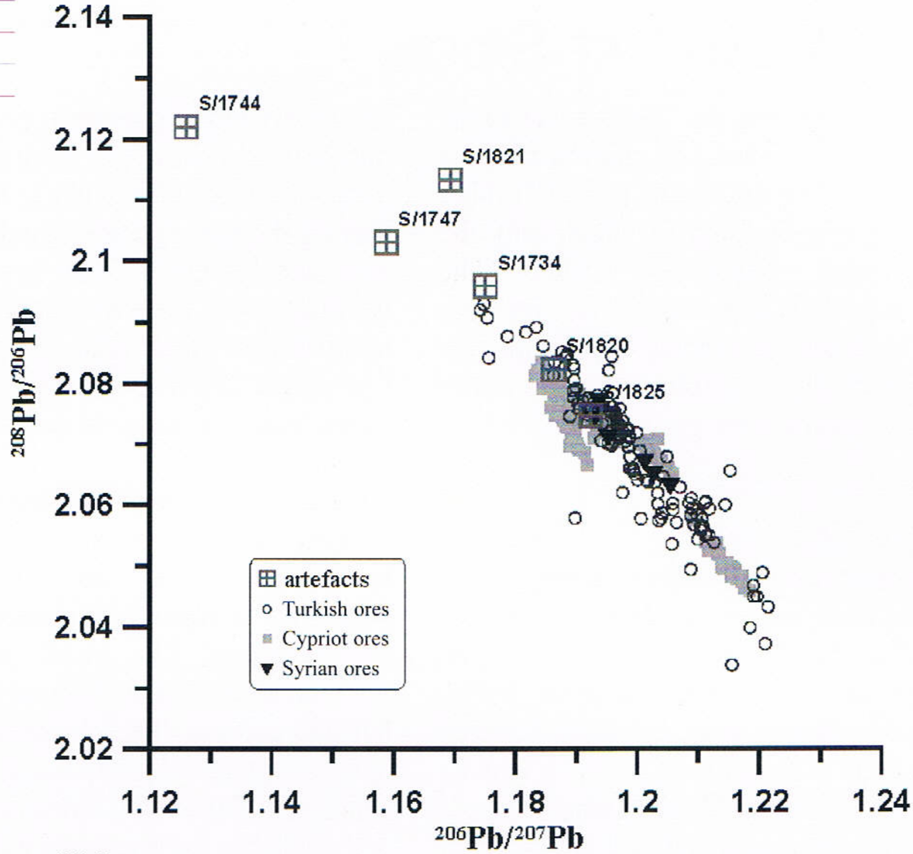
1 **$^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{204}Pb$ diagrams of the lead isotopes signatures of the metal weapons, and the signatures of possible used copper mines, for complete references about the lead isotopes database, please contact the first author.**


2.14
2.12
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^{208}Pb/^{206}Pb
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S/1744
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S/1747
S/1734
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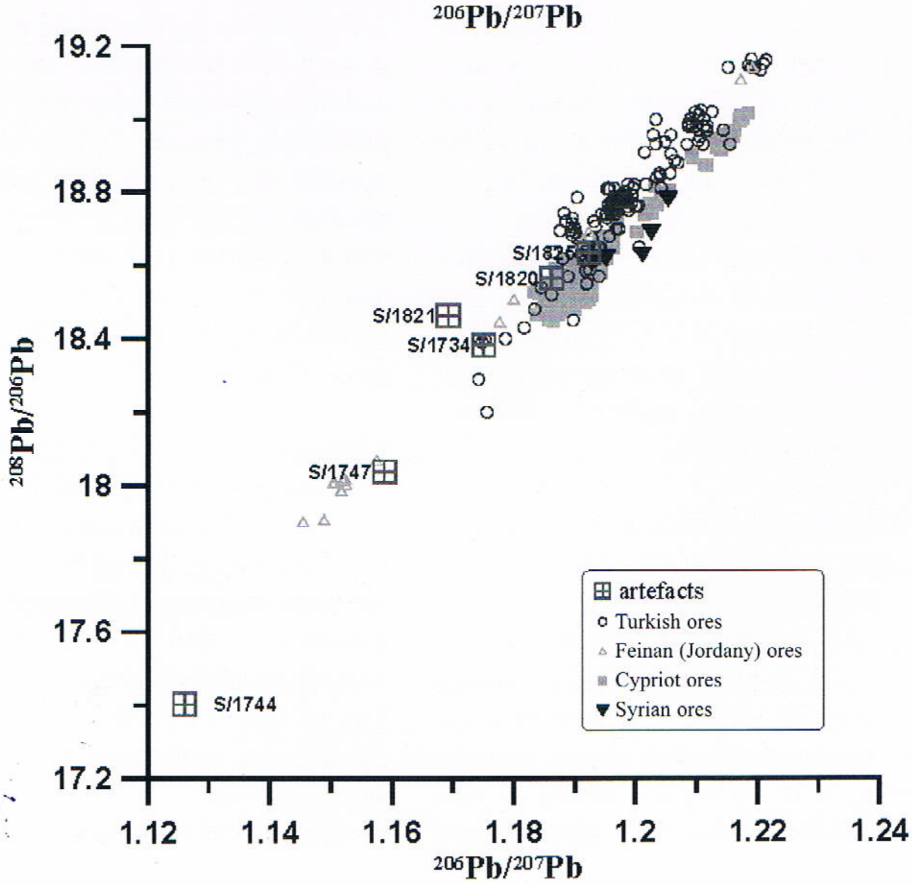
artefacts
Turkish ores
Cypriot ores
Syrian ores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^{208}Pb/^{206}Pb
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artefacts
Turkish ores
Feinan (Jordany) ores
Cypriot ores
Syrian ores