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Early bronze in two Holocene archaeological sites in Gansu, NW China

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ABSTRACT

Understanding of the origin and development of bronze technology in eastern Asia remains unresolved. Here we report on the distribution of copper and associated cations in sediments from Huoshiliang in northwestern Gansu, China, strontium and lead isotope analyses of ore and slag samples, and some artifact fragments at archaeological sites at Ganggangwa and Huoshiliang in the Black River valley.

We conclude that bronze production began perhaps as early as 2135 BC and that the Baishantang modern mine site at Dingxin was a possible source of copper ore. There was at least one other, but currently unidentified, source of ore. The Bronze Age people were also farmers and planted cereals such as wheat, and they may have abandoned the region when wood was exhausted and desertification took over.

Introduction

The ability to use metal was a great leap forward for weapon manufacture and made farming much easier. Initially, the principal metal was copper and its earliest identifications were associated with farming in Iran and Turkey. The use of copper began at least around 7250–6750 BC (Moorey, 1994) and smelting became common from about 4000 BC (Craddock, 1995; De Ryck et al., 2005). Bronze is an alloy of copper and tin, occasionally containing arsenic or antimony, and is harder and more resilient than copper. The development of bronze technology was complex and therefore a considerable step. Arsenic bronze appeared in Anatolia around 3300 BC (e.g. Potts, 1997), in India a few hundred years later, and an additional 500–600 yr later in Europe and China (Higham, 1996). Lee et al. (2008) have claimed that increases in concentration of Cu, Ni, Pb and Zn in Hubei lake sediments may indicate the beginnings of the Bronze Age in ancient China at about 3000 BC, but this is not associated with any clear archaeological site. It is not clear if bronze technology was invented in several places independently, or whether the technology was transferred from a single centre of origin. The complexity of the process suggests technological transfer is the favoured hypothesis.

In China, bronze first appears during the Xia Dynasty (a controversial term), or possibly the early Shang Dynasty (Liu, 2004; Thorp, 2005). In fact few sites have been dated in China, and until this is done questions regarding technology transfer, local invention, or even the origin of the technology in China remain open. The earliest metals identified are fragments of copper and bronze alloys associated with the Qijia and Siba cultures in Gansu. These possibly date between 2250 and 1900 BC (Thorp, 2005). However, based on current established evidence, the Bronze Age appears to have started first near Erlitou in Henan (near Zhengzhou). The Erlitou culture (ca. 1900–1500 BC) is well defined by pottery, ritual jades and cast bronze vessels, dated to roughly 1900 BC. Some bronze appeared before this date, according to Linduff et al. (2000), and bronze and/or copper objects have been found at several Longshan culture sites (ca. 2500–2000 BC) in the middle and lower Yellow River valley. A tin alloyed bronze knife has been unearthed at Dongxiang, with a supposed date of about 3000 BC, assigned on the basis that it is from the Majiayao culture (Sun and Han, 2000a,b).

Leaded bronze predominated amongst metal objects by the end of the Erlitou record (Jin, 2003; Jin et al., 2003). The lead included in it may have been brought from Shandong (Jin et al., 2003), whereas during the early and middle Shang period bronze may have been introduced from as far away as Sichuan or Yunnan where the lead isotopes of objects have similar isotopic signatures (Jin et al., 2003).

Recent archaeological studies in Gansu in northwest China have revealed many new finds of early metals. These include ornaments, knives, rings, hemispherical objects, spearheads and more (Mei, 2004; Sun and Han, 2000a,b). Commonly, these have been dated by referring to the culture they were associated with. The earliest of these are related to the Qijia culture which was centered on the Gansu–Qinghai–Mongolia region. Slag at these sites has been used to infer local manufacture near ore bodies (Gansu Museum, 1960). It is believed that the Qijia culture crossed from the Neolithic into the Bronze Age (Shui, 2001). While the data on metallurgy in northwest China grows, there is little objective evidence to clarify the possible origin of indigenous bronze technology or whether it was imported from the west.

By the time of the Erligang culture, 1600–1300 BC, usage of bronze was widespread in China. The fact that the oldest known dates may be in the Hexi Corridor region of Gansu is tentative evidence that east–west exchange of technology, perhaps along with cereals, may have occurred. The topography and distribution of deserts in the Hexi region of northwest China suggest the main corridor of travel was north of the

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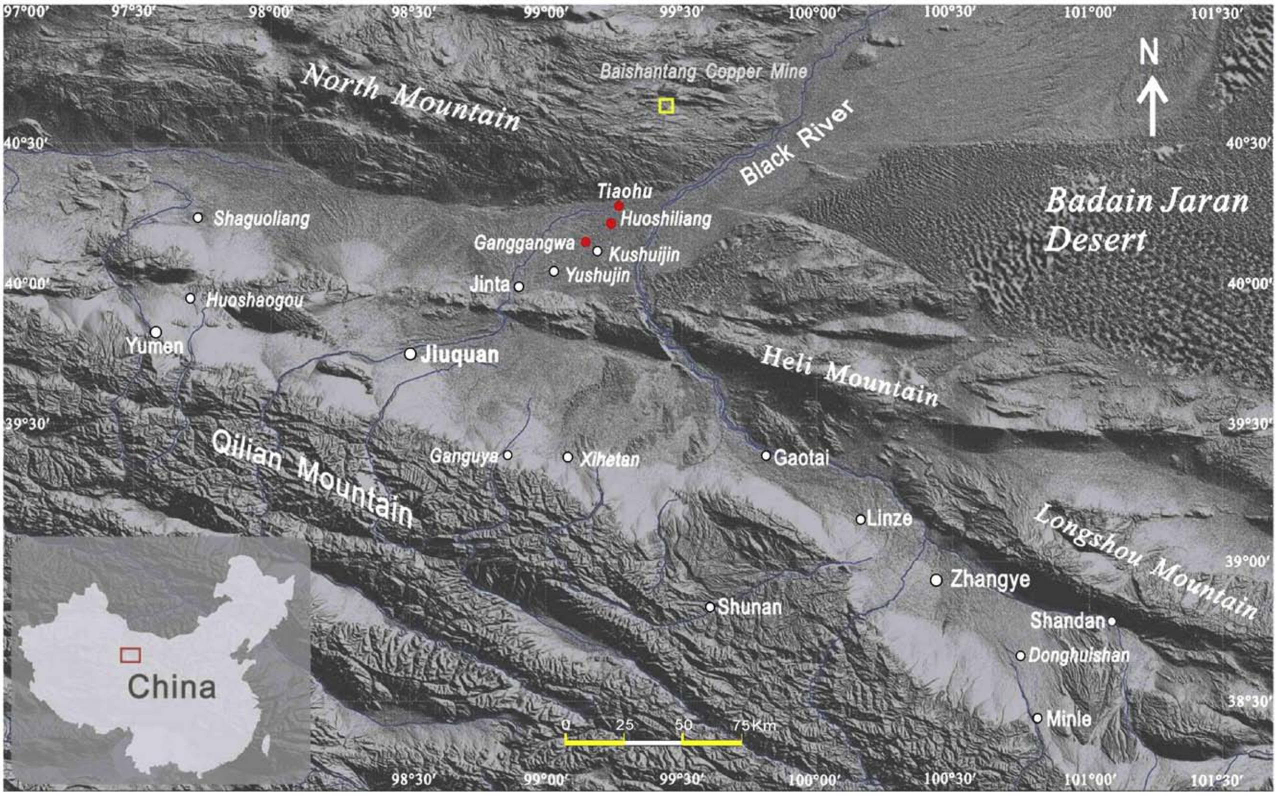

Figure 1. Map of the Hexi Corridor region of northwestern China showing location of study sites and key geographic features mentioned in the text.

Qilian Mountains and in the middle and lower reaches of the Yellow River. The topography and distribution of deserts in the Hexi region of northwest China suggest that the main corridor of travel was north of the Qilian Mountains and in the middle and lower reaches of the Yellow River. More dates on archaeological sites of mid Holocene age or younger are needed to help address this hypothesis. In particular, more data are needed on the nature and origins of early metal usage.

Hypotheses on the origins of metal artifacts were originally based on form and functional similarities. Later, chemical fingerprinting of metals and potential ore sources was developed and comparative interpretations were applied (e.g. Kuleff and Pernicka, 1995; Olariu et al., 1999; Spoto et al., 2000). This often led to problematic interpretations because of the chemical variability in ores and differences in techniques of manufacture.

Brill and Wampler (1965) were the first to recognize the potential of and perform lead isotope measurements to study the provenance of bronze, copper and glass samples, while Gale and Stos-Gale (1982) were amongst the first to apply lead isotope analysis for sourcing copper used in ancient societies after comparative chemical analyses had largely failed to provide insights into this problem.

Lead has several stable isotopes but only ^{204}Pb does not have a route from radioactive decay chains. Thus Earth has the same amount

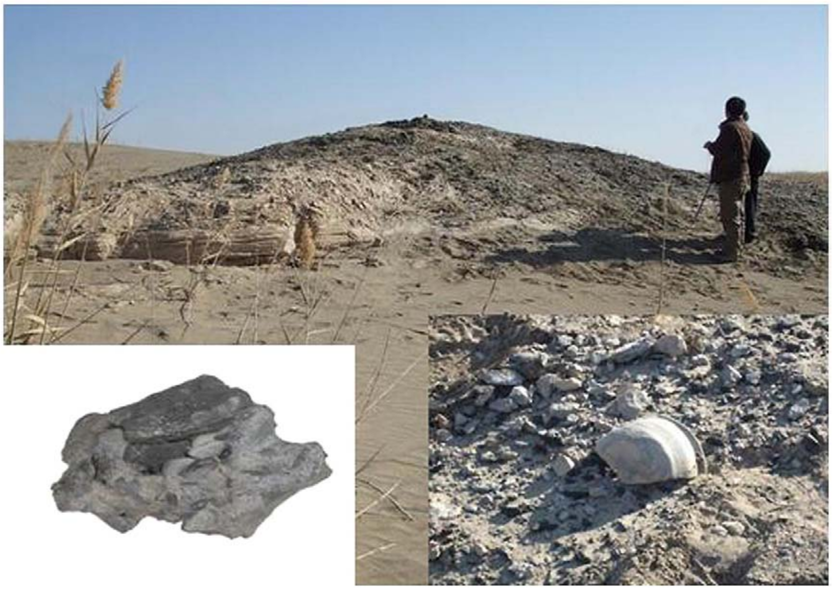

Figure 2. Presumed smelt site at Ganggangwa, northwestern Gansu. The inset shows surface detail with charcoal and smelt.

of this isotope since its formation. Other stable isotopes of lead result from uranium series decay. The isotopes ^{207}Pb, ^{208}Pb and ^{206}Pb are final decay products of U and Th with the decay chains beginning from ^{238}U, ^{235}U and ^{232}Th respectively. The ratios of ^{208}Pb, ^{207}Pb and ^{206}Pb to ^{204}Pb therefore reflect the amount of lead in the environment, the starting amount of U and Th, and the age of the sample. Oceanic basalts for example have ratios of about 17.8–18.8 for ^{207}Pb/^{204}Pb because of the relatively large amount of uranium and thorium in the ocean (Tatsumoto, 1966), and the same rule will apply to other sites with high uranium content. The lead isotope ratios therefore have considerable use in fingerprinting likely sources of a sample.

Strontium has two relatively abundant stable isotopes with masses of 86 and 87. Both had starting abundances set at the formation of Earth. This provides another technique for provenance studies. The primordial ratio was about 0.699 (Faure and Powell, 1972). Strontium has chemistry very similar to calcium and is found in a wide range of minerals. ^{87}Sr has an additional source; it is formed by β-decay of ^{87}Rb and thus ^{87}Sr values have generally increased in time (^{87}Rb half-life = 4.88 x10^{10}yrs). Rubidium has chemistry similar to potassium and thus a component of ^{87}Sr in a material will reflect a different set of weathering, deposition and other pathways compared to primordial ^{87}Sr. The ^{87}Sr/^{86}Sr ratio value of a sample therefore reflects an inheritance from the past and strontium 87/86 ratios will theoretically differ in materials that have different ages and origins.

Present study

The aim of this study is to determine for the Hexi Corridor ages, possible sources of ore and possible evidence of bronze production in the form of artifact pieces. Random samples of slag and copper ore were collected from the hundreds present from two archaeological sites in northwestern Gansu Province (Fig. 1). The sites are extensive surface scatters of pottery, bone, seeds, charcoal and other materials including copper ore and slag. There are several cultural and lake sediment sequences in the region that provide an opportunity to examine time series of cation composition to assess possible evidence of metal working.

The scatter sites occupy several thousand square meters and are known as Ganggangwa and Huoshiliang. Such sites are common amongst the dunes of the area but no systematic excavations have been done. The deposits are possibly, in part, lag deposits left from the shifting dunes. Several charcoal and seed samples were collected at each site and radiocarbon dates were obtained to estimate the site ages. There are a small number of raised mounds with abundant charcoal and slag (Fig. 2). Two charcoal samples from slag sites were also submitted for radiocarbon dating. In one case the charcoal was embedded in a piece of slag (see inset in Fig. 2).

At Huoshiliang cultural sediments were excavated to about 2 m depth. We chose this opportunity to use fossil charcoal to determine the age of the sites and measured a number of geochemical parameters to help determine whether there was trace evidence of metal smelting.

Lead and strontium isotope analysis was carried out on four slag and ore samples selected from the Ganggangwa and Huoshiliang archaeological sites in order to test whether the ores and slag from the ores had a similar provenance. Presently, a productive copper mine is located nearby at Baishantang near Dingxin (see Fig. 1) and is the only known copper ore site within 100 km of the study sites. Samples of ore at the mine were collected for isotope analyses to check if the

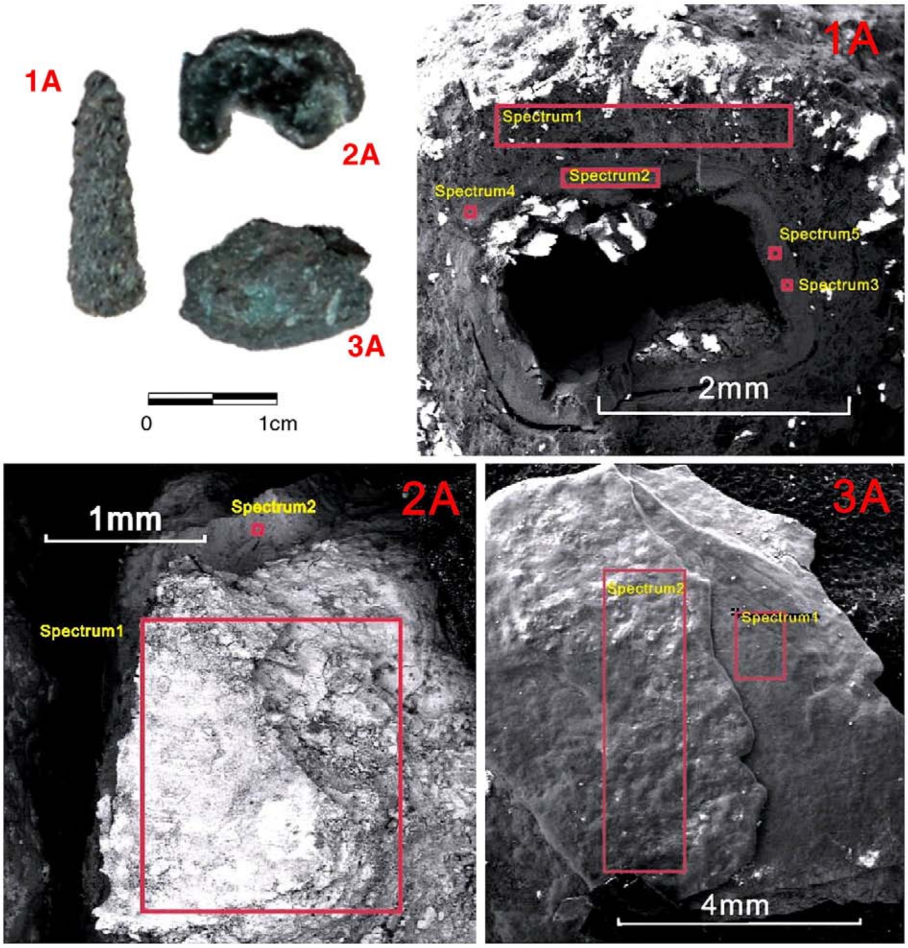

Figure 3. Three artifact pieces from Huoshiliang showing the location of the spectra for energy dispersive X-ray (EDS) analysis.

Table 1
Accelerator mass spectrometry (AMS) dates from Huoshiliang (HSL), and Ganggangwa (GGW).

Sample location, depth and code	Sample type	Lab. no.	$\delta^{13}C$ (‰)	Radiocarbon age (^{14}C yr BP)	Calibrated age range (Cal yr BC, 2σ)
GGW-1	Charcoal	OZK657	−23.7 ± 0.1	3735 ± 50	2292–2015
GGW-2	Wheat seed	OZK658	−23.2 ± 0.1	3560 ± 50	2026–1766
GGW-3	Charcoal[a]	OZK659	−25.0	1560 ± 120	841–730
HSL (0–5 cm)	Charcoal	OZK596	−224.4 ± 0.1	3520 ± 60	1976–1733
HSL (40–45 cm)	Charcoal	OZK597	−21.8 ± 0.1	3540 ± 50	1980–1745
HSL (80–85 cm)	Charcoal	OZK598	−24.7 ± 0.1	3565 ± 50	2032–1757
HSL (140–145 cm)	Charcoal	OZK599	−24.9 ± 0.1	3510 ± 50	1957–1730
HSL (163 cm)	Charcoal	OZK600	−24.7 ± 0.1	3600 ± 60	2135–1869
HSL-4	Wheat seed	OZK603	−22.9 ± 0.1	3635 ± 45	2135–1895

All assays were run on the STAR Accelerator, ANSTO, Australia. Calibrations refer to the Radiocarbon Calibration Program (Reimer et al., 2004).

[a] Small sample, $\delta^{13}C$ estimated and small mass correction applied to sample

archaeological sites had possibly used chalcopyrite and malachite from Baishantang.

Separate dissolutions were done for the Sr and Pb isotope analyses. The samples were dissolved in HF-HNO_3 in Teflon bombs for 48 h at ~175 °C. For the Sr chemistry, the samples were dried and then redissolved in 4 N HC1. All samples produced clear solutions and after drying again, the samples were dissolved in 2 M HNO_3, and centrifuged before elution through Eichrome® Sr-spec resin columns. The samples were loaded in a HNO_3–H_3PO_4 solution onto single outgassed Ta filaments and analyzed using a Finnigan 261 mass spectrometer. Mass fractionation during the analysis were corrected by normalizing the isotopic compositions to $^{86}Sr/^{88}Sr = 0.1194$. The composition of the NBS-987 Sr isotope standard measured on this instrument is $^{87}Sr/^{86}Sr = 0.71020 \pm 0.00002$.

After dissolution of the sample in HF-HNO_3, the solution was dried and brought up in 1 ml of 0.8 N HBr. Lead forms an anionic complex in HBr that is retained on Biorad AG-1X8 anion exchange resin. The sample was loaded on 150 µg of resin, washed several times with HBr to remove U and other elements, and the Pb was eluted with 8 N HC1. This solution was dried on a hotplate, brought up again in 1 ml of 2% HNO3, and spiked with 100 ppb of the NIST 997 thallium isotopic standard ($^{205}T1/^{203}T1 = 2.38$ m^3) for instrumental mass bias corrections to the Pb isotopic ratios. Isotopic compositions were measured on a Finnigan Neptune multi-collector ICPMS using a quartz concentric nebuliser and double-pass spray chamber to aspirate the sample into the plasma. Corrections for ^{204}Hg interferences were applied by measuring ^{202}Hg and assuming $^{204}Hg/^{202}Hg = 0.23$. Analyses of unknowns were interspersed with analyses of the common Pb standard NBS-981. More detail of the methodology are given in Theriault and Davis (2000) and Deniel and Pin (2001).

The cation analyses from the Huoshiliang cultural sediments were carried out on air-dried and powdered samples. For the latter, about 5 g was compacted into a disc with 32 cm diameter under 30 tf/m^2 for measurement by Axios advanced wavelength dispersive X-ray fluorescence at the Institute of Earth Environment, Chinese Academy of Sciences in Xi'an. Calibration of results was carried out by using 28 carefully chosen international reference samples, and analytical precision was tested by parallel analysis of national standard GSS-8. Thus precision was better than 1–2% for major elements and better than 5–10% for trace elements.

Ore samples from Baishantang (4), Huoshiliang (1) and Ganggangwa (2) were ground and analyzed by X-ray diffraction to determine the main chemical components. Fragments of artifacts found at Huoshiliang (Fig. 3) were clearly worked by human hands and their composition was analyzed by energy dispersive X-ray analysis (EDS) under a scanning electron microscope.

The charcoal, seed and organic matter samples were pretreated by washing in 10% NaOH and 10% HCl and reduced to neutral pH. They were then converted to graphite and radiocarbon ages were calculated after measurement in the STAR Accelerator at the Australian Nuclear Science and Technology Organisation. The ages were corrected from $\delta^{13}C$ values measured on graphite derived from the same fraction that was used for the radiocarbon measurement.

Results

The radiocarbon results associated with the seeds and charcoal associated with slag at Ganggangwa and Huoshiliang are presented in Table 1. The description of ages below follows the calibrated ages described in Reimer et al. (2004). The results indicate that the archaeological material is up to 3700 yr old and that smelting was being carried out as late as 1300 yr ago. Indeed the whole suite of radiocarbon ages is remarkably consistent for a site that is essentially a surface scatter. The dated seeds are of wheat and therefore it is probable that the sites were farming villages. The results of radiocarbon determinations from sediments of the Huoshiliang cultural sediment sections are also shown in Table 1.

Huoshiliang sediments are silts and muds and above about 160 cm contain evidence of human impact through fragments of pottery and abundant charcoal. The radiocarbon ages (Table 1) suggest rapid sedimentation of the top 160 cm within about 400 yr between 1730 BC and 2135 BC. The lower sediments are lake clays, probably older than about 2200 BC and these contain no clear signals of local human occupation.

Figure 4 shows the geochemical measurements for Cu, As, Zn, Pb, Ni and Fe through the Huoshiliang sediment section. Cu, As and Zn show significant upward trends from about 2100 BC. The period after about 160 cm depth defines a section with relatively high Cu values. Lead, Ni and Fe show little variation by comparison. Values of Cu and As are highest at about 100 cm depth (calibrated age of about 1800 BC). These sediments are about 100 km from any known copper source and since Cu and As can be key components in bronze manufacture we hypothesize that first occurrence of Cu and As in the sediments arose from smelting and runoff into the site between about 2135 and 1869 BC. The records for Zn, Pb, Ni and Fe also show small

Table 2
Huoshiliang cultural sediments, correlation coefficients.

	As	Pb	Zn	Ni	Fe
a. Section 1: Holocene samples with low copper values (below 160 cm depth)					
Cu	NS	NS	NS	NS	NS
As		NS	NS	NS	NS
Pb			0.752	NS	0.691
Zn				NS	0.906
Ni					0.752
b. Section 2: Holocene samples with high copper values (above 160 cm depth)					
Cu	.415	NS	NS	NS	NS
As		NS	NS	NS	NS
Pb			−0.391	0.547	0.558
Zn				−0.564	−0.723
Ni					0.922

NS = not significant at $P \leq 0.05$.

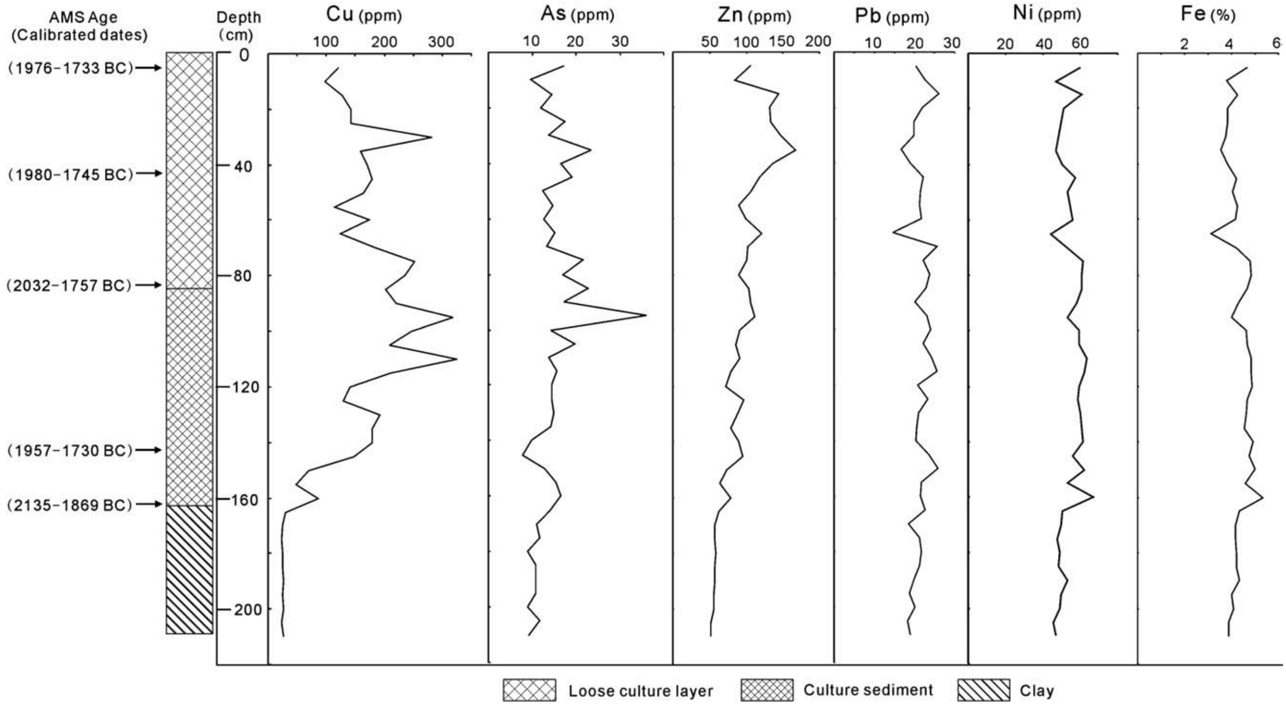

Figure 4. Cation profiles in Huoshiliang sediments.

peaks at this time possibly indicating the beginning of an increase in erosion. This may have been caused by human impact on the vegetation through the use of agriculture or domesticated animals, as evidenced by abundant sheep bones at the site.

At Huoshiliang, Cu is not significantly correlated with any cations if copper values were low (Table 2a) (i.e. below 160 cm depth), but become significantly correlated with arsenic if copper values were high (Table 2b) (i.e. above 160 cm depth). Copper and arsenic were not correlated with the other cations measured. In all samples the statistics indicate there were depositional relationships between Pb, Ni, Fe and Zn, but none of these showed any association with Cu or As, suggesting the sources of the cations differed throughout the record.

X-ray diffraction analysis of the ore samples from Baishantang (4 samples), Huoshiliang (1 sample) and Ganggangwa (2 samples) confirmed they were dominated by quartz (generally >70%, but some were as low as 22–29% quartz). Copper was present as chalcopyrite, botallacktite, atacamite, delafossite and malachite, and was quite variable with values generally between 0 and 4%, but in three cases mineral values above 10% were measured.

Elemental analysis using EDS for the three artifact samples from Huoshiliang is shown in Table 3. The areas where the elemental spectra were measured are shown in Figure 3. The results demonstrate that Cu is the most abundant element (although Si and O were high in some samples — values not presented here) and As was present in all samples. Tin was only observed in Huoshiliang 1. These confirm that the samples are bronze.

The results of the strontium and lead isotope analyses are shown in Table 4. One sample, Ganggangwa 3S, had a very high $^{87}Sr/^{86}Sr$ ratio compared to the others. This probably indicates it was located near a radioactive source containing ^{87}Rb. A group of independent *t*-tests on the means of the groups shows that means are not significantly different for the Baishantang, Huoshiliang or Ganggangwa samples excluding sample 3 of the latter.

Lead isotope analyses (Table 4) reveal that most samples have Pb 207/204 ratios of about 15.5 to 15.6. With a ratio of 17.4, Ganggangwa 3S was an exception. Although the means were not significantly different, their range was reduced when Ganggangwa 3S was excluded from the analysis. The relatively high 87Sr and 207Pb values for Ganggangwa 3S are strong evidence that the sample did not originate from Baishantang, whereas the other samples from the archaeological sites possibly did come from Baishantang.

The relatively high ^{87}Sr and ^{207}Pb values for Ganggangwa 3S are strong evidence that it did not originate from Baishantang, whereas the other samples from the archaeological sites possibly did come from Baishantang.

Discussion

The EDS analyses confirm that the artifacts are bronze with copper and arsenic, although these elements combined with tin can also be present. We suggest that the earliest record of possible bronze manufacture in the study region comes from elevated copper and arsenic values in the sediment from Huoshiliang sediments and possible charcoal associated with slag. The sediment material is from about 2200 BC and is associated with increased sedimentation rates, which may indicate increased disturbance of soils in the catchment. Since copper and arsenic have no likely local sources and are either not or negatively correlated with other cations, human involvement in

Table 3
Elemental analysis for (selected elements) using EDS on three artifact pieces from Huoshiliang relative units.

Sample (and number of EDS spectra)	Cu, ppm	As, ppm	Sn, ppm	Al, %	Fe, %	Mg, %	Ca, %	K, %
Huoshiliang 1A (5)	37.5–77.5	0.4–0.9	0.4–1.2	1.1–1.5	0.7–1.0	0	0.6–1.2	0
Huoshiliang 2A (2)	47.1–86.3	0.6–2.3	0	0	0.4–0.8	0	0.3–0.4	0
Huoshiliang 3A (2)	9.4–32.9	0.3–2.4	0	3.0–6.0	0.6–1.6	1.7–2.3	0.9–2.3	0.4–1.0

The values show the observed range in composition and are rounded to one decimal point.

Table 4
Results of isotope analyses on ore (O) and slag (S) samples.

Results of strontium and lead isotope analyses				
Sample #	$^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$	$^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$	$^{207}\mathrm{Pb}/^{204}\mathrm{Pb}$	$^{208}\mathrm{Pb}/^{204}\mathrm{Pb}$
Baishantang 1O	0.754	18.522	15.643	38.430
Baishantang 2O	0.713	18.235	15.635	38.182
Baishantang 3O	0.756	18.707	15.662	38.584
Baishantang 4O	0.721	18.677	15.672	38.569
Ganggangwa 1O	0.713	18.964	15.705	38.349
Ganggangwa 2S	0.713	17.826	15.546	38.035
Ganggangwa 3S	3.846	59.081	17.403	40.940
Ganggangwa 4S	0.713	18.418	15.625	38.360
Huoshiliang 1O	0.714	18.235	15.637	38.198
Huoshiliang 2O	0.714	18.223	15.623	38.150
Huoshiliang 3S	0.714	18.324	15.644	38.249
Huoshiliang 4S	0.714	18.285	15.640	38.242

Notes:
(1) Measured $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios (± 2 S.E), normalized to $^{86}\mathrm{Sr}/^{88}\mathrm{Sr} = 0.1194$.
(2) The $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios are reported relative to a value of 0.71022 ± 10 ($\pm 2\sigma$) the NBS standard SRM987.
(3) The errors show the uncertainty ($\pm 2\sigma$) for the last significant figures in the reported ratios.
(4) The lead isotopes are reported relative to the NBS-981 standard.

their increase is likely. We hypothesize that local bronze manufacture became visible in the sediments at about 2200 BC.

Direct radiocarbon ages on charcoal associated with slag range from about 2000 BC and last until about 700 AD. These are later than the dates from the sediment age estimate from Huoshiliang. No charcoal younger than 700 AD and associated with slag has been identified.

Some of the charcoal in the slag mounds is 5 cm or more in diameter suggesting substantial areas of woody vegetation occurred around the sites. Today the region is dominated by sand dunes and occasional grasses and sparse shrubs are present. There is no reliable wood supply and it is tempting to suggest that the archaeological sites were abandoned once the wood supply was exhausted.

The communities that occupied the sites also practiced cropping and animal husbandry, with horse and sheep bones being common. Cereal grains from wheat and millet have been identified and dated. The seed date in Table 1 is from wheat and has an age of 3800 BP, contemporaneous with the direct date of evidence of slag.

The lead and strontium isotope records suggest at least two sources of ore were used in the area. From the small sample of analyses it seems possible that the major source of ore was from the nearby Baishantang mine site. The enriched sample (Ganggangwa 3S) has not been provenanced but suggests either there is at least another unidentified ore source nearby or that trading of commodities with other people was practiced. This sample was from a location with a considerable amount of uranium present. There are no known copper sources with high uranium content in the region although Guo et al. (2005) believe that Mesozoic to Cainozoic basins in Gansu may be potential uranium mineralization sites.

While the present study contains evidence of copper-based metallurgy as early as about 2200 BC as reported for the Qijia and Sibu cultures (Thorp, 2005), it also shows that Gansu was a possible key region for the spread of bronze technology into eastern China. The dates from Ganggangwa and Huoshiliang do not go close to challenging even earlier dates for bronze which are known from Anatolia.

Here we conclude that the ore at the modern mine site of Baishantang was a likely source for bronze manufacture in the region, but that there were other ore sources as well. Further work on other potential ore sources is needed to provide a data base to support further archaeological investigations. A vast number of archaeological sites in Gansu, Xinjiang and elsewhere in the northwest of China are poorly studied and they are likely fruitful areas of investigation to broaden our knowledge of the technology and cultural development of eastern Asia.

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References

Brill, R.H., Wampler, J.M., 1965. In: Young, W.J. (Ed.), Application of Science in Examination of Works of Art. Boston Museum of Fine Arts, Boston, p. 155.

Craddock, P.T., 1995. Early Metal Mining and Production. Edinburgh University Press, Edinburgh.

Deniel, C., Pin, C., 2001. Single-stage method for the simultaneous isolation of lead and strontium from silicate samples for isotopic measurements. Analytica Chimica Acta 426, 95–103.

De Ryck, I., Adriaens, A., Adams, F.A., 2005. An overview of Mesopotamian bronze metallurgy during the 3rd millennium BC. Journal of Cultural Heritage 6, 261–268.

Faure, G.., Powell, J.L., 1972. Strontium Isotope Geology. Springer-Verlag, New York.

Gale, N.H., Stos-Gale, Z.A., 1982. Bronze Age copper sources in the Mediterranean: a new approach. Science 216, 11–19.

Gansu, Museum, 1960. Gansu Wuwei Huangniangniang tai yizi fajue baogao. Kaogu Xuebao 2, 53–71 (in Chinese).

Guo, Q., Chen, Z., Liu, H., 2005. Evolution of Mesozoic to Cenozoic basins in the Beishan–Gansu corridor region with respect to uranium ore formation. In: Mao, J.-W., Bierlein, F.P. (Eds.), Mineral Deposit Research. Meeting the Global Challenge. Springer, Berlin.

Higham, C., 1996. The Bronze Age of South Asia. Cambridge World Archaeology, Cambridge.

Jin, Z.-Y., 2003. Achievements in applying Pb-isotope analysis to ancient Chinese bronzes. Acta Geoscientica Sinica 24, 548–551.

Jin, Z.Y., Zheng, G., Hirao, Y., Hayakawa, Y., Chase, W.T., 2003. Lead Isotope Study of Early Chinese Bronze Objects. Show Forum: The Humanities Study, Bureau of International Co-Operative Chinese Academy of Social Sciences.

Kuleff, I., Pernicka, E., 1995. Instrumental neutron activation analysis of native copper — some methodological considerations. Journal of Radioanalytical and Nuclear Chemistry 191, 145–161.

Lee, C.S.L., Qi, S-H., Zhang, G., Luo, C-L., Zhao, L.Y.L., Li, X-D., 2008. Seven thousand years of records on the mining and utilization of metals from lake sediments in central China. Environmental Science and Technology 42, 4732–4738.

Linduff, K.M., Han, R., Sun, S.-H. (Eds.), 2000. The Beginning of Metallurgy in China. The Edwin Mellen Press, New York.

Liu, L., 2004. The Chinese Neolithic: Trajectories to Early States. Cambridge University Press, Cambridge.

Mei, Jianjun, 2004. Early copper-based metallurgy in China: old question, new perspective. Bulletin of Archaeology, The University of Kanazawa 27, 109–118.

Moorey, P.R.S., 1994. Ancient Mesopotamian Materials and Industries: The Archaeological Evidence. Oxford University Press, Oxford.

Olariu, A., Constantinescu, M., Constantinescu, O., Badica, T., Popescu, I.V., Besliu, C., Leahu, D., 1999. Trace analysis of ancient gold objects using radiochemical neutron activation analysis. Journal of Radioanalytical and Nuclear Chemistry 240, 261–267.

Potts, D.T., 1997. Mesopotamian Civilization, the Material Foundations. The Athlone Press, London.

Reimer, P.J., Baillie, M.G., Bard, E., et al., 2004. Intcal04 terrestrial radiocarbon age calibration, 0–26 cal kyr BP. Radiocarbon 46, 1029–1058.

Shui, T., 2001. Papers on the Bronze Age Archaeology of Northwest China. Science Press, Beijing (in Chinese).

Spoto, G., Ciliberto, E., Allen, G.C., Younes, C.M., Piccardo, P., Pinasco, M.R., Stagno, E., Ienco, M.G., Maggi, R., 2000. Chemical and structural properties of ancient metallic artefacts: multitechnique approach to the study of early bronzes. British Corrosion Journal 35, 43–47.

Sun, S.-Y., Han, R., 2000a. A preliminary study of early Chinese copper and bronze artefacts. In: Linduff, K.M., Han, R., Sun, S.-H. (eds.). The Beginning of Metallurgy in China. The Edwin Mellen Press, New York.

Sun, S.-H., Han, R., 2000b. A study of casting and manufacturing techniques of early copper and bronze artifacts found in Gansu. In: Linduff, K.M., Rubin, H, Sun, S.-H. (Eds.). The Beginning of Metallurgy in China. The Edwin Mellen Press, New York.

Tatsumoto, M., 1966. Genetic relations of oceanic basalts as indicated by lead isotopes. Science 153, 1094–1101.

Thériault, R.J., Davis, W.J., 2000. Rapid extraction of Sr and Pb by ion-specific chromatography for thermal ionization mass spectrometry: an update. Geological Survey of Canada, Current Research 2000-F1; Radiogenic Age and Isotopic Studies: Report 13, pp. 3.

Thorp, R.L., 2005. China in the Early Bronze Age. Shang Civilization. Pennsylvania University Press, Philadelphia.