AN ANCIENT CHINESE BRONZE FRAGMENT RE-EXAMINED AFTER 50 YEARS: CONTRIBUTIONS FROM MODERN AND TRADITIONAL TECHNIQUES*

M. L. YOUNG,1 F. CASADIO,2† J. MARVIN,1 W. T. CHASE3 and D. C. DUNAND1

1Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA
2The Art Institute of Chicago, Chicago, IL 60603, USA
3Chase Art Services, 508 Route 169, Woodstock, CT 06281, USA

Modern analytical techniques, such as secondary ion mass spectrometry, inductively coupled plasma optical emission spectroscopy, in-situ synchrotron X-ray diffraction and Raman microscopy, alongside scanning electron microscopy with energy-dispersive X-ray analysis and powder X-ray diffraction, were used to investigate bronze fragments from an ancient Chinese bronze vessel (also known as a hu) in the collection of the Art Institute of Chicago. Previous compositional results obtained by R. J. Gettens in 1951, using traditional optical metallography and powder X-ray diffraction, were compared with the present analysis. The investigation provided a complete description of the composition of the ancient metal alloy and spatially resolved identification of the major and minor corrosion products. Furthermore, the study also provided the opportunity for a better understanding of the possibilities and limitations of the various instrumental techniques available to the analyst for the study of ancient bronzes.

KEYWORDS: SIMS, ARCHAEOMETALLURGY, RAMAN MICROSCOPY, SYNCHROTRON RADIATION (SR)-XRD, ICP–OES, CHINESE BRONZES

INTRODUCTION

Beyond written sources, the study of ancient civilizations often relies on the investigation of their utilitarian and decorative artefacts. This methodological approach is relevant to one of the highest achievements of ancient China: bronze technology. Extensive scientific archaeological excavations in China have brought to light a profusion of bronze vessels and artefacts traceable to a known context and, as a result, the knowledge accumulated on ancient Chinese bronzes has greatly increased in the last 50 years (Bagley 1980, 1987, 2001; Rawson 1990; Linduff et al. 2000; Thorp 2005; von Falkenhausen 2006). At the same time, the techniques available to investigate ancient bronzes have greatly improved as compared to the simple, albeit effective, tools of metallography and X-ray diffraction (XRD) available half a century ago.

In this research, several bronze fragments (known as the ‘Kelley bronze’ fragments) from an ancient Chinese vessel (hu) in the collection of the Art Institute of Chicago (Illinois, USA) were subjected to a series of tests based on modern analytical techniques. The present paper presents results from this new analytical campaign involving the use of traditional techniques (optical microscopy and powder XRD) together with a battery of modern analytical techniques, including secondary ion mass spectrometry (SIMS), inductively coupled plasma optical emission spectroscopy (ICP–OES), Raman microscopy, scanning electron microscopy/energy-dispersive X-ray
analysis (SEM/EDX) and electron microprobe, which provided a complete, spatially resolved description of the complex layering of corrosion products and the bulk metal both at the elemental and molecular level. Results from a separate study using high-energy synchrotron X-ray diffraction (SR-XRD) (Young et al. 2006), on the same region where samples have been removed from the fragment for the present study, are also summarized to evaluate a non-destructive method for the study of ancient metallic artefacts.

HISTORICAL CONTEXT

The photograph in Figure 1 of an ancient Chinese vessel (hu) originally came from Gettens’ notes (detailed below) and has long been assumed to have been taken from the original, intact ‘Kelley’ bronze. Purchased as a collectible from China, the vessel broke into pieces during shipping to the United States in the mid-1940s, revealing it as a collection of fragments (Figs 2 and 3). The original fragments had been soft-soldered to new replacement pieces made from copper plates used to fill missing fragments (Fig. 3 (b)). The surface of the replacement pieces was then covered with artificial patina and missing decorative elements were re-created in order to camouflage the partial forgery. This vessel is of particular interest, since both an authentic patina, accumulated over centuries of burial, and a 19th or early 20th century artificial patina coexist on adjacent areas, as
observed by Gettens (1951, 1969). Upon arrival in the United States, the fragments were dispersed. Archival research based on the Art Institute of Chicago registrar’s records, publications by Gettens (1951, 1969), and the unpublished diary of Charles Fabens Kelley (1885–1960, the curator of Asian Art at the Art Institute of Chicago at the time) indicate that Mr Irvin S. Layton of Boise City

Figure 2  A compilation of photographs of 11 of the ‘Kelley’ bronze fragments from an ancient Chinese bronze vessel (hu) in a provisional restoration. Only one fragment shows the upper rim. Two masks appear on each side of the vessel; the eyes of the lower masks have a delineated pupil. Three bowstrings appear just down from the upper rim, and the clear band separating the two masks vertically is also present, though fragmentary. The variations in colour and contrast are due to differences in the original photographs. The AIC fragments are shown on the left-hand side. (See online for a colour version of this figure.)

Figure 3  (a) The ‘Kelley’ bronze fragments studied here, from an ancient Chinese bronze vessel (hu). The white letters (B and C) indicate sample locations. The area framed by the white rectangle on the largest fragment is the location where in-situ SR-XRD was performed. (b) Modern copper plates with applied patina used to compensate for missing fragments on the ancient Chinese vessel. (Photographs courtesy of S. R. Schnepp, Conservation Department, The Art Institute of Chicago; see online for a colour version of this figure.)

observed by Gettens (1951, 1969). Upon arrival in the United States, the fragments were dispersed. Archival research based on the Art Institute of Chicago registrar’s records, publications by Gettens (1951, 1969), and the unpublished diary of Charles Fabens Kelley (1885–1960, the curator of Asian Art at the Art Institute of Chicago at the time) indicate that Mr Irvin S. Layton of Boise City
(Oklahoma) shipped an unknown number of fragments of this vessel to the Art Institute as a personal gift to Mr Kelley, who received them on 9 September 1946 (recorded in the museum’s collection database with the unique identifier of ‘R of O 10478’), was much impressed by the quality of the shattered vessel fragments (E. L. Pearlstein, Art Institute of Chicago, pers. comm.) and attributed the vessel to ‘the Zhou period (1112–255 B.C.)’ (Gettens 1951, 1969). Kelley brought four of these fragments to Rutherford J. Gettens (1900–74), the scientific conservator at the Fogg Art Museum, Harvard University and founding Director of the Technical Laboratory, Freer Gallery of Art, Smithsonian Institution, during his visit to Cambridge, Massachusetts in October 1946, and shipped additional pieces to Gettens on 27 November (AIC shipping order 38969). Later, Gettens described his scientific analyses of cross-sections of the fragments by optical metallography, powder XRD and spectroscopy, thus identifying the bulk metal to be a Cu–Sn alloy composed of 72–74 wt% Cu, 20–22 wt% Sn and 4.1–4.6 wt% Pb (Gettens 1951, 1969). Gettens characterized the majority of the corrosion products; however, he was unable to identify all of them using the techniques available at the time.

In the course of this investigation, it was possible to use digital photography to bring together the pieces housed in the Art Institute of Chicago with the ones housed at the Freer and Sackler Galleries. Figure 2 shows a virtual restoration of the bronze vessel, illustrated here for the first time. Careful examination of the partially reconstructed vessel shown in Figure 2 indicates that it is similar but not identical to the hu shown in Figure 1. For example, the central forehead and nose on the upper mask on the ‘Kelley’ bronze (directly under ‘Side A’ in Fig. 2) has small protruding elements on each side; these are absent in Figure 1. Also, the decoration on the foot of the ‘Kelley’ bronze is squared spirals with protruding elements at the corners. The decoration on the foot of Figure 1 is a plainer spiral, more like the common lei-wen spirals. The original source of the photograph shown in Figure 1 has been lost, but even though it does not show the ‘Kelley’ bronze, it does give a valuable clue as to the actual shape of the ‘Kelley’ bronze—a flattened oval. Perhaps, in the future, all the fragments can be brought together in one place and assembled, photographed and dispersed again.

To better understand the discussion below, a brief description of early Chinese chronology is necessary. The exact chronology of the three early dynastic periods (Xia, Shang and Zhou) is still controversial. Current scholarship suggests that the Xia Period spanned from c. 2100 bc to 1600 bc, the Shang Period spanned from c. 1600 bc to 1046 bc and the Zhou Period spanned from 1046 bc to 221 bc (Loewe and Shaughnessy 1999; Xueqin 2002; Rawson 2009). The late Shang Period (c. 1300 bc to 1046 bc) is further divided into four parts; Anyang Period II (the time of Fu Hao) will be mentioned below (Jin et al. 1998a). The Zhou Period is further divided into two parts; Western Zhou (1046 bc to 771 bc) and Eastern Zhou (770 bc to 221 bc), which is also further subdivided, with the relevant period to our discussion being the Warring States (403 bc to 221 bc).
steps using silicon carbide grinding pads (180, 320, 400 and 600 grit) with water and diamond water-based suspensions (9, 3 and 1 μm) on a microcloth pad for the final polish. SEM/EDX was performed on cross-sections B and C using a Hitachi S-3500N variable-pressure SEM operated at 12 kV.

**Micro-Raman spectroscopic analysis**

Micro-Raman spectroscopy was performed directly on polished cross-sections of samples B and C with a Horiba Jobin-Yvon Labram 300 confocal Raman microscope, equipped with a multi-channel air-cooled open electrode charge-coupled device (CCD) detector (1024 × 256), a holographic notch filter and a dispersive grating with 1800 grooves per millimetre. The excitation line of an air-cooled frequency-doubled Nd:Yag solid state laser (λ₀ = 532 nm) was focused through a 100× Olympus objective on to the samples and Raman scattering was back-collected through the same microscope objective. Laser power on the samples was kept very low (never exceeding a few mW) by a series of neutral density filters in order to avoid any thermal damage.

**Micro-Fourier transform infrared spectroscopic analysis**

Micro-Fourier transform infrared (FTIR) spectroscopy of a small flake of the fake patina removed from the bronze fragment was performed using a Bruker Tensor 27 FTIR spectrophotometer with mid-IR glowbar source and Hyperion 2000 Automated FTIR microscope with nitrogen cooled mid-band and broad-band MCT detectors. Samples were analysed in transmission through the microscope after compression in a diamond micro-compression cell, at a resolution of 4 cm⁻¹.

**Synchrotron radiation X-ray diffraction analysis**

High-energy X-ray diffraction measurements were carried out at the Advanced Photon Source (Argonne National Laboratory, IL), using a monochromatic 85 keV (λ = 0.015 nm) X-ray beam with a cross-section of 20 × 200 μm² for exposure times of approximately 60 s. The largest bronze vessel fragment (from which sample C was excised) was positioned with its vertical face at a 30° angle relative to the beam. An on-line image plate (345 mm diameter, 100 μm pixel size and 16-bit dynamic range) was used to record complete Debye–Scherrer diffraction cones from the crystalline phases present in the diffraction volume, as well as from ceria powder, which was placed on the back surface of the bronze fragment for calibration purposes. The sample-to-detector distance was 500 mm. The software programs Matlab and Jade were used to create intensity versus d-spacing graphs and for phase identification, respectively. The general set-up for these experiments is the same as that described in Young et al. (2006) and is similar to that described in Newbury et al. (2004, 2006) and Stephenson et al. (2001).

**Secondary ion mass spectrometry analysis**

SIMS was performed on a polished cross-section of sample C. A highly polished surface is needed to obtain sharp elemental, spectral peaks, which aids in the distinction from the background and also helps to avoid overlapping peaks. The instrument used was a static SIMS–PHI TRIFT III (Physical Electronics), using a pulsed primary Ga⁺ ion beam with an energy of 15 keV and a very low current density allowing for the outermost surface (~0.5 nm) of the specimen to be probed. Typically, the primary ion dose is <10¹² ions cm⁻² for mass analysis and <10¹³ ions cm⁻² for secondary ion mass spectrometry.
cm⁻² for imaging. Before each SIMS scan, the selected area was sputtered using a 200 × 200 μm² beam for 20 s to remove the surface layer and any impurities from polishing. A test scan was performed for 1 min before each scan to verify instrument accuracy and to achieve a clean surface. Once the measurement scan was started, no adjustments were made to the instrument. All scans were performed using a 100 × 100 μm² beam for 12 min each. Five different areas of the bronze sample were scanned. Before and after scans of the bronze sample, one to three different areas of a polished lead standard (NIST SRM 981) mounted next to the sample were scanned to verify instrument accuracy. The use of a standard with known isotope ratios allows for absolute measurements of isotope ratios in the sample after performing a calibration calculation.

The peaks for the four main Pb isotopes (²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb) were measured. The measuring range was approximately 0.3 in atomic mass for each spectral peak. The background was taken from atomic mass regions 202.85–203.15 and 208.85–209.15, where no other spectral peaks were observed, averaged and subtracted from the spectral peak areas. After background subtraction, a small ²⁰⁹Pb peak was observed, despite the lack of a Pb isotope with that mass. It was assumed that this peak consisted of ²⁰⁸Pb + ¹H cluster. Counts from this peak were thus added to those for the ²⁰⁸Pb peak. It was assumed that all other isotopes showed similar ‘spillage’ with the same ratio as for ²⁰⁹Pb/²⁰⁸Pb, and corrections were made accordingly for all peaks. For instance, for ²⁰⁸Pb, 2747 ions were added from the spillage to the ²⁰⁹Pb peak (as ²⁰⁸Pb + ¹H), and 1075 ions were subtracted, as they belong to ²⁰⁷Pb + ¹H.

Inductively coupled plasma atomic emission spectroscopy

ICP–OES was performed at the Analytical Services Laboratory (ASL) at Northwestern University (NU) using a Varian model ICP spectrometer with spectral range from 175 to 785 nm and resolutions of 0.008, 0.015 and 0.040 nm at 160–335, 335–670 and 670–850 nm, respectively. A sample of approximately 10 mg of bulk material was collected by drilling a small hole (diameter: 1/16 in using cobalt steel drill bits) in the largest bronze fragment in the same place, where sample C was excised. Additional standard samples from commercial bronzes (copper alloys: 83300, 84400 and 85200 from SIPI Metals Corporation; 90300, 93200 and 93700 from Atlas Bronze; and 1107, 1110, 1112 and 1115 from NIST) with similar compositions to the ancient bronze sample were also collected using the same methodology. The samples were then diluted to approximately 5, 10, 20, 100 and 200 ppm in ~3% aqua regia. To each dilution, 1 ppm of Eu was added as an internal standard for ICP–OES. In addition to an internal standard, ICP–OES standards were also created for each selected element (As, Bi, Cr, Cu, Fe, Ni, Pb, Sb, Sn and Zn). Each set of ICP–OES standards consisted of 0.1, 0.5, 1, 5, 10 and 25 ppm concentration of each element present. A blank consisting of 3% HNO₃ was also created to provide a background subtraction for a concentration of 0 ppm.

RESULTS AND DISCUSSION

UV light, metallography, SEM/EDX, Raman and FTIR spectroscopy

As observed by Gettens (1951, 1969), both an authentic patina, accumulated over centuries of burial, and a 19th or early 20th century artificial patina, which coexist on adjacent areas, can be clearly seen in Figure 4, where ultraviolet (UV) light illumination causes orange autofluorescence of the binder used to apply the fake patina.
Although SEM/EDX is useful in providing visualization of the microstructure and elemental information about the corrosion products and the bulk metal, it is significantly more powerful when coupled with other techniques such as Raman and FTIR as shown here. A line scan performed on the cross-sections with the Raman microscope allowed for the molecular speciation and depth-profiling of the corrosion products whose elemental distribution was visualized in SEM/EDX maps. Additionally, Raman microscopy performed in parallel with optical microscopy allowed direct correlation of chemical composition with the observed colours of corrosion layers. The following paragraphs highlight the results from these techniques applied to cross-sections of samples B and C from the bronze fragment in Figure 3 (a), where sample B (a cross-section of which is shown in Fig. 13) is significantly more corroded than sample C (a cross-section of which is shown in Fig. 5 at three different magnifications).

Outer wall of sample C  Figures 6 (a)–(c) show elemental SEM maps of three areas from sample C corresponding to a cross-section from the body of the original vessel (Fig. 5). The corrosion phenomena can be divided in three principal areas proceeding outwards from the bulk of the metal to the outer wall of sample C: (a) an interpenetration zone, (b) a corrosion band and (c) an outer layer characterized by the build-up of porous corrosion products; the latter also includes elements, such as Si and Cl, foreign to the bronze and derived from the burial soil.

As illustrated in Figure 6 (a), X-ray maps of the bulk of sample C reveal Cu-rich dendrites in a Cu–Sn matrix with small Pb inclusions measuring 5–10 µm. Although the bulk of this sample appears uncorroded, corrosion is visible in the interpenetration zone, preferentially attacking the matrix phase (Figs 6 (a) and 6 (b)). The Cu dendrites near the surface are completely corroded and the corrosion band, illustrated in Figure 6 (b), shows accumulation of Sn corrosion products with interdispersed Pb corrosion products. As described more extensively later, Raman micro-
scopy also highlighted the presence of a cuprite (Cu$_2$O) layer and increased concentration of copper chlorides at the interface between the corrosion band and the metal. The presence of a cuprite layer associated with intergranular corrosion can be used as an indicator that the patina is authentic and has not been artificially produced (Eichhorn 1988). In the outermost porous corrosion layer (Fig. 6 (c)), the widespread presence of Cl and significant amounts of angular Si-rich particles, presumably quartz (SiO$_2$) grains, are observed, together with a localized corrosion band rich in Sn and Pb.

Chlorine distribution in the ‘Kelley’ bronze was previously studied in detail at the Freer Gallery of Art and at the National Institute for Standards and Technology, where samples similar to the Art Institute of Chicago samples were taken from a foot fragment in the Freer Gallery of Art Study Collection (SC-B-18), mounted as cross-sections and examined using traditional metallography (Gettens 1951, 1969). In this previous study, it was found that chlorine, commonly found in salts in excavation sites, plays a significant role in the formation of many of the corrosion products. To extend this previous research, an area at the interface of the corrosion and solid metal, similar to that shown just under ‘a’ in Figure 5, was chosen for investigation with electron microprobe. Conditions were like the lower left part of Figure 6 (a), where the front of corrosion penetration can be easily seen. Chlorine was clearly detected in the corroded portion of the bronze and area mapping allowed for visualization of the association of chlorine with the corrosion front. An area map showing concentrations of chlorine (red), copper (green) and tin (blue) is shown in Figure 7, along with a line scan. The scans confirmed the presence of chlorine at the spots where corrosion was beginning in the interior of the ‘Kelley’ bronze, with levels detected through spot analysis ranging from 3 wt% up to 10–11 wt% Cl.

The microstructure and its characteristic elemental distribution depicted in Figures 6 and 7, as well as the loss of shape of the original surface, are consistent with the well-known phenomenon of Type I corrosion (Chase 1994; McCann et al. 1999). This form of natural weathering involves volumetric changes at the corrosion interface and preferential corrosion of Sn from the $\alpha+d$ eutectoid to form either Sn oxide or mixed Sn and Cu oxides at the surface. This mechanism typically leaves behind the $\alpha$ phase (~90 wt% Cu), which is more corrosion resistant in the alkaline and reducing conditions typically found in Chinese deep tombs (Pelton 2006; Chase et al. 2007). The electrochemistry of this process is driven by anionic control, involving migration of Cl$^-$ ions from the environment deep into the bronze (Robbiola et al. 1998), a phenomenon confirmed by electron microprobe analysis (Fig. 7).
Figure 8 shows the chemical composition of the various corrosion layers, as detected by Raman microscopy on the outer side of sample C, with spectra collected from positions shown in the optical image in Figure 9. Starting at the bulk of the metal and progressing outwards, several sub-regions (a–f) are observed and their composition identified as follows: (a) in the interpenetration zone, copper sulphide \( (\text{Cu}_2\text{S}) \) was identified in the dark regions of corroded

Figure 6  SEM images and elemental distribution maps from the outer wall of sample C from the bronze fragment. Three areas from the bulk of the metal to the outer wall are observed: (a) an interpenetration zone, (b) a corrosion band, and (c) an outer layer of porous corrosion products as labelled in the optical image in Figure 5. (See online for a colour version of this figure.)
eutectic around the Cu dendrites (McCann et al. 1999); (b) in the corrosion zone, cuprite (Cu₂O) and anglesite (PbSO₄) were identified in the red corrosion band adjacent to the dendrites; (c) in the corrosion zone, atacamite (CuCl₂·3Cu(OH)₂) and PbSO₄ were detected in the greenish blue area. Interestingly, the uppermost portion of this greenish blue layer in the corrosion zone (d) also contains claringbullite (Cu₄Cl [Cl₀.2⁹(OH)₀.⁷₁] (OH)₆) (Scott 2002), unambiguously identified on the basis of the very intense, characteristic OH-stretching bands observed at 3351 and 3436 cm⁻¹ (Frost et al. 2003), mixed with PbSO₄. Beyond this layer, but still in the corrosion zone, a thin yellow-coloured layer (e) that was mostly abraded away during the polishing operation was observed to be particularly sensitive to irradiation with laser light. The spectrum, reproducibly recorded in several other similar yellow areas, is shown in Figure 8 (spectrum e) and was also observed by McCann et al. (1999) in the corroded δ phase of the α + δ eutectoid of a corroded Chinese bronze money tree from the Eastern Han Period (AD 25–220). The spectrum of this layer resembles that of Cu₂O but lacks the band at 219 cm⁻¹ (McCann et al. 1999). Finally, the outermost layer of corrosion (f) is dominated by a thick layer of Cu₂O.

Sulphur-containing corrosion products appear widespread in the subsurface layers of the patina. In particular, the detection of PbSO₄ dispersed throughout most of the corrosion layers seems to indicate that the artefact was exposed to a sulphur-rich environment, very likely anaerobic soils rich in bacterially produced H₂S: this would also justify the presence of black copper sulphides in the previously described interpenetration zone (a). When Gettens performed his analysis (Gettens 1951, 1969), he was unable to isolate enough of the black product originating from the corrosion of the eutectic and leaving dendrites of α bronze behind. His original XRD analysis of a fragment of material after removal of the outer corrosion product revealed Cu,
An ancient Chinese bronze fragment re-examined

Figure 8  Raman spectra of the various corrosion products from the outer wall of sample C for each region of interest (a–f) as shown below in Figure 9.

Figure 9  An optical image of the outer wall of sample C with regions of interest (a–f). (See online for a colour version of this figure.)

a faint line for cassiterite (SnO₂) and one unidentified line. The present analysis, which can identify phases with improved resolution, allowed for identification of the dendritic black crystals as copper sulphide.

**Inner wall of sample C** The inner wall of sample C (and, consequently, of the vessel) shows different corrosion phenomena than what was described for the outer wall of the same sample (Fig. 10). As illustrated in Figure 11, the X-ray maps acquired with SEM/EDX show a well-preserved, clear outline of the surface of the original bronze, with Si-, Ca- and Cu-based corrosion products present in both the inner and outer corrosion layers. The detection of Si and Ca suggests that oxides from the environment are also embedded in the corrosion layer.

In the inner side of sample C, Raman microscopy identified malachite (CuCO₃·Cu(OH)₂) mixed with some calcite (CaCO₃) in the inner corrosion layer (b, Figs 11 and 12) and CaCO₃ and PbSO₄ in the uppermost, whitish portion of the patina (c, Figs 11 and 12). No Sn corrosion products were identified with either Raman or SEM/EDX. These results underscore that the mechanism and products of corrosions vary from place to place on the fragments and seem to...
suggest that in this particular spot the bi-layer of corrosion formed on the surface acts as a passivating, protective layer that inhibits further corrosion. Patinas such as the one observed here are said to be controlled by the cationic migration of Cu ions from the metallic bulk to the surface of the bronze and are typically characterized by the presence of CuCO₃·Cu(OH)₂ and absence of Cl-containing minerals (Robbiola et al. 1998).

**Sample B** When compared to sample C, sample B exhibits a less complex patina structure. The cross-section highlights that the sample consists of a metallic core with a coarse dendritic structure consistent with casting, which is sandwiched between two corrosion layers with alternating Cu- and Sn-rich phases (Figs 13 and 14) with a high level of porosity. For the bulk region of this sample, the matrix is widely corroded, but the dendrites are mostly intact (Fig. 14 (b)). The dendritic structure is typical of Sn-rich bronzes, such as this one, known from Gettens’ wet-chemical analysis to be composed of 72–74 wt% Cu, 20–22 wt% Sn and 4.1–4.6 wt% Pb (Gettens 1951, 1969). Raman spectra of the red corrosion layers identified the Cu-rich corrosion as Cu₂O, while SnO₂ and PbSO₄ were identified in the whitish, Sn-rich corrosion layers (Fig. 15). Although Sn is abundant in these layers, the Raman spectrum of SnO₂ is quite weak. A similar observation was also reported by McCann et al. (1999) and supports Gettens’ suggestion that tin oxide may be in a near-amorphous state (Gettens 1951, 1969). Robbiola et al. (1998) also state that Sn-containing compounds in bronze corrosion layers are to be considered mainly as amorphous hydrated oxides, since these compounds are thermodynamically stable over a large range of pH and potentials.

In the centre of sample B, Pb globules are quite large and sometimes irregular in shape (Fig. 14 (b)), while in sample C, the Pb globules appear much smaller and with a regular spherical shape (Fig. 6 (b)). Some of the Pb globules in sample B surround small, pure Cu inclusions, a phenomenon that may be explained by either a solidification process at the time of casting or a corrosion process during burial (Chase 1979, 1994; Smith 1981; McCann et al. 1999).
Comparison of modern analysis with historical scientific data

The description of the patina on the inner and outer walls of both fragments reported here highlights the fact that corrosion varies significantly even across a single vessel, with localized corrosion phenomena affecting different areas on the fragments. Overall, the corrosion products identified on the bronze fragments by the different techniques are listed in Table 1. A marked difference in corrosion products is observed not only between the inner and outer walls of the vessel, but also between the patina of the body of the vessel (sample C) and the patina at the foot (sample B). These observations underscore the occurrence of very localized corrosion processes, highly influenced by the micro-environment created in the burial soil and any other implements in direct contact with the object.

Due to this variability in corrosion products, it is difficult to exactly correlate the phases described above with Gettens’ original observations (Gettens 1951). In fact, Gettens described the presence of nantokite (CuCl) in contact with the corroding dendrites, followed by an

Figure 12  Raman spectra of the various corrosion products from the inner wall of sample C in Figure 10.
Figure 13  Optical images of sample B, showing an etched dendritic core (etching occurred naturally during metallographic preparation) with two layered regions of corrosion products on the exposed surface of the vessel walls. (See online for a colour version of this figure.)

Figure 14  SEM images and elemental distribution maps of sample B from the bronze fragment corresponding to (a) corrosion layers and (b) the bulk of the metal as labelled in the optical image in Figure 13.
intermittent layer of redeposited metallic Cu, and, finally, a thick band of Cu$_2$O with white SnO$_2$ deposited in little disconnected seams throughout the Cu$_2$O, like ‘streaks of fat’ visible only at high magnification for one fragment. In other areas, the main corrosion product identified was CuCO$_3$·Cu(OH)$_2$, mixed with paratacamite (Cu$_2$Cl (OH)$_3$). Notwithstanding these differences, which are probably due to spatial variations of the corrosion phenomena, the most notable advancements made by using modern analytical techniques are the characterization of the corrosion products of Pb and the unambiguous identification of black copper sulphide corrosion products, which were impossible to isolate and hence identify with the tools available at the time of Gettens’ studies (e.g., powder XRD) (Gettens 1951), due to their lower sensitivity on the micro-scale, and to the impossibility of performing spatially resolved analysis in situ on the cross-sections.

**Identification of artificial patina on sample B** It is worth noting that Raman and FTIR microscopies also elucidated the composition of the outermost layers applied to disguise the joints in the original bronze fragments: a layer of superficial, applied stucco that is particularly

---

Figure 15  *Raman spectra of the various corrosion products from sample B in Figure 13.*

---
Table 1 Description, elemental composition, molecular composition and overview of chemical phases identified for two samples (B and C) from a bronze fragment from an ancient Chinese vessel (hu).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Colour</th>
<th>Description</th>
<th>Elemental composition (SEM/EDX)</th>
<th>Molecular composition (Raman microscopy)</th>
<th>SR-XRD Phases identified (overall)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C top</td>
<td>Shiny</td>
<td>Metallic core</td>
<td>Cu, Sn, Pb</td>
<td>Cu and Cu$<em>{4}$S$</em>{11}$, Pb</td>
<td>α-Cu densities with α, β, δ eutectic matrix and isolated Pb globules, Cu$<em>{5}$S$</em>{2}$, CuO, PbSO$<em>{4}$, Sn$</em>{2}$O$_{3}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Corrosion product on top of metallic core</td>
<td>Cu, Sn, Pb</td>
<td>Cu, Pb</td>
<td>CuCl$_2$, Cu(OH)$_2$, PbSO$_4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lower portion closer to metal core</td>
<td>Cu, Sn, Pb</td>
<td>Cu, Pb</td>
<td>CuCl$_2$$\cdot$3Cu(OH)$_2$, PbSO$_4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Upper portion closer to upper surface</td>
<td>Cu, Sn, Pb</td>
<td>Cu, Pb</td>
<td>Cu$_2$O species with altered Raman spectrum or different species</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bright red</td>
<td>Cu, Sn, Pb, Si, Cl</td>
<td>Cu$_2$O</td>
<td>Cu$<em>4$Cl$<em>3$$\cdot$Cl$</em>{0.29}$(OH)$</em>{0.71}$ (OH)$_6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Light greyish green</td>
<td>CuCl$_2$$\cdot$3Cu(OH)$_2$, PbSO$_4$</td>
<td>PbSO$_4$</td>
<td>Cu$<em>4$Cl$</em>{3}$$\cdot$Cl$<em>{0.29}$(OH)$</em>{0.71}$ (OH)$_6$, PbSO$_4$, CuCO$_3$, PbSO$<em>4$, CaCO$<em>3$, Pb Cl$</em>{0.29}$(OH)$</em>{0.71}$, Cu$_2$O</td>
</tr>
<tr>
<td>C bottom</td>
<td>Light green</td>
<td>Corrosion layer closer to metallic core</td>
<td>Cu, Sn, Pb</td>
<td>Cu, Sn, Pb</td>
<td>Cu$<em>2$O, PbSO$<em>4$, PbCl$</em>{0.29}$(OH)$</em>{0.71}$, CuCO$_3$, PbSO$<em>4$, CaCO$<em>3$, Pb Cl$</em>{0.29}$(OH)$</em>{0.71}$, Cu$_2$O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Intermediate corrosion layer</td>
<td>Cu, Sn, Pb, Si, Cl</td>
<td>Cu, Sn, Pb</td>
<td>PbSO$<em>4$, PbCl$</em>{0.29}$(OH)$_{0.71}$, CuCO$_3$, PbSO$<em>4$, CaCO$<em>3$, Pb Cl$</em>{0.29}$(OH)$</em>{0.71}$, Cu$_2$O</td>
</tr>
<tr>
<td>C bottom</td>
<td>Light greyish green</td>
<td>Outermost corrosion layer</td>
<td>Cu, Sn, Pb, Si, Cl</td>
<td>Cu, Sn, Pb</td>
<td>PbSO$<em>4$, PbCl$</em>{0.29}$(OH)$_{0.71}$, CuCO$_3$, PbSO$<em>4$, CaCO$<em>3$, Pb Cl$</em>{0.29}$(OH)$</em>{0.71}$, Cu$_2$O</td>
</tr>
<tr>
<td>B</td>
<td>Reddish brown, ruby red or dark red</td>
<td>Alternating with whitish green corrosion</td>
<td>Cu, Sn, Pb, Si, Cl</td>
<td>Cu, Sn, Pb</td>
<td>PbSO$<em>4$, PbCl$</em>{0.29}$(OH)$_{0.71}$, CuCO$_3$, PbSO$<em>4$, CaCO$<em>3$, Pb Cl$</em>{0.29}$(OH)$</em>{0.71}$, Cu$_2$O</td>
</tr>
<tr>
<td>B</td>
<td>Whitish green</td>
<td></td>
<td>Cu, Sn, Pb, Si, Cl</td>
<td>Cu, Sn, Pb</td>
<td>PbSO$<em>4$, PbCl$</em>{0.29}$(OH)$_{0.71}$, CuCO$_3$, PbSO$<em>4$, CaCO$<em>3$, Pb Cl$</em>{0.29}$(OH)$</em>{0.71}$, Cu$_2$O</td>
</tr>
</tbody>
</table>
evident in cross-section B (Fig. 13: bright green layer at very top and very bottom, marked ‘s’).
As illustrated in Figure 16, the FTIR spectrum showed that the stucco is a mixture of barium sulphate (BaSO₄), emerald green (copper acetoarsenite-Cu(C₂H₃O₂)₂·3Cu(AsO₂)₂), shellac and CaCO₃, while Raman microscopy confirmed emerald green as pigmenting material, mixed with ultramarine blue (Fig. 17). The new analysis confirmed and refined initial findings by Gettens (1969), who suspected the presence of shellac by a characteristic smell upon burning and by spectroscopic analysis after resin extraction, which detected large amounts of Zn and Cu, and lesser amounts of Si, Al, Ba (as barite, confirmed with XRD) and As (as emerald green, identified by microscopical examination). The identification of emerald green as pigmenting material ascribes the application to a date after 1800, when the pigment was discovered and successively commercially manufactured in Europe (Fiedler and Bayard 1997); however, it should be noted that emerald green pigment distribution and availability in China is unknown.

Synchrotron radiation X-ray diffraction

Although full account of the SR-XRD results has been given previously in Young et al. (2006), non-destructive SR-XRD results are summarized here and compared with the destructive examination carried out on the polished cross-section of sample C. The location where sample C was removed on the larger bronze fragment (Fig. 3 (a)) is the same as that where SR-XRD was performed.

In summary, SR-XRD patterns were collected every 20 μm step from the upper edge of the outer wall to 1.1 mm into the bulk of the fragment at an angle of 30° with respect to the sample surface. A gradual transition from surface corrosion products (Cu₂O and SnO₂) to the bulk metallic phases (Cu, Cu₁₁Sn₁₁ and Pb) is observed. The depth of corrosion varies depending on where the sample is positioned; in this case, the corrosion layer is about 370 μm deep, as indicated by phase disappearances/emergences, suggesting that the corrosion layer is relatively thin and that the bulk of the fragment is uncorroded. These conclusions are confirmed by the metallographic cross-section shown in Figure 5. Diffraction patterns indicate that the corrosion products have a fine, untextured grain structure and the bulk metal has a coarse, untextured grain structure, the latter indicating that the vessel was produced by casting instead of cold- or hot-working where a fine, textured grain structure would be observed for the bulk metal.

Figure 16  A micro-Fourier transform infrared (FTIR) spectrum of a region of fake patina in sample B from the bronze fragment.
From this earlier study (Young et al. 2006), three distinct advantages of using SR-XRD are that: (a) both the bulk and corrosion layers of the sample are analysed non-destructively and their approximate thicknesses can be measured; (b) the major phases present are identifiable; and (c) the original fabrication technique can be determined. The potential of SR-XRD to elucidate bronze corrosion products non-destructively has already been extensively described (De Ryck et al. 2003; Pantos et al. 2005; Salvado et al. 2005). Furthermore, in addition to SR-XRD, other SR techniques such as XRF, XAS, FTIR and radiography can also be used alone or in combination to non-destructively study ancient metal artefacts (Harbottle et al. 1986; Janssens et al. 2000; Stephenson et al. 2001; Araujo et al. 2003; De Ryck et al. 2003; Schreiner et al. 2003; Grolimund et al. 2004; Newbury et al. 2004, 2006; Pantos et al. 2005).

Inductively coupled plasma optical emission spectroscopy (ICP–OES)

ICP–OES on the bulk region of the cross-section of sample C revealed a composition of 77.03 wt% Cu, 18.17 wt% Sn, 4.44 Pb, 0.03 Zn, 0.02 Fe, <0.01 Ni, 0.10 As, <0.01% Cr and <0.01% Sb, which refines the composition observed by Gettens, where the bulk metal was found...
to consist of 72–74 wt% Cu, 20–22 wt% Sn, 4.1–4.6 wt% Pb and 0.1–1.0 wt% As (Gettens 1951, 1969). Using the more accurate ICP–OES technique, it is also possible to detect trace elements not detected earlier by Gettens, such as Zn, Fe, Ni, Cr and Sb, which can be important in the authentication and origin of ancient objects (Niederschlag et al. 2003; Pollard and Heron 2008).

Secondary ion mass spectrometry (SIMS)

During SIMS analysis, a beam of Ga ions is sputtered on to the surface of a sample, in this case, an uncorroded region in the cross-section of sample C. The sputtered elements are ionized and analysed by time-of-flight spectroscopy, in a manner similar to mass spectroscopy (MS). Unlike MS, which consumes a whole sample and thus provides average values for all ions, SIMS provides a measurement on a very small local area (~100 × 100 μm²) and therefore is nearly non-destructive, only requiring a very small amount of sample (~<1 mm³). Similar low sample quantities are used in thermal ion mass spectrometry (TIMS), where a small amount of sample is dissolved in acid, the Pb is separated electrochemically on to an electrode, the electrode with the deposited Pb is heated in a mass spectrograph and the intensities of the Pb isotopes are measured. SIMS and TIMS have both been used extensively for geological studies of Pb-containing artefacts (Gale and Stos-Gale 1982; Pernicka et al. 1990; Stos-Gale et al., 1997; Weeks, 1999; Spoto 2000) and more specifically on Chinese artefacts (Mabuchi et al. 1985; Barnes et al. 1987; Mabuchi and Hirao 1987; Chase et al. 1990; Hargrove 1997; Yeung et al. 2000).

SIMS has several advantages over other analytical methods. Unlike ICP–OES, SIMS can provide the full spectrum of elements present with very high sensitivity (Benninghoven et al. 1987) as well as information about the isotopes present. Specifically, Pb isotopes are of interest in the study of ancient bronzes. Pb isotopes are the stable result of the natural decay of radioactive elements (e.g., 238\text{U} decays to 206\text{Pb}, 235\text{U} decays to 207\text{Pb} and 232\text{Th} decays to 208\text{Pb}) (Rosman and Taylor 1998), providing insight into the geological history of the ore and its mode of formation (Faure 1977). The range of the Pb-isotopic compositions varies significantly depending upon the mining site, as shown specifically for Chinese mining sites (Ikonnikov 1975; Mabuchi and Hirao 1987; Jin 1991; Jin et al. 1998b,c). Peng et al. (2000) examined the geographical origin of Pb isotopes in China and divided the Chinese ore sources into three areas by Pb isotope ratios; high radiogenic lead (208\text{Pb}/206\text{Pb} less than 2), middle ratios (208\text{Pb}/206\text{Pb} from 2 to 2.16), and northeastern sources (208\text{Pb}/206\text{Pb} greater than 2.16). High-radiogenic lead, which is relevant to our discussion below, probably originated from polymetallic ore deposits formed from uranium in southwestern China.

Here, SIMS was performed on the bulk region of the cross-section of sample C. As shown in Figure 18, a surface map of total ion counts and elemental maps of ion counts for selected elements (Cu and Pb) was collected in scanning mode and shows similar microstructure to that observed in the SEM image of the bulk region of sample C (Fig. 6 (a)), with small Pb inclusions ~5–10 μm in size. In this particular image (Fig. 18), a larger than average Pb particle (~20 μm) was examined to achieve higher Pb count rates. In addition to the major (Cu) and minor elements (Sn, Pb) present in the bulk of the bronze fragment, trace elements (Ag, As, Ge, K, Na, Se, Si, Sr and Zn) were also observed and most probably originate as impurities within the metal ore used for casting. However, the source of Ge, Se and Sr is unclear: these elements may be artefacts from the chamber.

By analysing a highly polished surface, the individual spectral peaks corresponding to the four main Pb isotopes (204\text{Pb}, 206\text{Pb}, 207\text{Pb} and 208\text{Pb}) are well separated from each other, thus indicating excellent mass resolution, as shown in Figure 19.
Table 2 presents the $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios for six areas of the NIST Pb standard (SRM 981) and five areas of sample C. Averages for these areas are also given, together with the standard deviation, and are within error of the values found when conducting a weighted average based on the ion numbers (the weighted averages are thus not given in Table 2). The NIST measurements (the first three performed immediately before and the last three after the measurements on sample C) provide isotope ratios very close to the theoretical NIST values, showing that the instrument is well calibrated and not drifting during the bronze measurement. The small difference between measured and theoretical NIST ratio was used as a calibration factor to correct the measured ratio for the bronze fragment. Its isotopic ratios listed in Table 2 thus incorporate three types of corrections: background subtraction, spillage correction (described in the previous paragraph) and NIST calibration correction. After correction, the $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratio of 1.8933 for the ‘Kelley’ bronze falls clearly in the area of high-radiogenic lead.

Table 2 presents the $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios for six areas of the NIST Pb standard (SRM 981) and five areas of sample C. Averages for these areas are also given, together with the standard deviation, and are within error of the values found when conducting a weighted average based on the ion numbers (the weighted averages are thus not given in Table 2). The NIST measurements (the first three performed immediately before and the last three after the measurements on sample C) provide isotope ratios very close to the theoretical NIST values, showing that the instrument is well calibrated and not drifting during the bronze measurement. The small difference between measured and theoretical NIST ratio was used as a calibration factor to correct the measured ratio for the bronze fragment. Its isotopic ratios listed in Table 2 thus incorporate three types of corrections: background subtraction, spillage correction (described in the previous paragraph) and NIST calibration correction. After correction, the $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratio of 1.8933 for the ‘Kelley’ bronze falls clearly in the area of high-radiogenic lead.

Also listed in Table 2 are ranges of isotopic ratios for several other ancient Chinese artefacts from the St Louis Art Museum (11 artefacts: Hargrove 1997), from the Arthur M. Sackler Collections (222 artefacts: Barnes et al. 1987; Chase et al. 1990) and from two controlled excavations in China (seven artefacts: Yeung et al. 2000; Z. Jin, pers. comm.). The results from Yeung et al. (2000) show Pb isotope values determined by both SIMS and TIMS on the same samples, with good experimental agreement. The ranges of the Pb isotopic ratios for 11 ancient
Chinese bronzes from the St Louis Art Museum collection were measured by TIMS at NIST and reported by Hargrove (1997). These ratios are all higher than those measured here on the fragment and only one (a *Gu*, St Louis acc. no. 217.1950) of the vessels falls into the high-radiogenic Pb area.

Ranges for Pb-isotopic ratios from 132 TIMS measurements for 125 ancient Chinese bronzes from the Western Zhou Period (Chase et al. 1990) and 123 TIMS measurements for 97 ancient

### Table 2 Pb-isotope ratios from SIMS measurements and from the literature (Barnes et al. 1987; Chase et al. 1990; Hargrove 1997; Yeung et al. 2000) or personal communication from Dr Jin (Jin)

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Area</th>
<th>Measurements</th>
<th>Total no. of Pb counts</th>
<th>204Pb/206Pb</th>
<th>207Pb/206Pb</th>
<th>208Pb/206Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–6</td>
<td></td>
<td>Sum 1–6*</td>
<td>836 748</td>
<td>0.0590</td>
<td>0.9099</td>
<td>2.1406</td>
</tr>
<tr>
<td></td>
<td></td>
<td>St. dev. of sum 1–6†</td>
<td></td>
<td>0.0016</td>
<td>0.0074</td>
<td>0.0168</td>
</tr>
<tr>
<td>4–9</td>
<td></td>
<td>Pb standard (SRM 981)§</td>
<td></td>
<td>0.0590</td>
<td>0.9147</td>
<td>2.168</td>
</tr>
<tr>
<td>1–5</td>
<td></td>
<td>Sum 1–5¶</td>
<td>649 344</td>
<td>0.0456</td>
<td>0.7218</td>
<td>1.8933</td>
</tr>
<tr>
<td></td>
<td></td>
<td>St. dev. of sum 1–5†</td>
<td></td>
<td>0.0015</td>
<td>0.0061</td>
<td>0.0134</td>
</tr>
</tbody>
</table>

### Literature values

<table>
<thead>
<tr>
<th></th>
<th>204Pb/206Pb</th>
<th>207Pb/206Pb</th>
<th>208Pb/206Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>St Louis Art Museum (11 artefacts) (Hargrove 1997)</td>
<td>0.046–0.058</td>
<td>0.74–0.90</td>
<td>1.94–2.20</td>
</tr>
<tr>
<td>Sackler Museum (97 artefacts—Shang Period) (Barnes et al. 1987)</td>
<td>0.041–0.059</td>
<td>0.68–0.90</td>
<td>1.87–2.24</td>
</tr>
<tr>
<td>Sackler Museum (three <em>hu</em> vessels—Shang Period) (Barnes et al. 1987)</td>
<td>0.044–0.055</td>
<td>0.72–0.86</td>
<td>1.93–2.12</td>
</tr>
<tr>
<td>Sackler Museum (125 artefacts—Western Zhou Period) (Chase et al. 1990)</td>
<td>0.045–0.059</td>
<td>0.72–0.91</td>
<td>1.91–2.20</td>
</tr>
<tr>
<td>Sackler Museum (two <em>hu</em> vessels—Western Zhou Period) (Chase et al. 1990)</td>
<td>0.049–0.055</td>
<td>0.78–0.85</td>
<td>2.01–2.10</td>
</tr>
<tr>
<td>Sackler Museum (<em>hu</em> vessel, cat. #60) (Barnes et al. 1987)</td>
<td>0.04412</td>
<td>0.7181</td>
<td>1.9268</td>
</tr>
<tr>
<td>Sackler Museum (<em>hu</em> vessel, cat. #58) (Barnes et al. 1987)</td>
<td>0.04808</td>
<td>0.7867</td>
<td>1.9905</td>
</tr>
<tr>
<td><em>pan</em> basin (no. zy334, SIMS) (Yeung et al. 2000)</td>
<td>0.0441</td>
<td>0.7109</td>
<td>1.876</td>
</tr>
<tr>
<td><em>zun</em> vase (no. zy332, SIMS) (Yeung et al. 2000)</td>
<td>0.0444</td>
<td>0.703</td>
<td>1.869</td>
</tr>
<tr>
<td>Fu Hao tomb ZY-093 <em>fang yi</em> M5: 791 (Jin)</td>
<td>0.04389</td>
<td>0.7175</td>
<td>1.8953</td>
</tr>
<tr>
<td>Fu Hao tomb ZY-142 <em>zun</em> M5: 320 (Jin)</td>
<td>0.04541</td>
<td>0.7287</td>
<td>1.9161</td>
</tr>
<tr>
<td>Fu Hao tomb ZY-139 Steamer M5: 865 (Jin)</td>
<td>0.04261</td>
<td>0.6993</td>
<td>1.9272</td>
</tr>
<tr>
<td>Fu Hao tomb ZY-138 <em>hu</em> M5: 795 (Jin)</td>
<td>0.04540</td>
<td>0.7326</td>
<td>1.9443</td>
</tr>
<tr>
<td>Fu Hao tomb ZY-141 <em>jia</em> M5: 751 (Jin)</td>
<td>0.05532</td>
<td>0.8626</td>
<td>2.1237</td>
</tr>
</tbody>
</table>

*Ion counts were added for all six measurements for each isotope.
†Standard deviations of ratios.
§Standard reference lead (SRM 981) from NIST.
¶Counts were added for all five measurements for each isotope.
Chinese bronzes from the Shang Period (Barnes et al. 1987) in the Sackler Collections are also listed in Table 2. Assessing values for the $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratio below a value of 2.0, a third (65/97) of the Shang bronzes contain high-radiogenic lead. Furthermore, only five of the 125 Western Zhou bronzes (Chase et al. 1990) and one of the 85 Eastern Zhou bronzes (Chase et al. 1995) in the Sackler Collections have a value below 2.0 for the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio. Although not shown in Table 2 and beyond the scope of this study, it should be mentioned that 86 measurements from 82 ancient Chinese bronzes from the Eastern Zhou Period were also determined by Chase et al. (1995). The one Eastern Zhou bronze with high-radiogenic lead, a he-cup (no. 86) with inlay, is anomalous; interestingly, the inlay appears to have been applied in modern times. Like $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios, similar trends are also observed in the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{204}\text{Pb}/^{206}\text{Pb}$ isotope ratios.

Two of the 125 ancient Chinese bronzes from the Western Zhou Period are hu vessels similar to the hu fragment examined here. Their Pb-isotopic ratios are in the middle of the range and neither is close to the ratio ranges observed for the present fragment. Their compositions (88.3 wt% Cu, 9.9 wt% Sn, and 0.64 wt% Pb and 74.6 wt% Cu, 2.7 wt% Sn and 19.1 wt% Pb, respectively) are also significantly different from the present fragment (72–74 wt% Cu, 20–22 wt% Sn and 4.1–4.6 wt% Pb: Gettens 1951, 1969) and based on their Pb-isotopic ratios they probably do not have the same provenance as the hu fragment here.

Three of the 97 ancient Chinese bronzes from the Shang Period are hu vessels similar to the fragment examined here. As listed in Table 2, two of the hu vessels contain high-radiogenic lead. Although its composition (66.0 wt% Cu, 5.8 wt% Sn and 29.1 wt%Pb) is significantly different than the present fragment (72–74 wt% Cu, 20–22 wt% Sn and 4.1–4.6 wt% Pb: Gettens 1951, 1969), the first hu vessel (ring foot of hu vessel catalogue no. 60, Table 2) has isotopic ratios very close to those measured on the present fragment. The second hu vessel (ring foot of hu vessel no. 58, Table 2) is just at the cut-off point for high–radiogenic lead, but its composition (78.3 wt% Cu, 21.9 wt% Sn and 2.69 wt% Pb) is much closer to the present hu fragment. The second hu vessel and the ‘Kelley’ bronze vessel both have the decoration feature of three ‘bowstrings’ as the top décor register, and both employ the same squared double spiral with protruding elements; this double spiral occurs on the foot of the ‘Kelley’ bronze vessel and just below the three bowstrings at the top of the Sackler hu vessel. Bagley (1987) dates the Sackler hu vessel to the 13th century BC and relates it to the typologically more advanced oval-bodied hu in Fu Hao’s tomb, one of which (hu M5: 795) appears in Table 2.

Using the multivariate statistical methods pioneered by Edward V. Sayre et al. (Barnes et al. 1988), the lead isotope ratios and compositions of the Sackler bronzes have been grouped. A diagram of the chronological distributions of these groups has been created by Chase (1996). A revised version of this diagram, which highlights the high-radiogenic lead groups with black bars, is shown in Figure 20. Groups 7, 8, D and E lie in the high-radiogenic lead area. Group 8 contains bronzes from the middle Shang and early Anyang Periods. Group 7 contains bronzes from all Anyang Periods, as well as a small number (five) of Western Zhou bronzes. High-radiogenic leads are almost exclusively from the Shang Period.

Dr Jin of the University of Science and Technology of China has determined the isotope ratios in over 500 excavated bronzes from China, covering all periods of Chinese history (Jin et al. 1994, 1995; Jin 2000; Hirao 2001). Many of the analyses of early bronzes are published (Jin et al. 1994, 1995; Jin 2000; Hirao 2001), but the Shang Period material has not yet received full publication. The picture that emerges is complex. The earliest pre-Anyang bronzes are not made
with high-radiogenic leads, but rather from leads in the middle range and, in the case of Erlitou, leads in the northeastern range, above 2.16 for $^{208}\text{Pb}/^{206}\text{Pb}$. The enigmatic bronzes from Sanxingdui in Szechuan are made with extremely radiogenic leads. These leads, or similar leads, continue on into the Shang Period and are encountered in the bronzes from Xingan Dayangzhou. The bronzes from Erligang and Panlongcheng include both high-radiogenic lead and lead in the middle range. As the Anyang Period progresses, lead isotope ratios spread from the high-radiogenic area to the non-radiogenic part of the diagram. In subsequent periods (Eastern Zhou, Western Zhou and Han), most of the leads determined by Dr Jin fall into the middle or northeastern part of the diagram.

Based on these results, the Shang Period bronze casters had access to different lead sources at different times. During the early Anyang Period, sources of high-radiogenic lead were being used. In the statistical groups from the Sackler bronzes, two large groups (groups 7 and 8) fall into this high-radiogenic area. These groups correspond closely with lead isotope ratios from many bronzes in the Shang Periods II and III analysed by Dr Jin (the periodization of the bronzes analysed in that study was assigned from archaeological evidence). However, some of the bronzes from this period have lead isotope ratios from a less radiogenic lead source, possibly the same source used to make the Erlitou Period bronzes. During the later Anyang Period, bronzes in the non-radiogenic end of the distribution tend to fall on a different growth line than that used at the Erlitou Period.

Two bronzes from Sanxingdui, analysed by Yeung et al. (2000), are shown in Table 2. Their comparative study, using both SIMS and TIMS for lead isotope analysis of four ancient Chinese metallic artefacts, showed that SIMS was slightly less accurate, but still very useful to differentiate high-radiogenic leads in some ancient bronzes from other leads. In particular, they examined a pan basin made from leaded bronze (sample no. zy334, Shang Period, excavated at Sanxingdui in the Szechuan Province), consisting of 67.5% Cu, 10.9% Sn and 20.3% Pb. Their Pb isotope ratios by SIMS (Table 2) are, within experimental error, the same as our results for the present bronze fragment. This is also true for an unalloyed copper zun vase (no. zy332, Shang Period: 93.1% Cu, 1.4% Sn and 0.2% Pb). However, the Pb-isotope ratios for the other two less ancient artefacts, a hair pin (Western Zhou, 1100–771 bc) made from unalloyed tin and an artefact (Warring States, 475–221 bc) made from unalloyed lead, do not match our fragment and are

much closer to the ratios of artefacts from the Western Zhou Period, as reported in the Sackler study (Chase et al. 1990). Considering the lead isotope trends discussed above, Yeung et al. (2000) noted that a high-radiogenic Pb ratio content is found for most Shang bronzes, which is different from the value for ordinary (non-radiogenic) lead in China or the NIST standard. Our fragment is in the low range, with a value $0.722 \pm 0.006$, and thus closer to the values found for the two Shang Period artefacts studied by Yeung et al. (2000).

Five bronzes from the Fu Hao tomb, ‘the most remarkable single find ever made at the Anyang site’ (Bagley 1980), are also shown in Table 2. Dr Jin determined the Pb-isotope ratios of 14 bronzes from the Fu Hao tomb. Eight of these are high-radiogenic leads, and the lead-isotope ratios of the huge double $fang\ yi$ (M5: 791) correspond almost exactly to those from our ‘Kelley’ bronze fragment.

By plotting the ratios of $^{208}\text{Pb}/^{206}\text{Pb}$ against $^{207}\text{Pb}/^{206}\text{Pb}$, as shown in Figure 21, it can be shown that bronzes from the Shang Period tend to cluster in the bottom left region of the graph (high-radiogenic lead), while the bronzes from the Western Zhou Period tend to cluster in the middle region, and bronzes from the Warring States and Modern Periods tend to cluster in the upper right. Our bronze fragment falls on the low end of the Shang Period cluster, which corroborates the hypothesis that it originated from metal from the Shang Period, and very possibly from an Anyang foundry active in Anyang Period II or III.

It is worth noting that the Fu Hao bronzes cover a fairly wide range, and seem to be quite evenly spaced; the range is much wider and more even than many of the early tombs from Anyang represented in Dr Jin’s data. This result implies that the use of multiple ore sources and/or an active metals trade was occurring during this period. It should be noted here that a huge amount of bronze was found at the Fu Hao tomb, with a combined weight of over 1.6 metric tons (Buckley-Ebrey 2007). While the reuse of old metal as scrap will give lead-isotope ratios from sources that may not be contemporary with a casting, the fact that high-radiogenic lead is rare in the Western Zhou Period and almost non-existent in the Warring States Period suggests that scrap may not have played an important role in Chinese ceremonial vessel production.
CONCLUSIONS

Using modern analytical techniques, it is possible to deepen our understanding of the creation and subsequent corrosion of artefacts such as the ‘Kelley’ bronze fragments from a hu vessel originally attributed to the Zhou Period. The re-examination of the ‘Kelley’ bronze fragments 50 years after their first investigation allowed for the combination and comparison of traditional and more advanced analytical techniques, to arrive at a detailed morphological, metallurgical, chemical and elemental characterization of the bulk metal and associated corrosion products with good spatial resolution.

ICP–OES provides elemental information about the bulk material, with much higher accuracy than traditional methods previously performed by Gettens. Here, the alloy composition of the fragments was determined to be 77.03 wt% Cu, 18.17 wt% Sn, 4.44 wt% Pb and 0.03 wt% Zn and other minor elements using ICP–OES.

A combination of SEM/EDX, which allows for the effective visualization of the elements present within the core and in the interior and exterior corrosion layers, and Raman microspectroscopy, which allows for the determination of major and minor corrosion phases with high spatial resolution, on cross-sectioned samples allowed for complete molecular characterization and highly spatially resolved mapping of corrosion phases. Specifically, different corrosion products were highlighted: cuprite, copper sulphides, carbonates (malachite), chlorides (atacamite and claringbullite), tin oxides (cassiterite), lead sulphates and extraneous compounds derived from the burial soil such as calcium carbonates and silicates. Furthermore, a fake patina of barium sulphate, emerald green, ultramarine and shellac was also identified, which had been applied to camouflage the seams between original parts of the vessel and modern additions.

Microstructural data obtained with invasive means of analysis on sectioned samples were also compared with non-invasive SR-XRD measurements on the intact fragments and indicate that SR-XRD can accurately measure the thickness of the corrosion layer and also identify major phases in the corrosion layers (e.g., Cu₂O and SnO₂) and the bulk metal (e.g., Cu, Cu₄₁Sn₁₁ and Pb), thus demonstrating great potential as an accurate, non-destructive technique for the characterization of ancient bronzes.

As determined by SIMS, the Pb-isotope ratios from the bronze fragment overlap with other extensive literature measurements on Shang Period bronzes. Therefore, the present SIMS analysis supports the re-attribution of the ‘Kelley’ bronze fragments to the Shang Period. Furthermore, the Pb-isotope analysis provides clues to the origin of the ore used for the bronze object and enables speculation on the time period of manufacture.

In conclusion, complete characterization of ancient Chinese bronzes and, in this study, the ‘Kelley’ bronze fragments is achieved only with a combination of complementary techniques. In the future, spatially resolved SR-XRD has great potential for in-situ, non-invasive characterization of both corrosion layers and metallic core. As synchrotron facilities become more advanced and available, combined SR techniques (e.g., SR-XRD and SR-XRF) will allow in-situ non-destructive and spatially resolved studies of ancient artefacts, thus reducing or even eliminating the need to destructively sample ancient precious objects, which are important surviving testimonies of the societies that produced them.

ACKNOWLEDGEMENTS

The authors thank Suzanne R. Schnepp, Conservator of Objects at the Art Institute of Chicago (AIC), for sharing her visual, X-ray radiography and UV-light observations of the fragments,
and Elinor Pearlstein, Associate Curator of Asian Art at AIC, for her archival research on the provenance of the ‘Kelley’ bronze fragments. Dr James E. Love is gratefully acknowledged for permission to conduct scientific testing on the ‘Kelley’ bronze fragments on loan to AIC. This research also benefited from the financial support from the Andrew W. Mellon Foundation. W. T. Chase would like to thank Rayna Beth Marinenko of NIST for analysis of the Freer samples at NIST on 12 August 1993.

REFERENCES


Ikonnikov, A. B., 1975, Mineral resources of China, Geological Society of America, Washington, DC.


Jin, Z., 2000, Scientific research on the bronzes of the Erlitou culture and exploration of the Xia civilization, Wen Wu Archaeometry, 1–190, St Louis Art Museum, St Louis.


An ancient Chinese bronze fragment re-examined


Pelton, A. D., 2006, Calculation and analysis of EpH diagrams related to the corrosion of Chinese bronzes, in *Report from THERMF ACT LTD*, 1–39, Lehigh University, Quebec, Canada.


