Elemental composition and microstructure analysis of archaeological copper from Central Ganga Valley, India

Sidharth Shankar Rai*

Department of History, Babasaheb Bhimrao Ambedkar University, Lucknow 226 025, India

Copper alloys from an early-historic period site Kausambi, Uttar Pradesh, India were studied to understand the manufacturing technology and alloying practices through elemental analysis and microstructural examination. Most of the analysed samples were tin bronzes, and microstructure examination demonstrated casting, forging and annealing procedures adopted in manufacturing. Arsenic was absent in most of the samples, which may be due to recycling of the metal and awareness regarding the health hazards of this element among artisans. It is suggested that arsenic was not intentionally mixed in archaeological copper. On the other hand, tin was added in different quantities to meet the desired physical properties of the end-products. It is reported that copper metallurgy was developed in due course of time as a specialized craft in the Central Gangetic Valley, India and artisans of this region had mastered the copper-alloy technology since the early historic period.

Keywords: Archaeometallurgy, copper alloys, early historic period, elemental composition, microstructure analysis.

IN the Indian subcontinent, there is distinctive chronology of the Chalcolithic period and Copper–Bronze Age. Copper metallurgy in the Indian subcontinent developed uninterruptedly from the prehistoric Chalcolithic tradition to the advanced alloy tradition. Copper technology in the Ganga Valley is parallel to the integration era of the Harappan civilization. It is remarkable that in one part of the Indian subcontinent, there was Chalcolithic period and at the same time in other regions, there was Copper–Bronze Age. This tendency indicates separate metallurgical traditions practised in the broader zone which indeed meet at some point of time leading towards a steady development of metallurgy in the Indian subcontinent. This has been possible due to extended, trance-regional prehistoric and exchange networks spread extensively across the Indian subcontinent. The rivers and tributaries in this zone were useful to establish the vital line of exchange networks with neighbouring isolated hilly and forest areas which were prolific in raw materials and have developed close interaction with adjacent localities[1]. Lahiri[2] conducted a detailed analysis of such aspects in a seminal work on Indian trade routes. The Ganga Valley, India is vital to understanding ancient metallurgical practices. This region appears like a crossroad for different geographical zones of the country.

Evidences of Chalcolithic culture in this region are found from more than 150 sites. The large-sized Chalcolithic settlements like Manjhi, Oriup, Chirand, Chechar Kutubpur, Senuwar, Maner, Sonpur, Taradih, Khairadih, Imlidih Khurd, Narahan, Sohgaura, Kakoria, Lahuradeva, Jhusi in the Central Ganga Valley were inhabited around 2nd millennium BCE. From these sites, continuous habitation from the Neolithic period onwards is seen which sheds significant light on the beginning of the metallurgical tradition in the Ganga Valley. From most of the sites, copper was found from historical and early historic strata. The inhabitants of these sites played a significant role at the beginning of the metallurgical tradition by establishing resource access networks. The raw materials used by these people exhibit the extent of their regional and trans-regional networks[3].

Most of the discussion on this topic is limited to textual analysis rather than scientific examinations of archaeological findings. Comprehensive surveys of copper resources and their utilization have been conducted by several researchers[4–6]. Primary scientific analyses of copper artefacts from the sites of this region have been carried out and reported at a small scale. Such reports represent a minimal number of studies about historical and early historic copper artefacts from Rajghat, Ayodhya[7], Senuwar[8,9], Chirand, Narhan[9,10] and Agiabir[11]. These pioneering studies have been conducted through elemental analysis and metallography techniques.

Site and samples

Remains of the fortified city of Kausambi are found on the left bank of River Yamuna near the modern city of Prayagraj, Uttar Pradesh (UP), India (Figure 1)[12]. Excavations at Kausambi have revealed five cultural periods of habitation[13]. Period IV (6th–1st *c*. BCE) of Kausambi is

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*e-mail: sidsrai@gmail.com

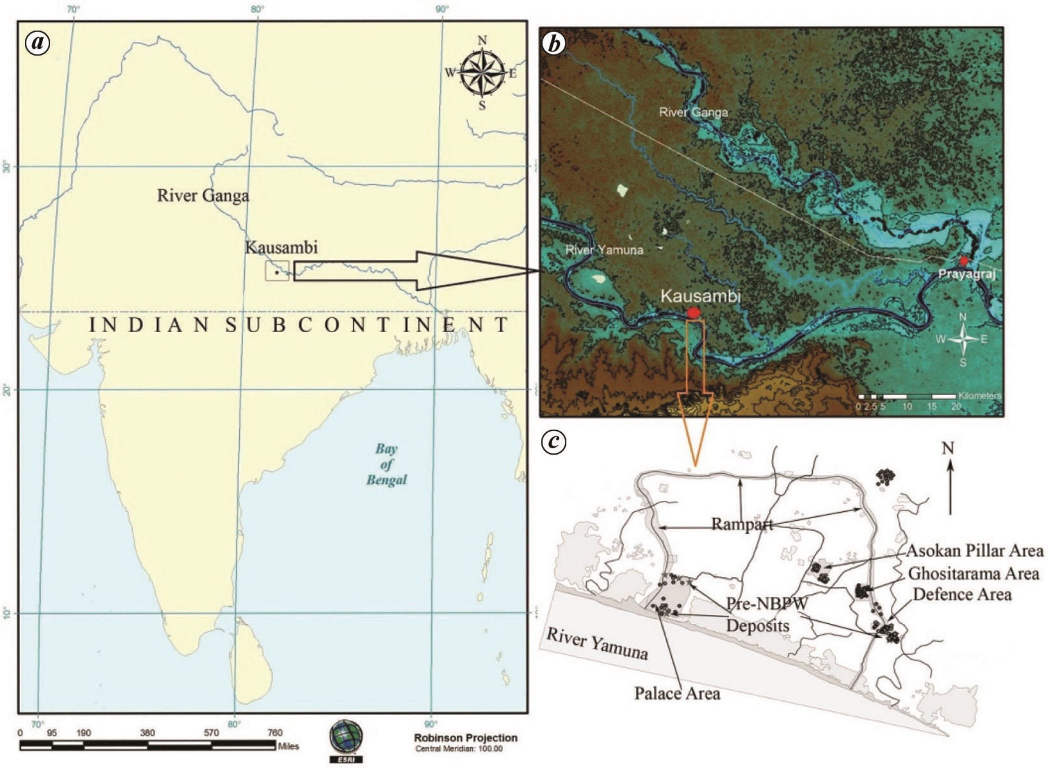


Figure 1. Map of the Indian subcontinent (***a***) showing Kausambi (***b***) and fortified area (***c***) (after Rai *et al.*)[39].

characterized by northern black polished ware (NBPW). This period witnessed large-scale constructions in Kausambi. It is pertinent to mention that during the historical period, people travelling to Vidisha, Saket and Shravasti had to pass through this area. That is why Kausambi appears as the junction of crossroads in this region. Bhita on the right bank of River Yamuna, near Kausambi, was a famous port site used for riverine trade in the historical period[14].

Kausambi is significant for the study of early interactions among Deccan Chalcolithic, Ganga Valley and Vindhya regions. Excavations at Kausambi have revealed several types of artefacts, viz. beads of different materials, potteries, metal objects, ivory, semi-precious stones, etc. Among metal artefacts, several copper and iron tools were recovered. Ten samples from the layer of 600–400 BCE of Kausambi have been selected for this study (Figure 2), to understand historical period metallurgy and the extent of alloying practices in the Ganga Valley.

Methodology

One of the most critical needs of archaeological science is the application of modern analytical methods. The primary objective of material analysis in archaeology is to obtain information regarding the mode of production, distribution, use, technology of manufacturing, and adaptation of production technology[15]. The study of metallic artefacts through elemental analysis provides valuable information regarding alloying practices and provenance. In contrast, metallography addresses the manufacturing technology, use and discard mechanism and functional aspects of an object[16].

Metallography

Metallography is the art of examining the microstructure of metals. Electron and optical microscopes are widely used to study metal microstructure and understand the manufacturing technology of ancient metal objects. Such analysis helps trace ancient technological competence, resource access and the resource-use pattern of ancient people. Metallography provides valuable details on grain structure, boundaries, inclusion pattern along with composition, solidification processes and thermo-mechanical treatment processes[17,18]. There are about five steps involved in sample preparation, viz. sectioning, mounting, grinding, polishing and etching[19]. These steps are followed, in sequence to produce a scratch-free, flat, smooth and mirror-like surface. The polished but unetched sample exhibits no microstructural details due to the absence of any contrast-producing features on the surface. However, it can provide valuable information about macroscopic cracks, pits and erosion. After polishing, samples are etched to reveal microstructural features of interest. The light microscope produces coloured

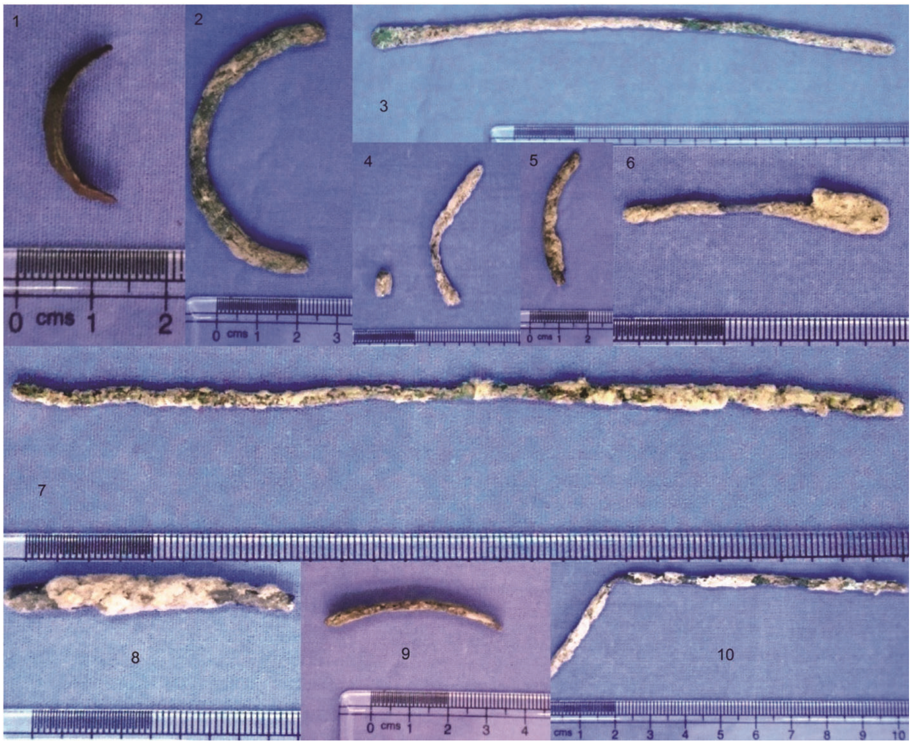


Figure 2. The Kausambi samples analysed and discussed in this study.

images of moderate resolution. The resolution is limited because metallurgical microscopes use light optics.

Scanning electron microscopy and X-ray microanalysis

The resolution limitation of the optical microscope can be solved with an electron microscope. The electron microscopy has revolutionized the micro-level investigations and proved their importance in archaeological and materials science[12,20]. The electron microscope uses electron optics instead of light optics which provides a very high resolution. In the scanning electron microscope (SEM), characteristic X-rays are generated when the electron beam interacts with the inner-shell electrons of the atoms present at the surface of the specimen. These X-rays are further used to form an image and for elemental quantification of the samples. The images formed by electron microscopes are black and white, but colours can be added to enhance their aesthetic value (Figure 3 *b*). Using an electron microscope images are mainly formed by secondary and back-scattered electrons (BSEs). Secondary electrons provide seamless topographic images with surface contours, whereas BSEs generated photomicrographs provide the relative density of the phases present at the sample surface. Both types of images are equally useful for metallography. BSE imaging is a potent tool for metallography. The as-polished specimen, which does not show much contrast, can be easily viewed in BSE image mode. The specimen prepared for optical microscope can be analysed directly using SEM without any additional sample preparation.

The most significant advantage of SEM in metallography is its ability of imaging at sub-micron scale and simultaneous quantitative elemental analysis with attached energy dispersive spectrometer (EDS) or wavelength dispersive spectrometer (WDS) detectors. Recent advances in detector technology and highly efficient silicon drift detectors (SDDs) have made quantitative analysis more precise and accurate.

Sample preparation and analysis

Ten samples from Kausambi were analysed at the Nano-Phosphor Application Centre, University of Allahabad, UP and Indian Institute of Technology Gandhinagar, Gujarat. The samples were tiny, and to avoid any thermal-induced changes, they were cold-mounted with acrylic in moulds. After mounting, the samples were ground with 1000 and 1500 grit size SiC paper and polished with 5μ alumina suspension. Special attention was given to avoid edge rounding of the samples. For final polishing, 3μ diamond paste and fine polishing velvet cloth made of synthetic fibres were used. Finally, aqueous solution of ferric chloride was used for etching. The samples were studied using an optical microscope (Leica) and SEM (JEOL JSM 7600 FE-SEM with Oxford Silicon Drift Detectors EDS system). Table 1 presents the analytical

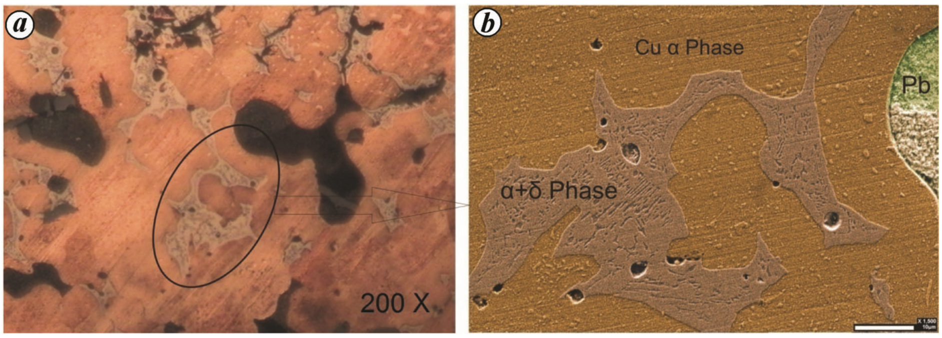


Figure 3. Microstructure of sample 1. (***a***) Optical metallograph; the circular area is examined using scanning electron microscope (SEM) and (***b***) SEM image showing Cuα phase, $\alpha + \delta$ eutectoid structure, lead globule and micro-shrinkage in $\alpha + \delta$ phase.

results. The combined use of an optical microscope and SEM is helpful in the study of metal samples because the same regions of interest can be observed in both instruments. In order to analyse significant microstructural features, marks were indented at the sample stub with metallic ink during observation in the optical microscope; the same marks were used to relocate the region of interest in SEM. The analysed artefacts of Kausambi are shown in Figure 2, which includes fragments of rings (1, 9), bangles (2, 4, 5), hook (6), nails (3, 7) and rods (8, 10). The rings and bangles were for ornamental purposes, while hooks and nails for utilitarian purposes. Nails and rods were multipurpose objects, used as finished products or intermediate products for further processing.

Results and discussion

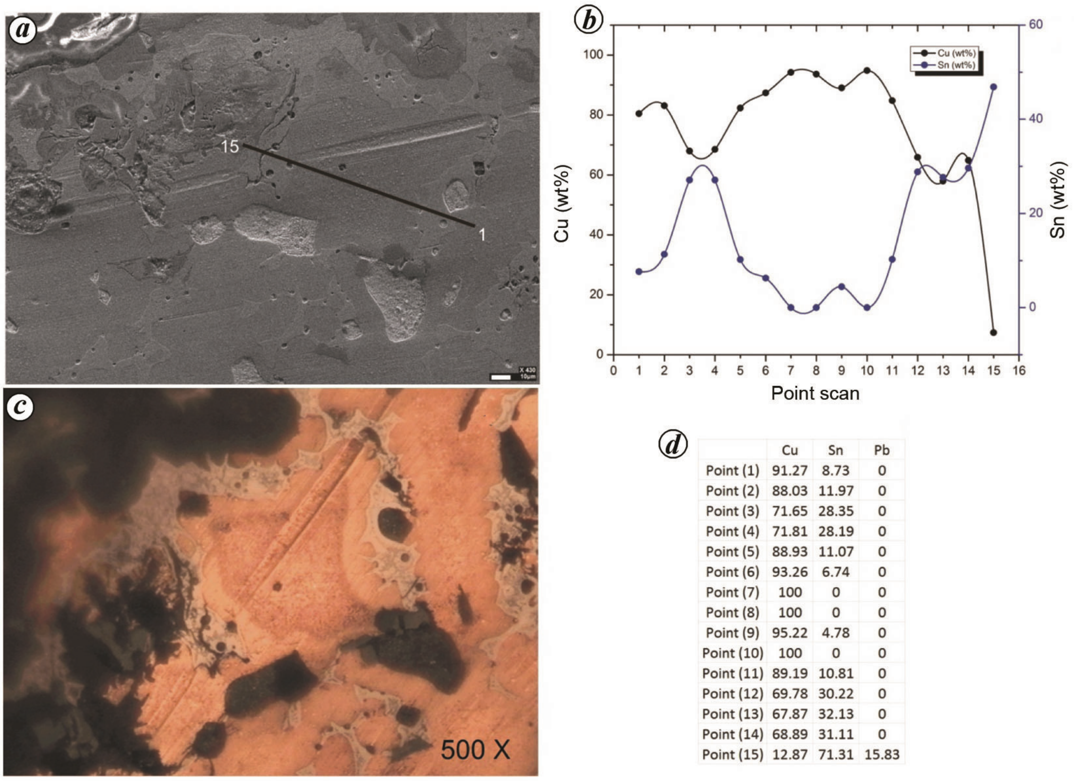
The elemental composition suggested that samples 1 and 2 were binary Cu–Sn alloy and sample 3 was unalloyed copper with some inclusions. Metallographic examinations of these three samples was conducted. The microstructure of sample 1 exhibited a typical as-cast structure of binary $\alpha + \delta$ eutectoid Cu–Sn alloy. Copper and tin are partially soluble in each other and form a solid solution in two-phase system; thus they may have many metallic and intermetallic phases. In the microstructure of sample 1, the Cu-rich α-phase was surrounded by the Sn-rich phase. The SEM–EDS characterization exhibited remarkable segregation of δ-phase Sn. There was highest concentration of Sn in the δ-region. The $\alpha + \delta$ eutectoid structure and small globules of Pb particles were distributed in the entire microstructure of the sample. Such type of microstructure is formed during slow cooling of metals under normal conditions. The small-sized pores are visible in $\alpha + \delta$ eutectoid structure (Figure 3 *b*). These micro-shrinkages are formed due to gas-bubble formation in the liquid where it floats. If no liquid surface is available to discharge, gas-bubble interacts with the solid–liquid interface[21]. Also, it has negative effect on quality and mechanical properties of an alloy, if formed in large amounts.

The δ-phase Sn in the sample is critical because it increases the hardness and wear resistance of the metal. The amount of Pb is significant in this sample. The composition profile obtained through EDS on 15 points of Cu-rich grain showed that in the middle of the grain, there was 100% Cu while towards the periphery there was an increase in the Sn content, finally, the δ-phase segregates (Figure 4). During sand-cast solidification, copper solidifies first and forms the α-phase of 100% pure copper. Further solidification initiates the formation of Cu + β Sn-phase, and finally, Sn segregates and forms the $\alpha + \delta$ phase. This study demonstrates that for ring fabrication bronze was used and sand casting under normal cooling condition was preferred. The alloy thus prepared was hard, workable up to some extent and was a perfect choice for objects like a ring.

Optical metallography of sample 2 exhibits an as-cast structure of bronze (Figure 5). This sample was a little corroded. The amount of Sn was moderate, and Pb globules were visible in limited quantities. The Cu-rich grains were rounded, suggesting a slow cooling rate. This microstructure presents a compelling case because Sn and Pb contents are present in ample amounts, but $\alpha + \delta$ phase is not visible. Pb is present as a small globule and Sn is localized around the Cu grains. Probably this was the result of Sn precipitation due to annealing at moderate temperature. In the microstructure, strain lines are visible, indicating that the alloy was worked by hammering and annealing to prepare the final product. It appears that artisans made semi-finished bangles by the casting method and further shaped them with annealing at moderate temperature and hammering. A similar technique was observed in a Narahan bangle[9]. The optical metallograph of sample 6 shows a cast structure of the homogenous Cu–Sn alloy. A *V* shaped, bent, inter-crystalline crack was observed in the sample (Figure 6). This sample was made of arsenical copper, as evident from EDS analysis (Figure 7).

Table 1. Elemental data of samples obtained from Kausambi, Uttar Pradesh, India (6th–1st century BCE)

Sample no.	Object	Zn	Cu	Sn	C	O	Al	Pb	As	S	Fe	Cl	Sb
1/a	Ring	0	79.72	6.61	11.01	2.66	0	0	0	0	0	0	0
1/b	Ring	0	69.75	10.5	6.87	6.09	0	6.19	0	0	0	0.59	0
1/c	Ring	0	80.23	5.39	11.5	2.88	0	0	0	0	0	0	0
2/a	Bangle	0	78.16	5.52	12.27	4.06	0	0	0	0	0	0	0
2/b	Bangle	0	79.79	4.4	12.34	3.46	0	0	0	0	0	0	0
3/a	Nail	0	88.07	0	9.41	1.77	0.75	0	0	0	0	0	0
3/b	Nail	0	88.25	0	9.19	2.56	0	0	0	0	0	0	0
4/a	Bangle	0	70.48	7.33	16.25	5.98	0	0	0	0	0	0	0
4/b	Bangle	0	77.64	7.46	12.22	2.68	0	0	0	0	0	0	0
5/a	Bangle	0	74.27	9.02	12.8	3.91	0	0	0	0	0	0	0
5/b	Bangle	0	74.28	7.33	12.65	5.75	0	0	0	0	0	0	0
6/a	Hook	0	71.03	11.12	11.79	2.62	0	0	1.72	1.73	0	0	0
6/b	Hook	0	77.08	6.11	11.61	3.08	0.56	0	1.55	0	0	0	0
6/c	Hook	0	74.48	12.92	8.92	3.69	0	0	0	0	0	0	0
7/a	Nail	0	81.45	0	14.05	4.51	0	0	0	0	0	0	0
7/b	Nail	0	84.3	0	11.83	3.87	0	0	0	0	0	0	0
8/a	Rod	0	58.02	23.92	12.6	5.46	0	0	0	0	0	0	0
8/b	Rod	0	56.25	26.85	12.95	3.96	0	0	0	0	0	0	0
8/c	Rod	0	69.42	21.2	6.74	0	0	0	0	0	0	0	2.64
9/a	Ring	14.99	67.97	0	8.68	3.82	0.63	2.57	0	0	1.33	0	0
9/b	Ring	14.53	68.77	1.21	8.31	3.87	0	3.31	0	0	0	0	0
10/a	Fragment of rod (?)	0	79.13	11.3	6.56	3.01	0	0	0	0	0	0	0
10/b	Fragment of rod (?)	0	78.18	11.04	8.64	2.14	0	0	0	0	0	0	0



	Cu	Sn	Pb
Point (1)	91.27	8.73	0
Point (2)	88.03	11.97	0
Point (3)	71.65	28.35	0
Point (4)	71.81	28.19	0
Point (5)	88.93	11.07	0
Point (6)	93.26	6.74	0
Point (7)	100	0	0
Point (8)	100	0	0
Point (9)	95.22	4.78	0
Point (10)	100	0	0
Point (11)	89.19	10.81	0
Point (12)	69.78	30.22	0
Point (13)	67.87	32.13	0
Point (14)	68.89	31.11	0
Point (15)	12.87	71.31	15.83

Figure 4. ***a***, Fifteen point scans were performed along the line to understand the elemental composition profile of Cu grain. ***b***, Results of 15 point line scan. ***c***, Optical metallograph of Cu grain, showing Sn segregation at the boundaries in sample 1. Colour differences in Cu grain are visible, which indicates the solidification process. The same grain was analysed using SEM-EDS. ***d***, Wt% quantitative data.

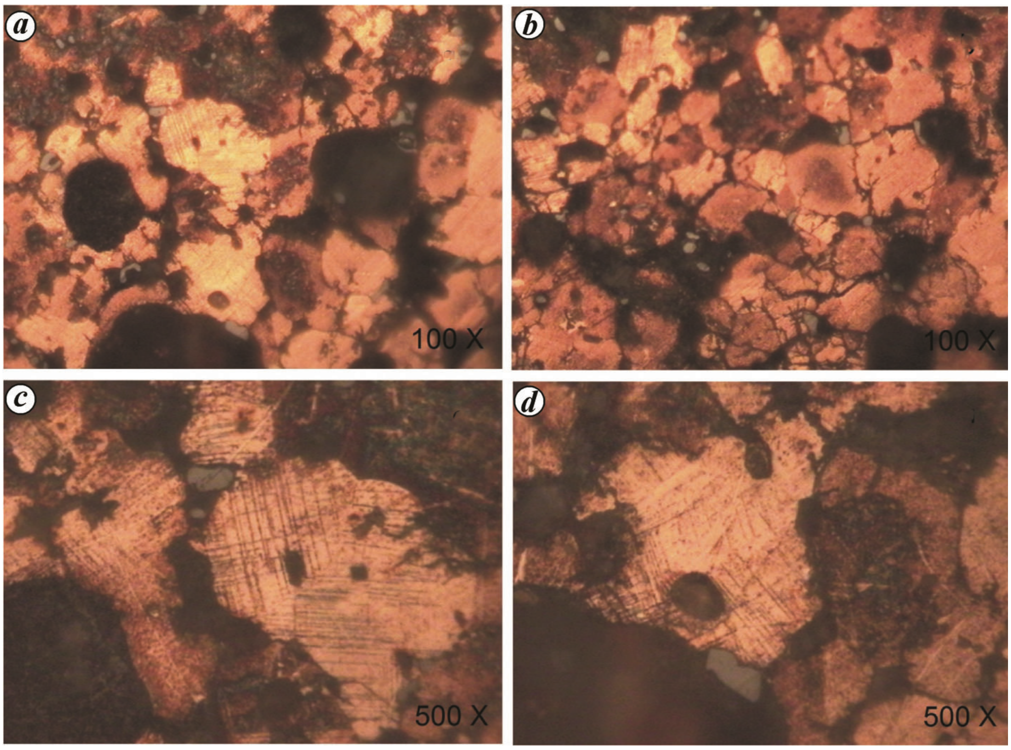


Figure 5. ***a***, ***b***, The microstructure of sample 2 at different magnifications. ***c***, ***d***, The strain lines are visible on copper grain.

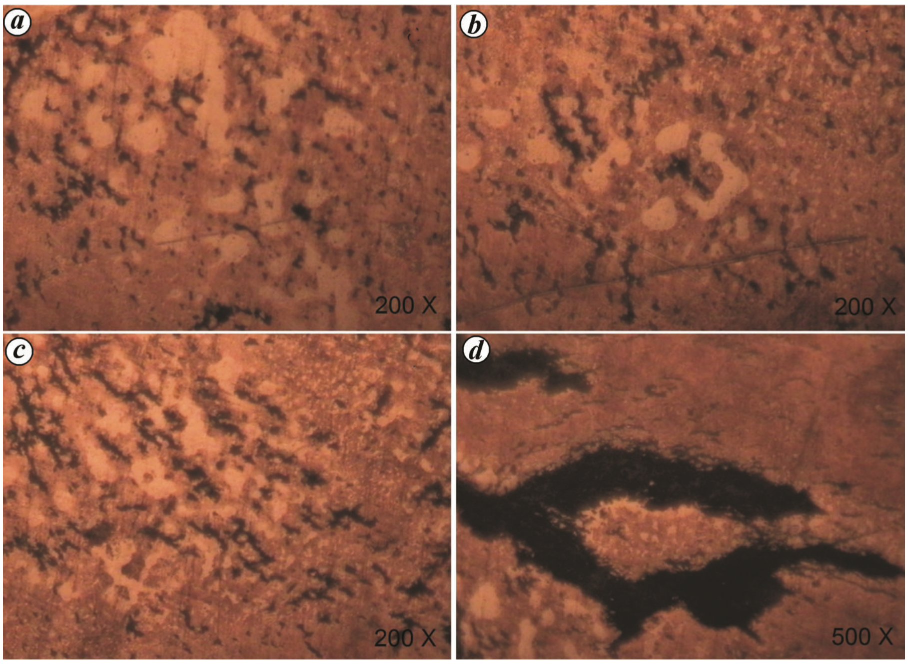
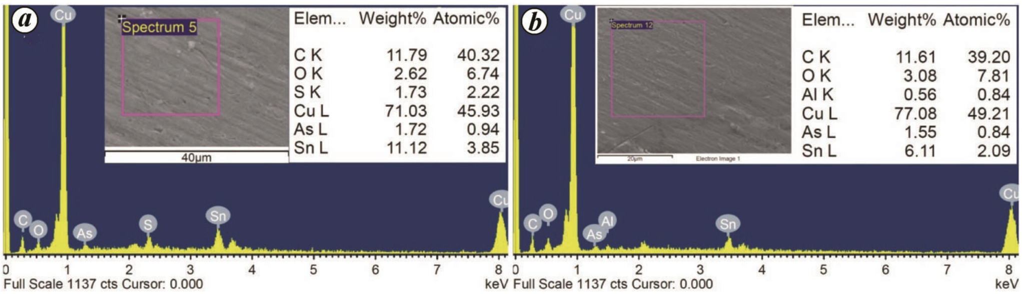


Figure 6. Microstructure of sample 6. An inter-crystalline crack is visible in the metal matrix.



Elem...	Weight%	Atomic%
C K	11.79	40.32
O K	2.62	6.74
S K	1.73	2.22
Cu L	71.03	45.93
As L	1.72	0.94
Sn L	11.12	3.85

Elem...	Weight%	Atomic%
C K	11.61	39.20
O K	3.08	7.81
Al K	0.56	0.84
Cu L	77.08	49.21
As L	1.55	0.84
Sn L	6.11	2.09

Figure 7. Elemental composition obtained at different locations of sample 6 using EDS. Arsenic is evident in the EDS data.

The EDS analysis identified several elements with Cu and Sn in which lead, arsenic, sulphur, zinc, aluminium, iron and antimony were relevant.

Copper

This is the principal constituent of the alloy. It is found in native and metal forms. Artefacts made from native copper are not found from early historic or historical period sites. Most of the copper used in the Ganga Valley has been extracted from the ores of Singhbhum mines[9,22]. There was also substantial deposition of tin ore[23,24], which was quarried in the ancient period. Copper has strong corrosion-resistant properties. The major disadvantage of copper is its softness; hence other elements are alloyed to enhance the strength of the alloy. Also, forging of copper is comfortable in both cold and hot conditions. The ductility of the alloy decreases in cold forging method, which can be enhanced by annealing. Ancient metal-smiths were aware of these properties of copper and its alloys. Analysis of these samples indicates that metal-smiths were acquainted with solid solution strengthening properties of copper, where additional elements were added in the molten state according to their solubility. All samples from Kausambi had copper as a primary constituent, and its amount varied from ≈68 wt% to 88 wt%. When the amount of added elements increased, the second phase appeared in the alloy and physical properties of alloy became different from solute and solvent metals. Two kinds of copper alloys were frequently found in these antiquities – bronze (Cu + Sn) and brass (Cu + Zn). Among all elements, Sn is the most suitable metal to form the bronze alloy. Also, bronze is superior to most of the copper alloys.

Tin

This is a crucial metal for bronze. Several alloys of different physical properties can be formed within the Cu–Sn system. Most of the alloys are produced by casting method. The low tin content in copper alloy completely dissolves in copper and develops a solid solution of α-phase. The δ-phase, which is primarily responsible for hardening of alloy, can be formed frequently within Cu–8% Sn. With higher amount of tin in the Cu–Sn system, the copper-rich α-phase reacts with the liquid to form Sn-rich β-phase by a peritectic reaction. Further, β-phase disintegrates into an α- and γ-phase, and the γ-phase finally decomposes to form α- and δ-phase. This sequence is highly dependent on the cooling condition of metals and can be complicated[25]. However, low-tin cast bronze is difficult for forging[26]. Usually, two types of bronze are discussed in the archaeological literature. One is low-tin bronze where Sn content is lower than 18% and the other is high-tin bronze where Sn content is much higher, and it can reach up to 30% (refs 17,27). In the historical period, both kinds of bronze were produced. Tin addition in copper metal enhances the physical properties of the alloy. Also, tin acts as a flux and lowers the melting point of copper alloys. A study has demonstrated that the addition of 20% tin in copper can reduce the melting point by 800°C, which is useful for metal-smiths to forge tin–bronze[26]. Production of tin–bronze was a remarkable achievement in ancient times. Tin–bronze is harder than copper, but easy to fabricate. Like iron tools, bronze tools are equally durable for heavy duty like cutting trees and preparing agriculture fields. Durability and easy fabrication process made the bronze tools popular in society.

The samples from Kausambi showed a standard composition of low-tin–bronze. Tin content in these samples varied from ≈5.5 wt% to 12 wt%. One sample (hook), showed high tin content, viz. ≈11 wt% to 12 wt%. Also, the needle found from Senuwar had a significant amount of Sn. Both objects require hardness and high tensile strength. So increasing Sn in the alloy to obtain the required physical properties was a natural choice for the artisans. Rings, bangles and nails from Kausambi (Table 1), and Chirand and Rajghat (Table 2) showed a small percentage of Sn because increased hardness was not a desired property for these objects. A sample which appears to be a rod was made of high-tin–bronze. The high-tin–bronze was widely forged and used for making objects in ancient times[10,28,29]. The addition of tin was generally avoided in coins because the purity of copper was of utmost importance in bullion metals. These data indicate that in the historical periods, tin was alloyed deliberately and artisans were skilled in controlling the physical properties of the alloy.

Lead

This is commonly found in archaeological copper and alloys. Sometimes it was added intentionally, but most of the times it is found naturally with ores of copper. During ore-processing, it gets extracted in copper and is visible in archeo-materials. The solubility of lead in copper is low (about 0.007%); hence it does not affect the solidification structure and remains present as a globule in the copper matrix[25]. Pb has a negative effect on the physical properties of the final product, but it makes the molten metal less viscous and facilitates casting[17,27]. Lead was identified in two samples of Kausambi in significant amounts. Also, it is present in other samples in minimal amounts. It appears that lead was added intentionally in both samples 1 and 3 of Kausambi to facilitate casting. These samples exhibit knowledge of Pb alloying among ancient artisans. Small amounts of lead in other artefacts may be considered as an ore impurity which was not eliminated during smelting.

Arsenic

This is another critical element which is frequently found in Cu alloys, although it was not prominently seen in the studied artefacts. During EDS characterization arsenic was observed in many artefacts, but their quantities were too low to be detected EDS. Arsenic is found usually in copper ores, and if it is not removed during ore processing, it results in arsenical copper. The copper ore can be processed in reducing and oxidizing medium. It has been found that processing in oxidizing condition initiates greater loss of arsenic in comparison to processing in reducing condition[30]. The volatile arsenic forms arsenic-tri-oxide (As_2O_3) in an oxidizing atmosphere and subsequently evaporates. The experimental data suggest that alloys containing a higher amount of arsenic are more prone to arsenic evaporation[30,31]. Arsenic is completely soluble in copper and has a major impact on the physical properties of the alloy. The hardness of copper alloy increases gradually with increasing amounts of arsenic in copper. Arsenic also plays the role of flux. Presence of arsenic in the copper alloy decreases its melting temperature. Also, As gives a lustrous appearance to the copper alloy. Arsenic is found in most of the earliest Chalcolithic-period copper and copper hoards[4,32–34]. It is also found in later period alloys, but the intensity of occurrence is low. The data of historical period copper show very little amount of arsenic in the artefacts (Tables 1 and 2). In the Ganga Valley, most of the copper was procured from the Singhbhum region[9], which has been identified as arsenical copper ore[33]. In fact, arsenic was present in reasonable quantities in Chalcolithic copper, but due to further processing and recycling, there was a decrease in its concentration. Most probably, arsenic was not alloyed intentionally but was mixed naturally with the ore. During smelting, it was extracted in the alloy and gradually disappeared during further recycling. This aspect needs special attention for further research in Indian archaeometallurgy.

Table 2. Elemental data of samples obtained from other sites of Ganga Valley (after Bhardwaj and Singh[7–11]). NPW period regarding SNR (Senuwar) artefacts is 7th–6th century BCE to 5th–4th century BCE, for NRH (Narhan) artefacts 600–200 BCE and for CRD (Chirand) artefacts, it is 700–200 BCE

Artifacts	Period	Object	Cu	Sn	As	Pb	Fe	Ni	Ag	Sb	Cl	S	Si	CaO	MgO
SNR 1112	III (NBP Pd)	Needle	85.738	13.775	0	0.129	0.215	0.139	0.004	0	3.58	0	2.65		
SNR 853/1	III (NBP Pd)	Needle	87.38	10.209	0	0.77	0.979	0.57	0.083	0	1.62	0	2.33		
SNR 853/2	III (NBP Pd)	Needle	83.046	14.085	0	0.738	1.911	0.22	0.0002	0					
NRH 305/1	III (NBP Pd)	Bead	91.064	9.446	0	0.125	0.233	0.016	0.053	0					
NRH 305/2	III (NBP Pd)	Bead	89.028	8.853	0	0.051	0.205	0.028	0.022	0					
CRD 541/13	IV (NBP Pd)	Piece of bowl	82.884	16.852	0	0	0.263	0	0	0					
CRD 541/13A	IV (NBP Pd)	Piece of bowl	99.961	0	0	0.038	0	0	0	0					
CRD 14/1	IV (NBP Pd)	Bangle	96.199	3.135	0.122	0.282	0.278	0.037	0.024	0.66					
CRD 14/2	IV (NBP Pd)	Bangle	93.484	4.08	0.521	0.11	0.21	0.068	0.019	0.57					
CRD 14/3	IV (NBP Pd)	Bangle	95.398	3.087	0.2	0.034	0.211	0.055	0.038	0.63					
CRD 15/1	IV (NBP Pd)	Antimony rod	99.882	0.007	0	0.038	0.041	0	0.059	0.01					
CRD 15/2	IV (NBP Pd)	Antimony rod	98.705	0.054	0	0.125	0.176	0.253	0.005	0					
CRD 15/3	IV (NBP Pd)	Antimony rod	99.875	0	0	0	0	0	0	0					
Rajghat	400–200 BC	Bronze fragment	79.4	13.99	tr	0.09	2.23	0		tr		tr		2.46	0.74
Rajghat	400–200 BC	Bangle	93.93	1.82	+	tr	1.09	0.32		0		0.5		1.86	0.38
Rajghat	600–400 BC	Copper fragment	98.05	0	+	tr	0.37	0.08		0		tr		0.85	0.17
Rajghat	600–400 BC	Antimony rod	96.38	0	+	0	0.21	0.08		0		0.8		2.31	0.84
Rajghat	600–400 BC	Sheet	95.45	0	0.25	0	0.96	0.15		tr		0.2		1.75	0
Rajghat	400–200 BC	Copper coin	86.9	7.83	+	0.83	1.5	1.07		0		tr		1.1	0
Taxila	300–200 BC	Copper coin	96.24	0	0	0	0.56	0		0		0		0.56	tr
Taxila	300–200 BC	Copper coin	98.4	0	0	tr	0.8	0		0		tr		0	0
Ayodhya	200–100 BC	Copper coin	94.77	0	0	tr	1.2	0		0		0.5		0	0
Mathura	100 BC	Copper coin	95.27	0	+	0.25	0.85	0.98		0		0.5		1.02	0

This possibility may also explain the occurrence of arsenic in Harappan copper. The Harappan period saw a dramatic increase in copper and alloy production technology. Copper was used on a large scale in the Harappan civilization scale; it was mostly fresh and came from arsenic-bearing ores[35]. As it was not recycled much, traces of arsenic are still present in these samples.

On the other hand, copper of the later periods were both recycled and fresh. So there is no specific pattern of arsenic. Sometimes, arsenic content was minimum or nearly absent in the artefacts. This possibility further suggests that arsenic was never intentionally alloyed with copper and artisans were well acquainted with its health hazards.

Other minor elements

Other elements reported in the artefacts were sulphur, zinc, iron, aluminium and antimony. Many copper ores contain sulphur naturally. Sulphur was present in metals and alloys during smelting. Sulphur in bronze artefacts makes the alloys corrosion-resistant. Deliberate alloying of sulphur in ancient times has not been reported. Zinc was reported only in one artefact. Zn alloying was much prevalent in later periods. Addition of aluminium also improve hardness and corrosion resistance, but its occurrence in the artefacts does not provide any clue regarding alloying practices. Iron has been reported in most of the copper artefacts of the Ganga Valley. The artefacts from Kausambi showed no iron. Only one artefact (sample 9) had iron however, it was not homogeneous but localized at one place. Antimony was reported in one artefact. Most of the Ganga Valley artefacts showed the absence of Sb. In these artifacts carbon was present in sufficient amounts. In ancient times, charcoal was mixed with copper ore for reducing the ore to metal[36]. There is the possibility of some minor elements in the alloy, but due to detection limits of EDS, these elements could not be mapped accurately. Data from other sites of the Ganga Valley showed elements like Fe, Ni and Ag in very low quantities. The large-scale analysis of minor, trace elements and isotopes is required from several sites for provenance studies of copper in the Ganga Valley.

Conclusion

The Ganga Valley was the focus of urbanization during the 6th century BCE in the Indian subcontinent. The available data show that copper artefacts from north-central India in the historical period are primarily low-tin–bronze. Out of ten samples, one was high-tin–bronze; one was pure copper, and rest of the samples were standard bronze alloys with composition ≈Cu–7% Sn. These artefacts show a tendency of object-specific alloying. It appears that in the historical period, artisans were fully aware of the physical properties of different alloys compositions. During this period, objects were fabricated with a suitable alloy of correct proportion. The data show that low-tin–bronze was used for rings and bangles, while ≈Cu–11% Sn tin–bronze was used for hooks and rods. Pure copper was preferred for nails. The early historic period was the time when iron was gaining importance in the daily life of humans. Later it replaced copper in most of the metal assemblages which were forged for heavy duty. These data suggest that copper alloying technology was being developed parallel with iron technology. The bronze artefacts from a central Indian site showed an advanced γ-phase[37]. This phase is highly unstable phase and formed in a controlled atmosphere. It is well established that Central India was closely associated with north–central India through several connecting networks. So, the dispersal of ideas and technologies through interconnecting networks working in a wider perspective cannot be ruled out. It appears that technological know-how was disseminated among artisans, and through the process of trial-and-error, they acquired knowledge of the physical properties and metallurgical techniques of the alloy. Production of a perfect alloy, which may be called object-specific alloy, with composition was a remarkable achievement in the historical period in India because the Harappans were not able to control the correct composition of the alloy[38]. It is pertinent to mention that arsenic was never used intensely as an alloying component with copper in the early historic India. Arsenic can be used to distinguish fresh and recycled copper artefacts. In ancient times, copper was extracted since the 3rd century BCE and its availability continuously increased with the passage of time. This tendency augmented the chance of metal recycling for finishing objects. It appears that till the historical age, large amount of copper had been accumulated in society which was further recycled to produce fresh copper objects. Also during the historical period, use of iron gained popularity and it soon replaced copper in most of the heavy objects.

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