Archaeometric investigations of eagle-head buckles from Bulgaria

I Kuleff, M Junk and L Vagalinski

*ABSTRACT: Eagle-head buckles (*Adlerkopfschnallen*) are among the artefacts from the final stage of the Migration Period. Different types of eagle-head buckles were worn during the 5th–7th centuries AD, mainly by east germanic tribes. The elemental composition of eight buckles has been determined using ED-XRF. The results show that buckles were produced from brass (with 12–25% zinc). Two of the analysed objects are characterized by extremely high silver contents (10–15%). Some aspects of the production technology are elucidated on the basis of results of metallographic investigations.*

Introduction

Eagle-head buckles (*Adlerkopfschnallen*) are among the artefacts from the final stage of the Migration Period. Their name comes from the head of a bird of prey at the end of buckle's plate (see Figs 2–4). Until recently, only a single example was known from Bulgaria (Vagalinski *et al* 2000).

These buckles are classified into three types. The first includes 'standard' eagle-head buckles, found over a vast territory from the northern Black Sea littoral in the east to southern France in the west, and from northern Poland in the north to Spain in the south. Some finds perhaps belonged to late Sarmatian (Alans) women as well. Bulgarian examples date to the 6th century AD. Data for the find sites of the Bulgarian buckles (see Fig 1) support the assumption that their wearers were barbarians settled by the early Byzantine authorities in north-central and north-eastern Bulgaria to strengthen the defence of the region, a matter of strategic importance for the Byzantine capital.

The second type is called *Kaliakra* and is known at present only from NE Bulgaria (Vagalinski *et al* 2000, cat nos 8–9). Its examples are smaller and far less showy than type 1. They date from the end of the 6th century AD to the middle of the 7th century AD. Most probably these specimens were worn mainly by east germanic men in Byzantine service.

Type 3 covers the smallest (length 40–45mm) and earliest eagle-head buckles, also known as *Vogelkopfschnallen*. These items were popular in the middle Danube area during the 5th century AD and belonged to barbarian warriors, Huns and their east germanic and Sarmatian (Alamannic) vassals (Werner 1956, 72, 82, Taf 18/5; Tejral 1998, 282, Abb 41/3–5,14,16,17; Bona 1991, 283/No 77, Abb 34/C, Abb 77/1,2). Two examples are published in this paper.

The aim of the present study is to investigate eagle-head buckles from Bulgaria using energy dispersive X-ray fluorescence analysis (ED-XRF). Thus data for the chemical composition of eagle-head buckles has been obtained for the first time and the results have been used for initial interpretation of the technology of production. We hope the present survey will stimulate further research in this area.

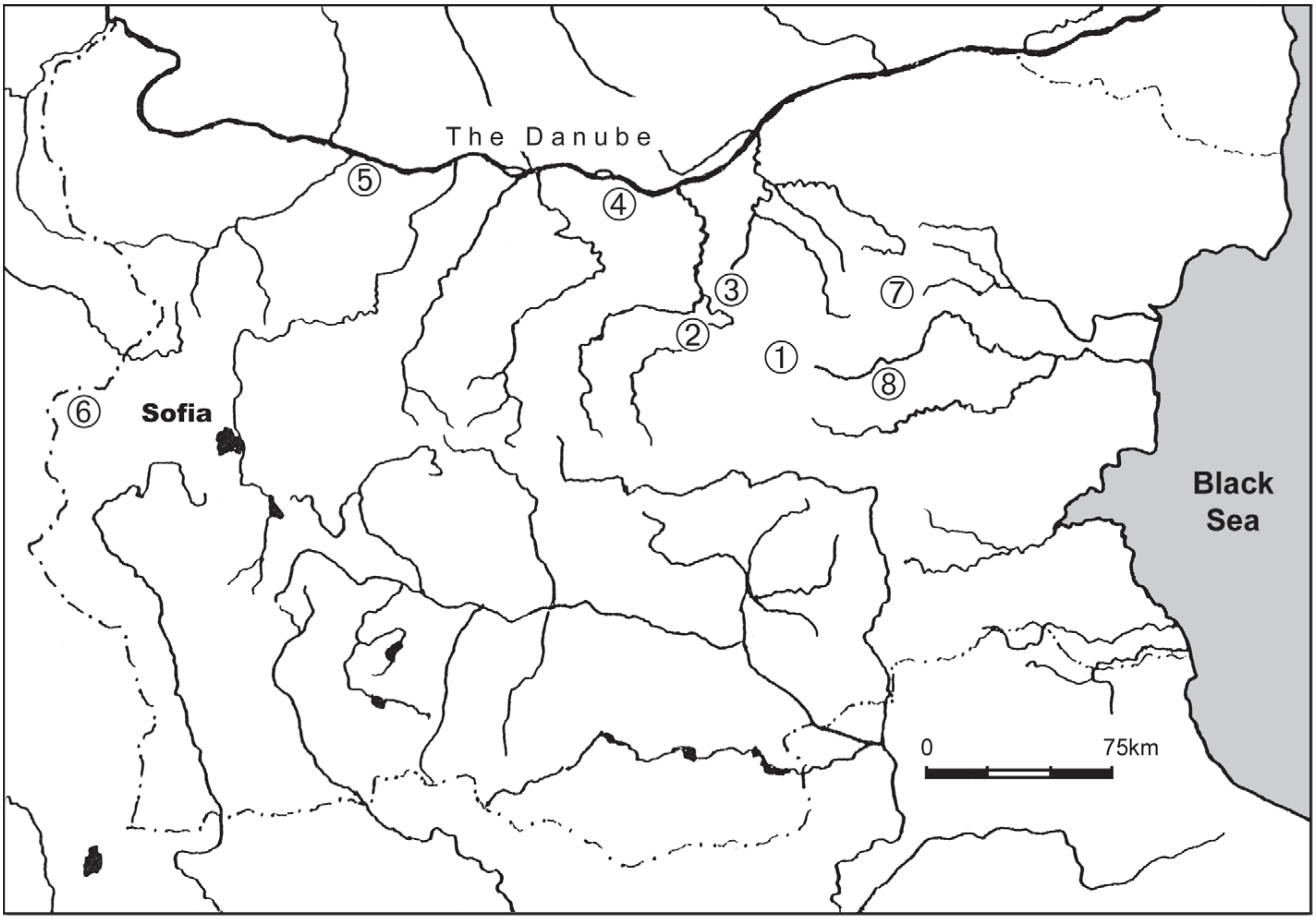

Figure 1: Find sites of eagle-head buckles in Bulgaria. 1 = village of Kostel, Veliko Turnovo district (W-B-1), 2 = Veliko Tarnovo (W-B-2), 3 = village of Gorski Goren Trumbesh, Veliko Turnovo district (W-B-3), 4 = Svishtov, Veliko Turnovo district (W-B-4), 5 = village of Leskovetz, Vratza district (W-B-5), 6 = Trun, Sofia district (W-B-6), 7 = village of Zhivkovo, Shoumen district (W-B-7), 8 = village of Rish, Shoumen district (W-B-8).

The analysed buckles

Eight buckles are investigated in the present paper. Table 1 contains a brief description of them, and the find sites in Bulgaria are shown in Figure 1. Four belong to the type 1 ('standard' eagle-head buckles). Sample W-B-3 was taken from the artefact illustrated in Figure 2. Sample W-B-1 comes from another, contemporary group of 'large buckles with rectangular plate' (see Vagalinski *et al* 2000, cat no 6) but never had an eagle head. It is included in our study because of its importance. Only one type 2 buckle (Vagalinski *et al* 2000, cat no 8) was sampled (W-B-7), and is illustrated in Figure 3.

Two examples of the third type of buckle were analysed. W-B-5 (Fig 4) was found by chance near the village of Leskovetz (ancient *Variana*) on the Danube, Vratza district, NW Bulgaria and is now kept in a private collection. This completely preserved buckle (length 41mm) has two lemon-coloured glass inlays, in the bird's eye and on the square plate. W-B-6 was found by chance in a late antique settlement at 'Tzarkvishte' in the suburbs of Tran, Sofia district, SW Bulgaria. The loop, the tongue and the two inlays are missing (preserved length 26mm). It is kept at the History Museum in Pernik.

Analytical method

ED-XRF has been used to determine the chemical composition of the buckles. Small pieces (a few milligrams) were cut from the finds and the analysis was carried out after mechanical removal of the patina by grinding (Lutz and Pernicka 1996). We used a Tracor Spectrace 5000 with a Si(Li) detector; energy resolution was 155eV at the Mn Kα line. The measurement conditions are given in Table 2. The content of the following 14 elements was determined: Ag, As, Au, Bi, Co, Cu, Fe, Ni, Pb, Sb, Se, Sn, Te, and Zn. The

Table 1: Description of the eagle-head buckles investigated.

Lab code	Find site (number in Fig 1)	Type	Dating (century AD)	Publication (cat no in Vagalinski *et al* 2000)
W-B-1	Village Kostel (1)	*	first half of 6th	6
W-B-2	Veliko Tirnovo (2)	1	6th	5
W-B-3	Gorski Goren Trumbesh (3)	1	6th	4
W-B-4	Svishtov (4)	1	6th	7
W-B-5	Village Leskovets (5)	3	5th	-
W-B-6	Tran (6)	3	5th	-
W-B-7	Village Zhivkovo (7)	2	end of 6th-mid 7th	8
W-B-8	Village Rish (8)	1	6th	2

Note: * = belongs to a contemporary group of 'large buckles with rectangular plate'

Figure 2: Big 'standard' eagle-head buckle of Type 1 (W-B-3). (Photo: K Georgiev).

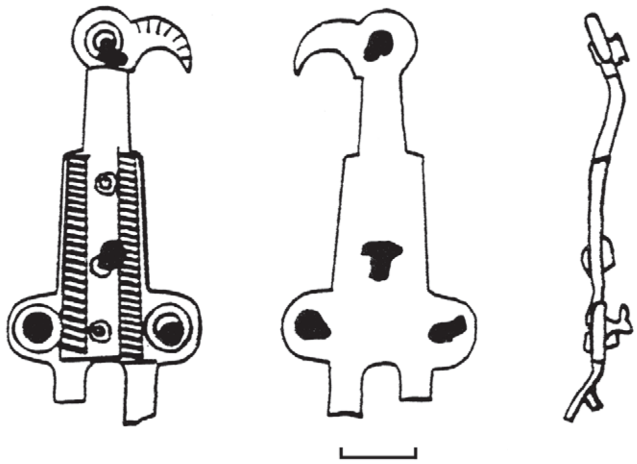

Figure 3: Eagle-head buckle of Type 2, called Kaliakra (W-B-7). Scale 1:1 (Drawing: L Vagalinski).

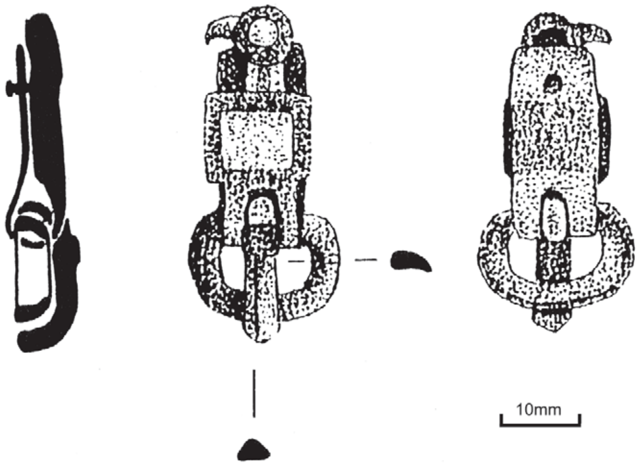

Figure 4: Small eagle-head buckle of Type 3 (sample W-B-5). Scale 1:1 (Drawing: I Cholakov).

Table 2: XRF measurement parameters

Parameter	Settings	
Energy range (keV)	6.4-15.2	22.1-31.0
Tube potential (kV)	35	50
Tube current (mA)	0.02	0.30
Filter	Rh (127μm)	Cu (630μm)
Live time (s)	500-3000	500-3000
Measured elements	Fe, Co, Ni, Cu, Zn, As, Se, Au, Pb, Bi	Ag, Sn, Sb, Te

quantification was performed using a fundamental parameter approach (Criss and Birks 1968; Broll and Tertian 1983).

Scanning electron microscopy (SEM-DSM 960 Zeiss) was used to determine the element distribution in the analysed samples which were mounted in synthetic resin, ground and polished. To increase the contrast, the metallographic sections were etched with ferric chloride (2.5g $FeCl_3$, 50ml H_2O, 5ml HCl). In some cases pre-etching with so-called three acid mixtures (63ml CH_3COOH, 27ml H_3PO_4, 10ml HNO_3) was used.

Results

Chemical analysis

The results of the analysis are given in Table 3. The analyzed finds are produced from brass with zinc concentrations between 12 and 25%. It seems that Bulgarian finds have a variety of provenances. Two of the samples (W-B-1 and W-B-2) are characterized by extremely high silver contents (11.1% and 15.1% respectively) that indicate intentional addition of silver or mixing of scrap. Another example, of type 1 (W-B-8), was probably gilded (2.8% Au on the surface) and has a relatively low silver concentration (~0.1%). Sample W-B-3 (type 1) contains 0.8% silver, but in the other samples silver is below 0.1%.

The single sample of type 2 (W-B-7) has a relatively high arsenic content (0.4%). Its 3.4% lead content is similar to that of the type 3 samples (W-B-5 and W-B-6) which have 2.6% and 6.2% lead respectively. One of these (W-B-6) also has a high tin content (4.3%). Its zinc content is quite low (11.8%). This alloy, a so-called red brass, could indicate mixing of brass with some scrap bronze. Generally speaking, sample W-B-6 is very similar in composition to the Avar copper alloy artefacts reported by Craddock (1985). This is in agreement with the proposed provenance of type 3 buckles, the middle Danube region.

Table 3: Chemical compositions of the buckles; mean and standard deviations (wt%).

Element	W-B-1	W-B-2	W-B-3	W-B-4	W-B-5	W-B-6	W-B-7	W-B-8
Cu	74.03±2.45	67.02±1.00	79.35±2.4	74.4±4.2	73.7±3.0	77.0±1.4	77.8±1.7	79.8±0.8
Zn	13.4±0.9	15.1±0.9	18.6±1.4	24.9±2.1	23.3±1.3	11.8±0.6	18.2±1.7	19.3±0.9
Ag	11.1±1.1	16.2±1.5	0.76±0.12	0.088±0.024	0.037±0.003	0.022±0.002	0.081±0.007	0.094±0.009
As	0.062±0.008	0.072±0.009	0.074±0.007	0.040±0.007	0.025±0.003	< 0.005	0.43±0.05	0.060±0.007
Au	0.23±0.03	0.67±0.08	0.025±0.07	0.03±0.01	0.09±0.02	0.12±0.02	0.040±0.009	0.012±0.003
Bi	0.007±0.004	0.008±0.003	< 0.005	< 0.005	< 0.005	0.038±0.04	< 0.005	< 0.005
Co	< 0.005	0.010±0.006	< 0.005	0.014±0.006	< 0.005	< 0.005	0.020±0.008	0.015±0.004
Fe	0.21±0.06	0.23±0.04	0.11±0.01	0.12±0.02	0.20±0.02	0.29±0.02	0.27±0.016	0.26±0.015
Ni	0.059±0.009	0.069±0.009	0.068±0.017	0.087±0.016	0.083±0.008	0.061±0.007	0.091±0.016	0.091±0.008
Pb	0.52±0.04	0.37±0.06	1.00±0.09	0.33±0.03	2.6±0.3	6.2±0.6	3.4±0.3	0.21±0.02
Sb	0.058±0.006	0.028±0.007	0.083±0.012	0.017±0.005	0.076±0.008	0.076±0.008	0.042±0.003	0.025±0.003
Se	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Sn	0.28±0.03	0.15±0.03	0.055±0.006	0.009±0.003	0.33±0.03	4.3±0.2	0.026±0.003	0.129±0.012
Te	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	0.009±0.005	< 0.008

The use of brass for the production of eagle-head buckles from Bulgaria may be accepted as indirect evidence of the assumption made by some authors (see Vagalinski *et al* 2000) that they are produced in workshops located south of the lower Danube. This assumption is supported by Craddock's results (2001), which show that during the second half of the first millennium AD, bronze remains the prevalent alloy for Slavs, Avars, and Magyars from the Carpathian Basin. For some Byzantine workshops brass is the main material for production of artefacts such as eagle-head buckles.

Regarding other elements, the two samples with high silver contents (W-B-1 and W-B-2) are not very different from the rest of the samples; only the gold content is a little higher. All samples have similar iron and nickel contents (0.1–0.3% and 0.06–0.1% respectively). The concentration of arsenic in sample W-B-7 (type 3) differs from that of the other samples, but they all belong to other types of buckles. Sample W-B-1 and samples of type 1 (W-B-2, W-B-3, W-B-8) have rather similar arsenic concentrations (about 0.065 %) and these are lower in W-B-4 and W-B-5, and below the detection level for W-B-6. All samples except W-B-6 have bismuth concentrations near the level of detection or below. The contents of antimony are 0.02–0.08% and those of selenium and tellurium are below the detection levels (0.005 and 0.008% respectively).

The data in Table 3 does not give us the possibility of proposing a mean chemical composition for each type of eagle-head buckles as there is considerable variation, even within a single type. Copper:zinc ratios are varied, as are the contents of lead, tin and silver. Whether the chemical characteristics are chronologically determined could be confirmed only by analyses of many more finds of eagle-head buckles from different places.

The chemical composition of the brass of the buckles with low contents of silver is similar to that of brass objects dated to Roman times and later that are found in Central Europe and England (Craddock 1985, Craddock and Lambert 1985, Craddock *et al* 1990, Gegus 1994, Hook and Craddock 1997, Jackson and Craddock 1995, Mortimer 1991), as well as in Egypt (4th–6th centuries AD) and Byzantium (7th–8th centuries AD) (Werner 1977).

Metallography

The polished metallographic section of sample W-B-1 showed a single-phase brass with uniformly distributed

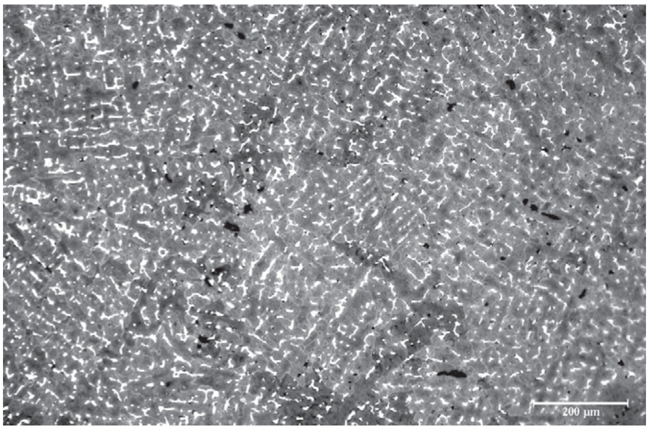

Figure 5: Etched metallographic section of silver-containing brass (W-B-2) showing a cast structure with silver dendrites. Scale bar 200μm (Photo: M Junk).

dendrites. The analysis by SEM showed that the dendrites are silver. In the etched sample a marked dendritic cast structure was visible with larger areas of same orientation. Sample W-B-2 showed a similar cored structure to W-B-1 but with a smaller dendrite arm spacing, illustrated in Figure 5.

Sample W-B-3 was a single-phase brass with microshrinkage. The grain boundaries were marked by grey globular inclusions. The etched section showed the initial coarse cast structure with microsegregation and areas of the same orientation. This structure was overlapped by slip traces.

The polished section of sample W-B-4 showed smaller inclusions than W-B-3. They were mainly found at the grain boundaries. The etched sample showed a cast structure with small dendrite arm spacing. Slip traces were found in some grains.

Sample W-B-5 was characterized by dark grey globular inclusions, which were uniformly distributed. The etched sample showed a recrystallized structure with annealing twins (Fig 6). Towards the edge of the sample slip traces were found.

Sample W-B-6 differed in its structure from the other samples. It was two-phase with a copper solid solution and a second dark grey phase. The etched sample showed a recrystallized structure with annealing twins.

Sample W-B-7 showed single-phase structure with dark grey globular and light blue inclusions that were found to be cuprite. The etched section showed remnant coring overlapped by a recrystallized structure with twins and slip traces in some grains.

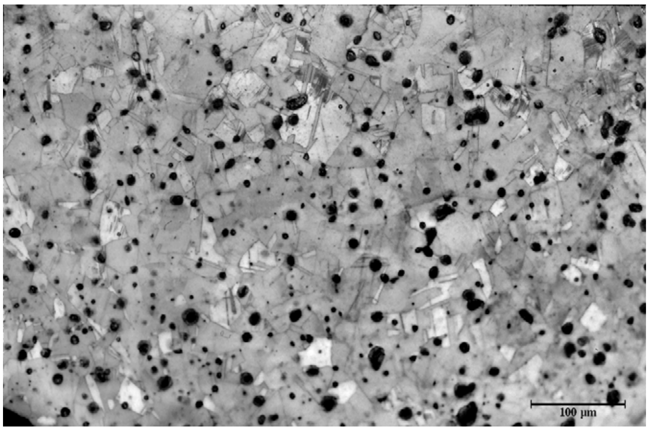

Figure 6: Etched metallographic section of brass (W-B-5) showing a recrystalized structure with annealing twins and slip traces. Scale bar 100µm (Photo: M Junk).

Sample W-B-8 showed intercrystalline corrosion. In the etched metallographic section a cast structure overlapping with slip traces was visible.

Summary

The earliest eagle head buckles (type 3) consist of brass (W-B-5) and red brass (W-B-6). The metallographic sections showed lead-rich inclusions. The basic form of the buckles was probably cast and subsequently cold worked with intermediate annealing.

The buckles of type 1 were produced by different technologies, depending on the alloy composition. The artefact made of high-silver brass (W-B-2) was left in the as-cast state (as was sample W-B-1). These alloys have low melting points and are therefore excellent for casting. In the polished state they appear silver, in contrast to common brass. The buckles made of brass (W-B-3, W-B-4, W-B-8) showed an overlapping of the dendrite cast structure with slip traces which indicate a cold deformation (*eg* hammering) of the material. Since they were found only in some grains the brass may be two-phase. In contrast to the earliest artefacts these buckles showed no evidence of annealing.

The latest buckle (type 2) was made of leaded brass (W-B-7). The cast item was likely cold worked (hammered?) and annealed. Slip traces indicated some further deformation after the annealing.

Discussion

Why did ancient craftsmen put silver in the brass? There are two possible explanations:

1. The silver was added to the brass for technological and aesthetic reasons. Silver improved the castability of brass, the metal could be polished better and, in contrast to leaded brass, it does not tarnish (the alloy is more stable against the oxidation);
2. The ancient craftsmen sought to prepare a metal which appears more valuable, but is cheaper and could be sold as silver.

Other analyses of brass show similar high silver contents (Gilmore 1980 and 1987, Gilmore and Metcalf 1998, Riederer 1975). Using AAS, Riederer analysed 17 fibulae (*Bügelfibeln*) and two belt buckles belonged to east germanic Ostrogoths. Three groups could be distinguished, based on silver and zinc contents. One of the groups has 18–28% silver and 11.8%–15.4% zinc, which is exactly the chemical composition of our buckles. The second of Riederer's groups has 77–88% silver (the rest is copper) and very low zinc concentrations (0.4–3%); the alloy is Ag-Cu. The third group contains 30–40% silver and 6–7% zinc.

This variability of silver contents is most probable not accidental. It shows that some traditional accessories of Ostrogoth costume were made from silver of high purity and others from brass containing some silver. The possibility of polishing the brass that contains silver, and the longevity of the polished surface in comparison to pure brass or brass containing lead, is one very important feature. We believe that the ancient craftsmen used this alloy because of its ability to take a durable polish. This could also probably be the explanation for adding silver to the Northumbrian coins (*stycas*) investigated by Gilmore (1980, 1987 and Gilmore and Metcalf 1998).

The second explanation is more attractive but less probable. The techniques for preparing silvery-bronze coins have been known since the end of the 2nd century AD. They were applied to copper-silver alloys as well a hundred years later (Moesta and Franke 1995, 130–132). Using such technologies copper-silver alloys with 10–20% silver can look like material with a high silver content. Such techniques could be used for the treatment of brass objects too, but our metallographic investigations of the objects with silver (W-B-1 and W-B-2) do not support this hypotheses.

Conclusion

This first archaeometric investigation of eagle-head buckles from the final stage of the Migration Period reveals they are made from brass with different chemical compositions that could be chronologically correlated. Some of the buckles of type 1 were produced with an intentional addition of silver to the brass, and others were probably gilded. These features could result from chronological differences and/or be determined by their place of manufacture. In the production of different types of eagle-head buckles different technologies were used, depending on the alloy. Some were cast, others were also subjected to cold working and annealing.

Investigation (chemical and metallographic) of further similar artefacts found in different parts of Europe would be very desirable.

Acknowledgements

The authors are indebted to Prof E Pernicka (Bergakademie, Freiberg) for valuable discussions and suggestions and for the possibility to carry out this study. We acknowledge the valuable information given by Prof Dr Riederer (Rathgen Forschungslabor, Staatliche Museen Preussischer Kulturbesitz zu Berlin), Dr G Gilmore (Nuclear Training Services Ltd, Warrington) and Dr P Craddock (British Museum, London). The authors would like to thank Mrs Wolf (TU-Bergakademie Freiberg) for preparing the metallographic samples. The authors are thankful to Mr D Dimitrov (New Bulgarian University, Sofia) and to Mrs V Paunova (History Museum at Pernik) for permission to publish samples W-B-5 and W-B-6. One of the authors (I K) is grateful to Volkswagenstiftung for financial support, which gave him the opportunity to work in the Bergakademie, Freiberg.

References

Bona I 1991, *Das Hunnenreich* (Stuttgart).

Broll N and Tertian R 1983, 'Quantitave X-ray fluorescence analysis by use of fundamental influence coefficients', *X-Ray Spectrometry* 12, 30–37.

Craddock P T 1985, 'Medieval cooper alloy production and West African bronze analyses', *Archaeometry* 27, 17–41.

Craddock P T 2001, 'Conservative metal alloyng traditions in the migration period', *Acta Metallurgica Slovaca* 7, 175–181.

Craddock P T and Lambert J 1985, 'The composition of the trappings', in I Jenkins, 'A group of silvered-bronze horse-trappings from Xanten (Castra Vetera)', *Britannia* 16, 141–164.

Craddock P T, La Niece S and Hook D 1990, 'Brass in the medieval Islamic world', in P T Craddock (ed), *2000 Years of Zinc and Brass* (London: British Museum Occasional Paper 50), 73–101.

Criss J W and Birks L S 1968, 'Calculation methods for fluorescent X-ray spectrometry, empirical coefficients vs. Fundamental parameters', *Anal Chem* 40, 1080–1086.

Gegus E 1997, 'Micro-spectrochemical analysis methods of ancient copper alloys and the organ of Aquincum', in H Eggebrecht (ed), *Proc Symp 'Organ of Classical Antiquity. The Aquincum Organ AD 228*' (Kleinblittersdorf), 92–98.

Gilmore G R 1980, 'The alloy of Northumbrian coinage in the mid-ninth century', in D M Metcalf and W A Oddy (eds), *Metallurgy in Numismatics 1* (London), 83–98.

Gilmore G R 1987, 'Metal analyses of Northumbrian stycas', in M Metcalf (ed), *Coinage in 9th Century Northumbria* (Oxford: British Archaeological Reports 180), 159–170.

Gilmore G R and Metcalf D M 1998, 'Neutron activation using a reactor', in A Oddy and M Cowell (eds), *Metallurgy in Numismatics* (London), 1–14.

Hook D and Craddock P T 1997, 'The scientific analysis of the cooper-alloy lamps: Aspects of classical alloying practices', in D M Bailey, *A Catalogue of the Lamps in the British Museum, IV. Lamps of Metal and Stone, and Lampstands* (London), 144–163.

Jackson R P J and Craddock P T 1995, 'The Ribchester hoard: A descriptive and technical study', in B Raftery (ed), *Sites and Sights of the Iron Age* (Oxford: Oxbow Monograph 56), 75–102.

Lutz J and Pernicka E 1996, 'Energy dispersive X-ray fluorescence analysis of ancient copper alloys: Empirical values for precision and accuracy', *Archaeometry* 38, 312–323.

Moesta H and Franke P R 1995, *Antike Metallurgie und Münzprägung* (Basel).

Mortimer C 1991, 'Northern European metalworking traditions in the fifth and sixth centuries AD', in P Budd, B Chapman, C Jackson, R Janaway and B Ottaway (eds), *Archaeological Sciences 1989* (Oxford: Oxbow Monograph 9), 162–168.

Riederer J 1975, 'Metallurgische Untersuchung ostgotischen Trachtzubehöres und ihre Auswertung', in V Bierbrauer (ed), *Die ostgotischen Grab- und Schatzfunde in Italien* (Spoleto), 231–238.

Tejral J 1988, 'Zur Chronologie der frühen Völkerwanderungszeit im mittleren Donauraum', *Archäologia Austriaca* 72, 223–304.

Vagalinski L, Atanassov G and Dimitrov D 2000, 'Eagle-Head Buckles from Bulgaria (6th–7th centuries)', *Archaeologia Bulgarica* 4(3), 78–91.

Werner J 1956, *Beiträge zur Archaeologie des Attila-Reiches* (München).

Werner O 1977, 'Analysen mittelalterlicher Bronzen und Messinge, Teil I. Werkstoffe und Analysen', *Archäologie und Naturwissenschaften* 1, 144–220.

The authors

I Kuleff
Address: Faculty of Chemistry, University of Sofia, 1 James Bouchier Ave, BG-1126 Sofia, Bulgaria.
E-mail: kuleff@chem.uni-sofia.bg

M Junk
Address: Lehrstuhl für Archäometallurgie, TU – Bergakademie Freiberg, Gustav-Zeuner Str. 5, D-09596 Freiberg, Germany.

L Vagalinski
Address: Archaeological Institute with Museum by Bulgarian Academy of Sciences, 2 Saborna St., BG-1000-Sofia, Bulgaria.