

Article

Corrosion Analysis of Bronze Arrowheads from the Minyue Kingdom Imperial City Ruins

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Abstract: This study investigates the material properties, metallurgical processes, and corrosion mechanisms of bronze arrowheads excavated from the Imperial City of the Minyue Kingdom, a UNESCO World Heritage site in Wuyishan, Fujian, China. Using optical microscopy, SEM-EDS, XRF, XRD, and Raman spectroscopy, the researchers analyzed the cross-section and corrosion layers of the artifacts. Results show that the arrowheads are Cu-Sn-Pb alloys, with Cu (70.76%), Sn (8.73%), and Pb (8.72%), optimizing hardness, toughness, and casting performance. Corrosion analysis reveals a surface layer rich in Cu₂O, CuO, SnO₂, and Cu₂(OH)₂CO₃, driven by oxidation, carbonation, and sulfidation reactions. The corrosion layer exhibits stratification, porosity, and cracks, indicating the influence of oxygen, carbonate ions, and sulfides in burial environments. This study provides crucial insights into ancient bronze metallurgy and the long-term preservation of cultural relics.

Keywords: bronze arrowheads; material properties; metallurgical process; corrosion mechanism; microstructure; oxidation reaction; carbonation; Raman spectroscopy; bronze heritage; Minyue Kingdom



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1. Introduction

In the field of archery in ancient China, the spring wood used to make bow handles, the animal and plant fibers used to make bowstrings, and the arrow shaft and feathers of feathered arrows are all organic materials that are difficult to preserve for a long time [1], and only arrowheads are mostly intact among unearthed bows and arrows. The primary materials used to make arrowheads in ancient China varied depending on the period. The late Paleolithic period (about 45,000 years ago until about 10,000 years ago) saw the appearance of stone arrowheads in China [2]. In the Stone Age, arrowheads were mainly made of flint, animal bones, clam shells, and hardwood [3,4]; in the Shang and Zhou Dynasties (c. 1600 B.C.–256 B.C.), arrowheads made of stone and bone still accounted for a large proportion, but, at the same time, the proportion of bronze arrowheads also increased [5,6]; in the Spring and Autumn Period and the Warring States Period (B.C. 770–B.C. 221), arrowheads were completely dominated by bronze; in the Qin and Han Dynasties (B.C. 221–A.D. 220), the proportion of iron arrowheads increased, but bronze was still the main material of arrowheads. Therefore, the study of arrowheads is essential to understanding ancient Chinese archery activities [7,8]. Bronze arrowheads (in Chinese, 青銅箭鏃), among other

weapons, played a significant role in ancient wars [9–11]. The evolution of their shape, craftsmanship, etc., reflects the development level of military technology at that time. For example, the evolution from double-winged arrowheads to three-edged arrowheads reflects people's continuous pursuit of arrowhead lethality, penetration, flight stability, and other types of performance, as well as changes in war forms and tactics [12]. The social environment of that era closely influenced the mass production and use of arrowheads [13]. Through the study of bronze arrowheads, we can understand the frequency, scale, and military organization of wars in ancient societies [14,15]. In periods of social unrest and frequent wars, there was a large demand for arrowheads, and their shape and production process changed accordingly. The bronze arrowheads unearthed in different regions are helpful in studying the cultural exchanges and integration between different regions in ancient times [16]. Arrowheads unearthed in some regions may have cultural characteristics of other regions, which shows that there was extensive cultural exchange and technology dissemination in ancient times. To date, bronze arrowheads have become an important cultural heritage for studying ancient bronze civilizations. In addition, bronze arrowheads have formed a natural layered corrosion structure under the long-term interaction with environmental factors. This structure originates from the interaction of multiple environmental factors such as oxidation, carbonation, and sulfidation reactions. These corrosion layers show obvious hierarchical characteristics in the microstructure, similar to the protective coatings or films commonly used in the field of modern cultural relic protection. Therefore, studying these layered corrosion structures can not only deeply reveal the ancient bronze metallurgical technology and corrosion phenomena, but also provide an important scientific basis for the design and application of modern cultural relic protection coatings.

There have been various research developments in the study of bronze arrowheads unearthed in China. For example, some scholars used metallographic microscopes, inductively coupled plasma atomic emission spectroscopy, and multi-collector inductively coupled plasma mass spectrometry to conduct archeological metallurgical analyses on 16 bronze arrowheads unearthed from the Yuwan cemetery, which provided new insights into the production process, methods, and sources of raw materials for bronze weapons of the ancient Chu State in China [8]. Other scholars studied 40,000 bronze arrowheads unearthed from the Terracotta Warriors and Horses of the Qin Shihuang Mausoleum in Xi'an. Using portable X-ray fluorescence spectrometry, they pinpointed chemical clusters that corresponded to individual metal batches. Combined with their contextual studies in the tomb group, they conclude that a unit production model comprising various multi-skilled units, rather than a production line, organized the arrowhead manufacture [17]. Other researchers applied nondestructive neutron technology to copper and iron arrowheads unearthed from a tomb of the Western Han Dynasty (B.C. 202–A.D. 8; B.C. means Before Christ and A.D. means Anno Domini) near the ruins of Chang'an City, China (the capital of the Western Han Dynasty). This is the first time that neutron resonance capture analysis, neutron diffraction, neutron tomography, and Raman spectroscopy have been combined to obtain useful information about arrowheads in the context of Chinese cultural heritage [18]. Scholar Xiansheng Yan and others discovered, for the first time, a large number of bronze casting relics from the Warring States Period at the ruins of ancient cities in various states in Shandong Province. They analyzed the microstructure, composition, and lead isotope ratio of slag and bronzes, and explored the origin and circulation of mineral materials for bronze-making in Shandong during the Eastern Zhou Dynasty, as well as its relationship with neighboring countries [19]. In addition, some research focuses on using bronze arrowheads to reveal issues such as social changes, rituals, social organization, and political significance at a particular time [20–24]. However, the characteristics of different bronze arrowheads vary depending on their location. Existing research has not

yet fully targeted the Minyue region. Furthermore, due to their prolonged underground burial, bronze arrowheads often face rust-related issues. By studying their rust mechanism and preservation status, we can explore effective cultural relic protection technologies and methods and provide a scientific basis for the protection of bronze arrowheads and other bronze artifacts.

The novelty of this study was to systematically analyze the material properties, metallurgical process, and corrosion mechanism of bronze arrowheads unearthed from the Ruins of the Imperial City of the Minyue Kingdom and to deeply reveal the production process of ancient bronze arrowheads and the chemical evolution law in a long-term burial environment. At the same time, this study aims to provide a reliable scientific basis for the protection and restoration of bronze cultural relics through modern scientific and technological means. This purpose not only helps further the understanding of the metallurgical technology level and cultural characteristics of the Minyue Dynasty but also provides a new perspective for studying the technological achievements and cultural exchanges of ancient Chinese bronze civilization. At the application level, the tasks of this study mainly include the following two aspects: First, through the study of the corrosion phenomenon and mechanism of bronze arrowheads, protection technologies that are suitable for bronze cultural relics, especially mitigation measures for common corrosion problems, such as copper oxide and carbonate corrosion products, can be developed. Second, based on the research findings, crossover research between the field of the archeology of cultural relics and the fields of materials science and environmental chemistry can be promoted, and a scientific reference for the future restoration, display, and long-term preservation of bronze cultural relics is provided.

2. Materials and Methods

2.1. *The Ruins of the Imperial City of the Minyue Kingdom*

The bronze arrowheads studied here come from the Ruins of the Imperial City of the Minyue Kingdom. The Ruins of the Imperial City of the Minyue Kingdom (also known as the Han Dynasty Ruins in Chengcun Village, Wuyishan City) are located on the hilly slopes southwest of Chengcun Village, Xingtian Town, Wuyishan City, Fujian Province, China (Figure 1) [25]. These are ruins of a Han Dynasty (B.C. 206–A.D. 23) city. The first national cultural relic census discovered the ruins in 1958, and they underwent a trial excavation in 1959. Fujian Province listed this as a cultural relic protection unit in 1961. From 1986 to the autumn of 1991, the East Gate site was excavated and cleaned up several times, revealing a total area of about 800 square meters. A large number of building materials, such as flat tiles, tubular tiles, and tiles, as well as various daily pottery and some iron and bronze artifacts, were cleared out. In addition, archeologists at the time also discovered important relics such as doorways and guardhouses, and established the structure and specific location of the East Gate. They unearthed a cluster of bronze arrowheads for the first time in the guardhouse at the north gate of the East Gate. In 1999, Wuyishan City applied for world cultural and natural heritage and included the Ruins of the Imperial City of the Minyue Kingdom in the World Heritage List. In 2013, it became a national archeological site park project unit [26]. It is the only large-scale ancient city ruin surrounded by city walls in Fujian Province and is known as the “Pompeii of the East”. The plan of the site is in the shape of an irregular rectangle. The square is 25 degrees north to west. The widest point from east to west is 550 m, and the longest point from north to south is 860 m [27]. It covers an area of about 480,000 m². The iron and steel handicraft tools, such as axes, adzes, chisels, saws, and nails, unearthed from the Ruins of the Imperial City of the Minyue Kingdom reflect the improvement of the production level of the handicraft industry. In particular, well-forged steel weapons, such as spears, halberds, swords,

knives, daggers, arrowheads, protective iron armor, and highly lethal copper crossbows, became the basic equipment of the Minyue army, greatly improving its combat effectiveness [28,29]. The Minyue Kingdom extensively utilized copper and iron tools for building components and daily necessities. The iron tools unearthed inside and outside the Ruins of the Imperial City of the Minyue Kingdom have been analyzed and tested according to their metallographic structure, and it can be seen that decarburized steel, fried steel, forged steel, and wrought iron occupy a major position, proving that the smelting technology of the Minyue Kingdom has reached a very high level.

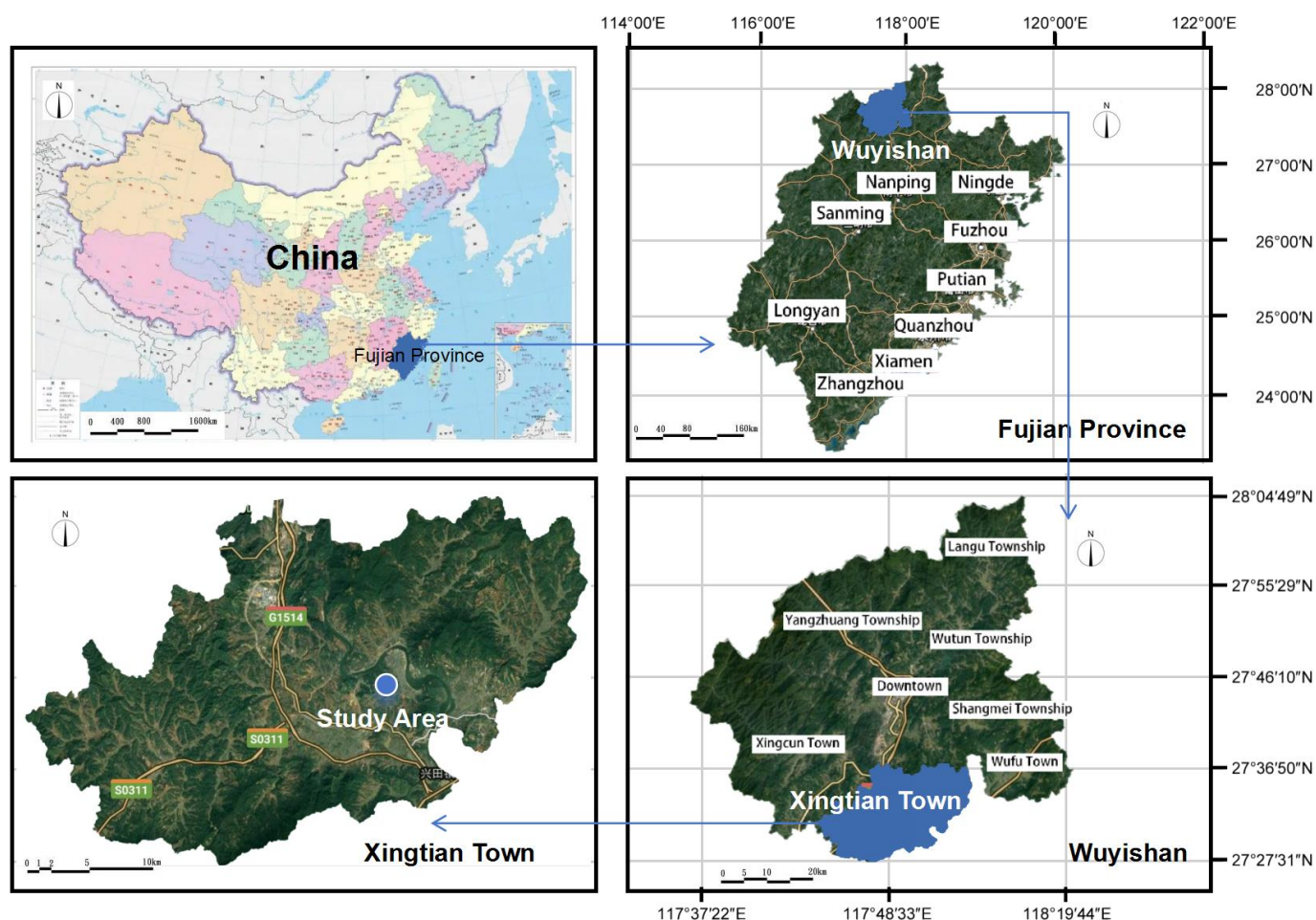


Figure 1. Location analysis. The small amount of Chinese characters in the picture are the original place names on the map and have no specific meaning (image source: drawn by the author via GIS).

The bronze arrowheads excavated from the East Gate Storehouse exhibit distinct characteristics of their respective times and regions. The majority of these arrowheads are sharp blades, and some feature unique patterns and decorations. The exquisite craftsmanship of these arrowheads not only reflects the superb skills of the Minyue Kingdom in bronze casting technology but also reflects the frequent military activities and the importance of war at that time. Specifically, the sharp heads of these bronze arrowheads easily penetrate the enemy's armor or shield, while the finely ground and polished arrow bodies ensure flight stability and accuracy. Additionally, some arrowheads feature unique patterns or symbols, serving not only as decorative elements but also potentially symbolizing special meanings or beliefs. Simultaneously, local villagers and enthusiasts of cultural relics organize excavation activities. By visiting the local gentry and viewing their collections of bronze arrowheads, we discovered that these arrowheads boast unique shapes and exquisite craftsmanship, showcasing the exceptional bronze casting skills of the Minyue Kingdom. The

excavation of the Ruins of the Imperial City of the Minyue Kingdom revealed clusters of scattered bronze arrowheads. Among the bronze arrowheads whose excavation sites could be verified, the bronze arrowheads unearthed from the storehouse at the East Gate were mainly in clusters. This significant capital site serves as a valuable resource for research on the cultural heritage of ancient civilizations.

2.2. *Bronze Arrowheads in This Study*

The research object was unearthed from the Ruins of the Imperial City of the Minyue Kingdom, which are more than 2000 years old. This was the capital of the former Minyue Kingdom and was a royal city built by Wuzhu (無諸), the king of Minyue (閩越王), after he was granted the title by Liu Bang (劉邦), the first emperor of the Han Dynasty. An arrowhead is a sharp edge installed at the front end of an arrow shaft, and an arrow can be shot far away by using a bowstring [30,31]. The complete sample and the complete bronze arrowhead model are shown in Figure 2. As a type of ancient long-range weapon, arrowheads hold a significant position in ancient Chinese weapons due to their long attack range and strong lethality. Looking back at history, the earliest bronze arrowhead discovered in China was unearthed from the Liuwan settlement site in Ledu, Qinghai, during the Neolithic Age [32]. The bronze arrowhead was forged. It is 3.4 cm long and 1.5 cm wide. It is thin and flat in shape, with a slight ridge in the middle. The wings are slightly longer, and the collar has three fronts. Furthermore, at the Erlitou site in Yanshi, Henan, bronze arrowheads from the early Shang Dynasty were unearthed [33,34]. At this time, bronze arrowheads had already taken on the initial form of a primary two-winged arrowhead. However, this type of arrowhead was unable to penetrate armor due to the arrowhead's forward tip, which was easily broken when it struck a hard object. When the two-winged arrowheads reached their peak, i.e., the Spring and Autumn Period, three-winged arrowheads began to appear [35,36]. Compared with the two-winged arrowheads, their casting process was more complex, requiring the use of three molds, yet they possessed a significant advantage in their ability to penetrate armor. The triangular cross-section made the arrowhead structure more stable, allowing it to effectively penetrate armored targets. In the late Spring and Autumn Period and the Warring States Period, three-winged arrowheads were popular, and they were most effective when combined with crossbows. A complete arrowhead includes the front, blade, spine, joint, wing, rear, base, throat, and beard. The object of this study is a bronze, three-edged arrowhead from the Han Dynasty unearthed from the Ruins of the Imperial City of the Minyue Kingdom [37,38]. The arrowhead's wing surface is narrow, closely aligned with the arrowhead body, and its rear is flat. Preservation issues have resulted in the loss of all parts, leaving only the relevant ones and those described above.

2.3. *Analytical Techniques*

This study uses a variety of analytical methods to investigate the microstructure, compositional characteristics, and chemical properties of bronze arrowheads unearthed from the Ruins of the Imperial City of the Minyue Kingdom. The experimental design includes the following three main stages: (1) sample selection and preparation, (2) microstructure and composition analysis, and (3) elemental and phase characterization. These stages use modern analytical techniques, including optical microscopy (OM), scanning electron microscopy–energy dispersive spectroscopy (SEM-EDS), X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), and Raman spectroscopy. At the same time, to ensure the repeatability and reliability of the data, measurements were performed in multiple areas of the sample to reduce the impact of the uneven distribution of corrosion. All of the instruments were calibrated using certified reference materials.

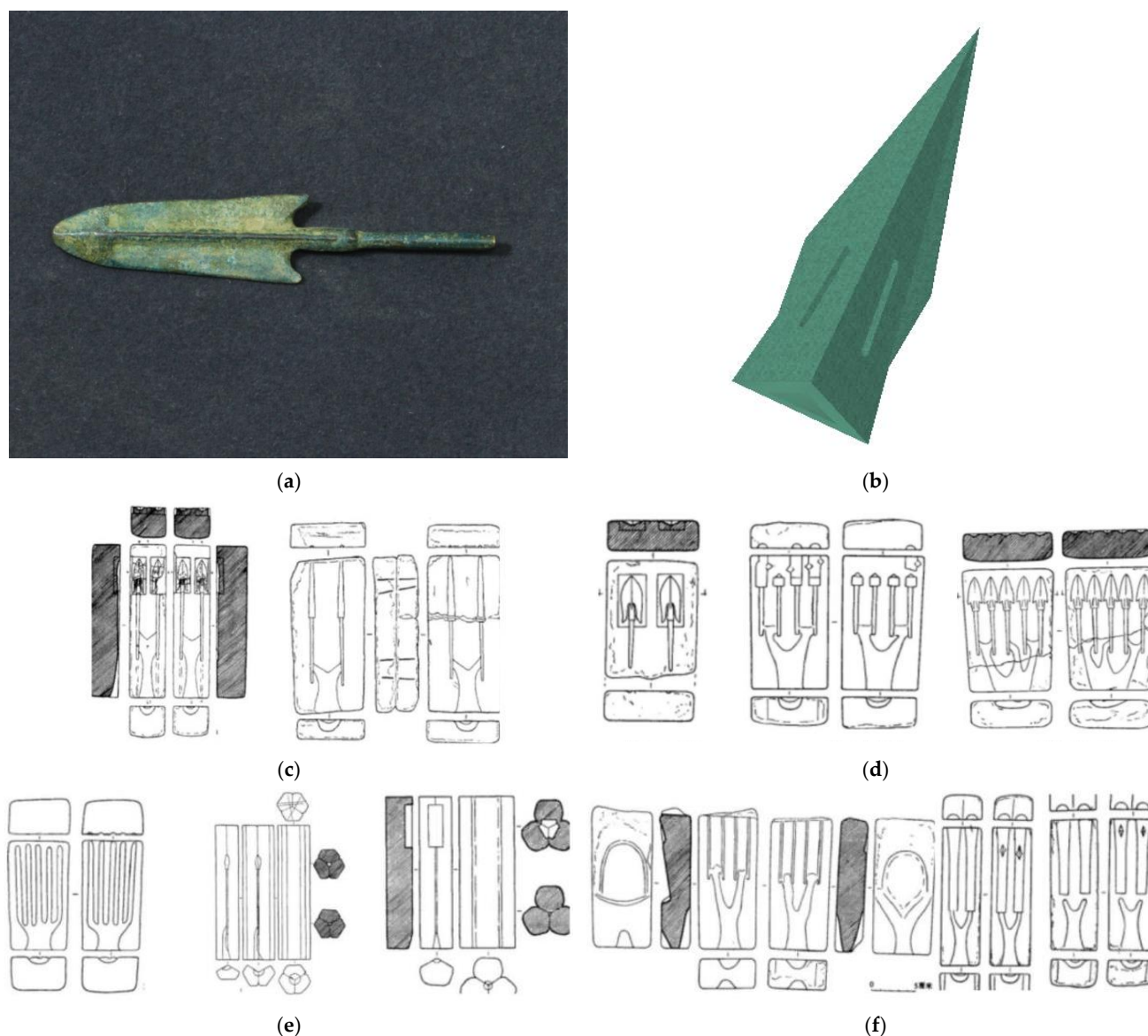


Figure 2. The complete sample and the complete bronze arrowhead model. (a) Bronze arrowheads from the Spring and Autumn Period in the collection of Wuxi Xinli Museum. (b) A complete model of a bronze arrowhead. (c–f) Line drawing of a bronze arrowhead (image source: (a) picture comes from Wuxi Xinli Museum, available online: <https://www.xlmuseum.com/index.php?s=/Mobile/Show/index/cid/313/id/1425.html> (accessed on 12 January 2025); (b) picture drawn by the author; the small pictures (c–f) are from the literature, *Research on the Manufacturing of Bronze Arrowheads in the Pre-Qin Period*, available online: https://chn.oversea.cnki.net/KCMS/detail/detail.aspx?dbcode=CMFD&dbname=CMFD202401&filename=1023587403.nh&uniplatform=OVERSEA&v=v1693yUkR9nTBrS25rtIC_N36eeNAYDQvU42TI8B8jhJ9d96-LEJKzmAvVqyMfQk, accessed on 12 January 2025).

For the sample analysis in this test, we selected the East Gate Storehouse of the Ruins of the Imperial City of the Minyue Kingdom as the sampling location (Figure 3). Based on the mold line and overall condition of the bronze arrowheads, it was preliminarily determined that the production process was to first cast a bronze arrowhead in a rough mold and then forge it to form the final shape. In the test, the sample was cut and finely ground to 1–3 microns, with no visibly obvious scratches (Figure 4).

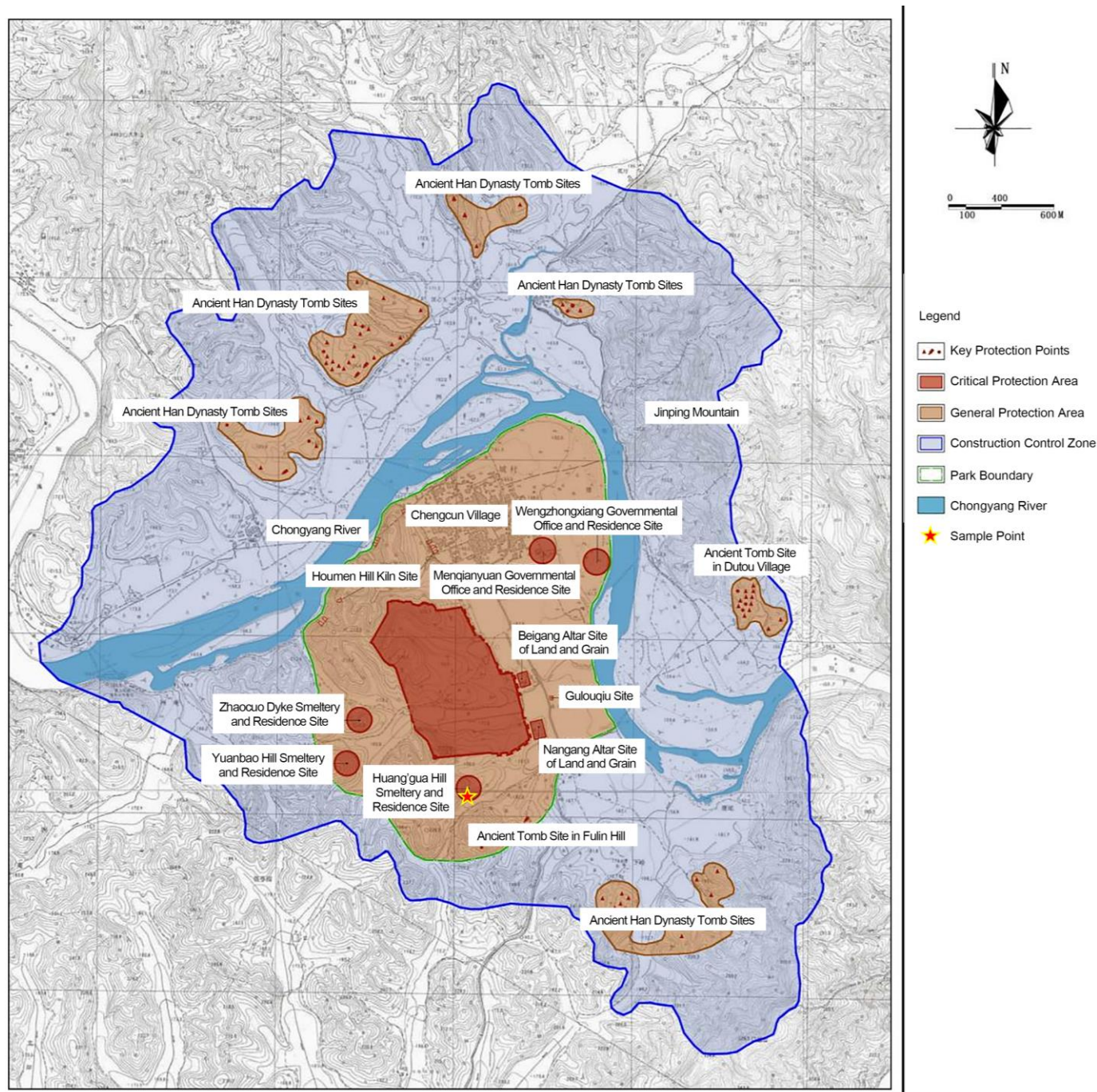


Figure 3. Sampling location (image source: drawn by the author via GIS).

2.4. Sample Treatment

2.4.1. Sample Pre-Processing: Overall Cleaning

In this study, bronze arrowheads were cut, their cross-sectional morphology was observed, internal and external copper rust powder was extracted, samples were prepared, and microstructural observation and analysis were carried out. First, the sample was cleaned as a whole, and restoration technicians used various brushes, hammers, chisels, carving knives, medical surgical instruments, and other tools to manually remove rust from the rusted parts of the bronze arrowheads. While this method is convenient, it cannot completely eliminate harmful rust, so it is more effective to combine it with other methods. Second, a large amount of dust was removed to ensure a tight inlay and prevent interference with the subsequent experiments. Medical ultrasonic cleaners manufactured based

on the principle of ultrasonic vibration are suitable for rust removal and the descaling of bronze. Anhydrous ethanol was used with an ultrasonic cleaner to deeply clean the samples when its working head came into slight contact with rust, resulting in a quick removal of the rust. This method was simple to operate, efficient, and highly selective, and the operator could control the location and degree of removal.



Figure 4. Detailed illustration of the samples used in this study. (1) Intact bronze arrowhead sample. (2) Image of copper rust on the arrowhead surface. (3) Cross-sectional image of the arrowhead (image source: photographed and annotated by the author).

2.4.2. Sample Preparation: Cutting, Polishing, and Grinding

The preparation of bronze arrowhead samples for the SEM/EDS analysis involved a sequence of cutting, mounting, grinding, and polishing procedures, ensuring minimal alteration of the material's original characteristics.

Cross-sectional samples were obtained using EDM cutting and subsequently embedded in resin using a UV-curing technique. The embedding resin was cured under 395 nm ultraviolet light to rapidly solidify, ensuring strong adhesion and minimal deformation. After mounting, the samples underwent sequential grinding and polishing using an automatic system (QATM Saphir 560, Mammelzen, Germany) with abrasive papers ranging from 100 to 4000 mesh, followed by mechanical polishing with abrasives from 2.5 microns to 0.5 microns under controlled pressure (15 N) and rotational speed (400 rpm). To enhance

the polishing efficiency and minimize contamination, ethanol-diluted polishing liquid was used. Optical microscopy (Zeiss EVO MA15, Oxford Instruments, Oxford, UK) at magnifications of $50\times$, $100\times$, and $200\times$ was employed to verify the surface quality and detect residual scratches.

Given the limitations of mechanical polishing for copper-based materials, a final metallographic vibration polishing step (Buehler, Lake Bluff, IL, USA) was employed. This process involved placing the sample in contact with an abrasive-lubricant suspension under controlled vibration, effectively eliminating residual deformation layers and fine scratches. This technique provided a superior, artifact-free metallographic surface, crucial for high-resolution microstructural analysis.

To optimize the SEM/EDS imaging and analysis, the prepared samples were subjected to a fine gold coating process, improving the electrical conductivity and minimizing the charging effects. Figure 5 illustrates the key steps and results, highlighting the cross-sectional structure of the bronze arrowhead and sampling locations, as well as the microstructural features of corrosion products revealed through high-magnification microscopy.

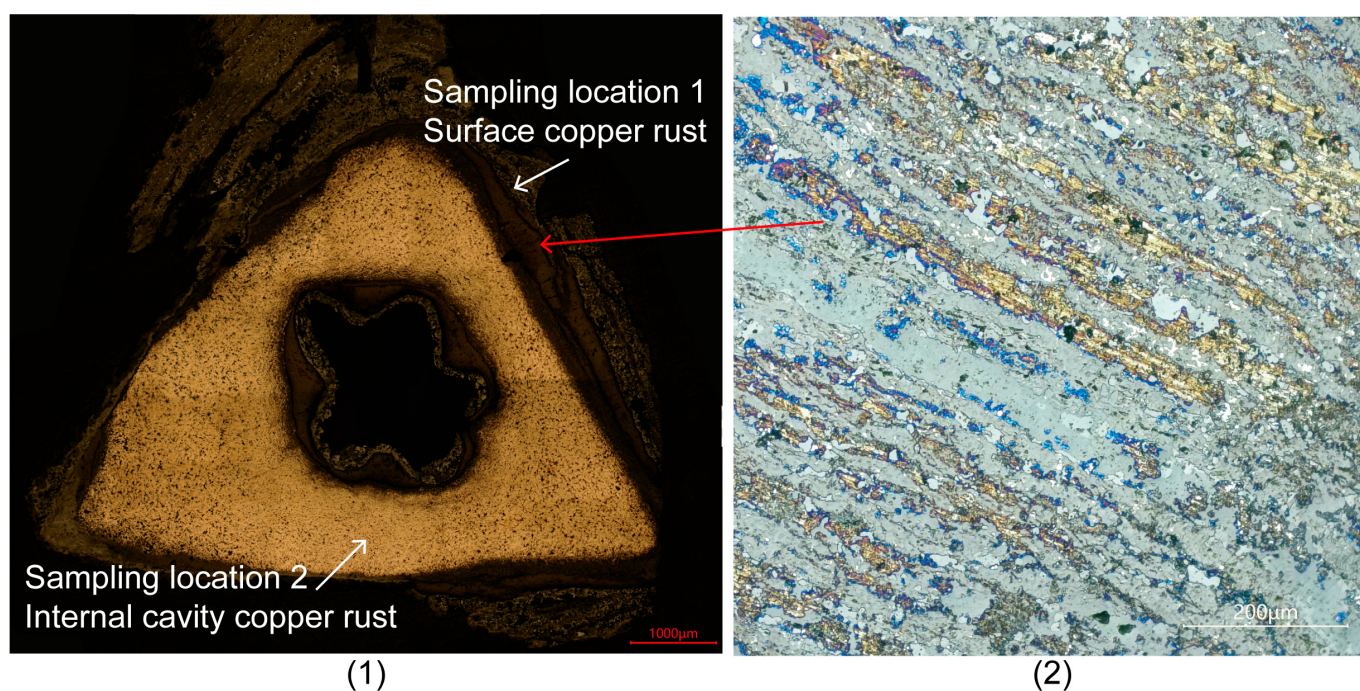


Figure 5. Preparation process of bronze rust on bronze arrowheads and the results of microscopic observation in this study. (1) Cross-sectional image of a bronze arrowhead. (2) Microstructural image of copper rust (image source: photographed and annotated by the author).

In order to gain a deeper understanding of the corrosion process and its mechanism, the research plan combines a variety of technical means, including X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), and Raman spectroscopy analysis, to conduct a comprehensive study of the chemical composition and phase characteristics of the corrosion layer and the substrate layer. These methods will provide qualitative and quantitative data support for the analysis of the corrosion behavior of bronze arrowheads and will help to distinguish the changes in the material properties between the corrosion layer and the substrate layer, laying the foundation for the formulation of cultural relic protection strategies.

3. Results

3.1. Metallographic Microscopy

The bronze arrowhead was dated to B.C. 206–A.D. 23 (the Han Dynasty) by radio-carbon dating. Figure 6 shows the metallographic micrographs from sampling location 1. The microstructural observations at different magnifications from 50 $\times$ to 1000 $\times$ reveal the layered and porous characteristics of bronze corrosion.

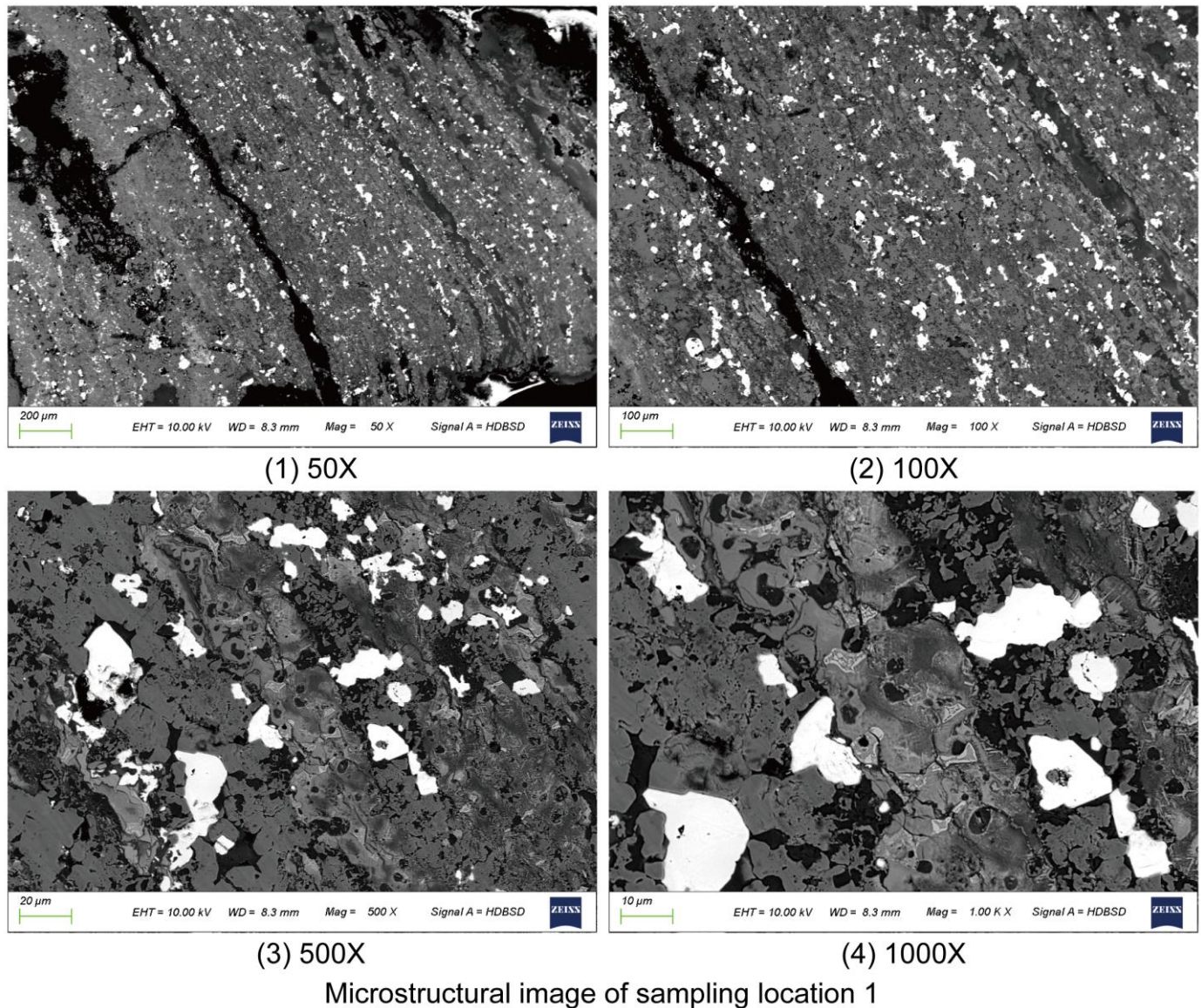


Figure 6. Microstructural image from sampling location 1: (1) 50 $\times$. (2) 100 $\times$. (3) 500 $\times$. (4) 1000 $\times$. (Image source: photographed and annotated by the author).

In Figure 6(1), the low-magnification (50 $\times$) microscopic image shows that the surface patina presents an obvious layered structure, reflecting the gradual accumulation process of corrosion products. There is significant heterogeneity between the upper and lower parts of the corrosion layer, where the black areas are mainly the corrosion voids of the copper matrix, while the white granular area could be identified as the crystal structure of the lead (Pb) element based on the subsequent SEM-EDS analysis. The appearance of the layered morphology indicates that the corrosion process gradually spreads along the metal surface, forming a complex layered structure.

The $100\times$ microscopic image in Figure 6(2) further shows granular and cracked structures inside the corrosion layer. The distribution of cracks shows that the corrosion of bronze materials is highly heterogeneous, which may be closely related to the stress concentration points in the metal matrix and the defects in ancient metallurgical processes, such as raw material mixing or insufficient control of the melting and casting process. In addition, the presence of cracks may provide a path for the penetration of corrosive media, accelerating the expansion of internal corrosion.

In the $500\times$ microscopic image in Figure 6(3), the distribution of fine particles in the corrosion layer and the existence of a porous structure can be clearly observed. The porous corrosion layer reflects the uneven crystal deposition of rust products during the corrosion process. This porous structure may significantly increase the active area of the corrosion reaction, thereby further aggravating the deterioration of the metal. The porous layer is a typical feature of “harmful rust”, and its expansion and development significantly weaken the integrity of the bronze matrix.

In Figure 6(4), by observing at the highest magnification ($1000\times$), the distribution of nano-scale needle-shaped or granular crystals in the corrosion layer could be identified. This corrosion product is not only destructive to the bronze matrix but may also undergo a self-catalytic reaction by absorbing moisture in the air, leading to the further expansion of rust and a chain reaction of damage to the surrounding metal structures.

As shown in Figure 7, the metallographic microscopic images from sampling location 2 show significant differences in microstructure and corrosion characteristics compared with those from sampling location 1, especially in terms of the crack distribution, corrosion layer morphology, and crystal structure.

In Figure 7(1), (2) ($50\times$ and $100\times$ magnification), the corrosion layer at sampling location 2 shows a more obvious wavy texture. This texture may be due to the long-term erosion of the bronze surface by the external environment (such as the accumulation of water inside the bronze arrowhead), resulting in periodic deposition of corrosion products along the stress concentration area. This wavy deposition structure was not observed at sampling location 1, indicating that sampling location 2 may be in a more dynamic environment, and the corrosion to which it is subjected is more complex and multi-directional.

In Figure 7(3), (4) ($500\times$ and $1000\times$ magnification), the fracture structure at sampling location 2 is more penetrating, and the interconnectivity between fractures is significantly enhanced. These cracks not only extend along the corrosion layer, but they also tend to penetrate into the matrix, indicating deeper damage. This is different from the phenomenon of the cracks at sampling location 1 being mainly concentrated in the corrosion layer, indicating that long-term exposure to a high-humidity environment at sampling location 2 is more likely to cause deep damage. The particle morphology of the corrosion products at sampling location 2 is more irregular, with some areas showing blocky shapes, rather than the more uniform needle-shaped or granular crystal distribution at sampling location 1.

3.2. SEM-EDS

3.2.1. Sampling Location 1

Figure 8 shows the SEM-EDS analysis results of sampling location 1, intuitively presenting the distribution characteristics of the main elements in the corrosion layer in this area and their mutual relationships. In the element superposition distribution diagram, one can see metal elements such as lead (Pb), tin (Sn), and copper (Cu), as well as oxygen (O) and trace amounts of carbon (C). The distribution in the corrosion layer is complex and heterogeneous.

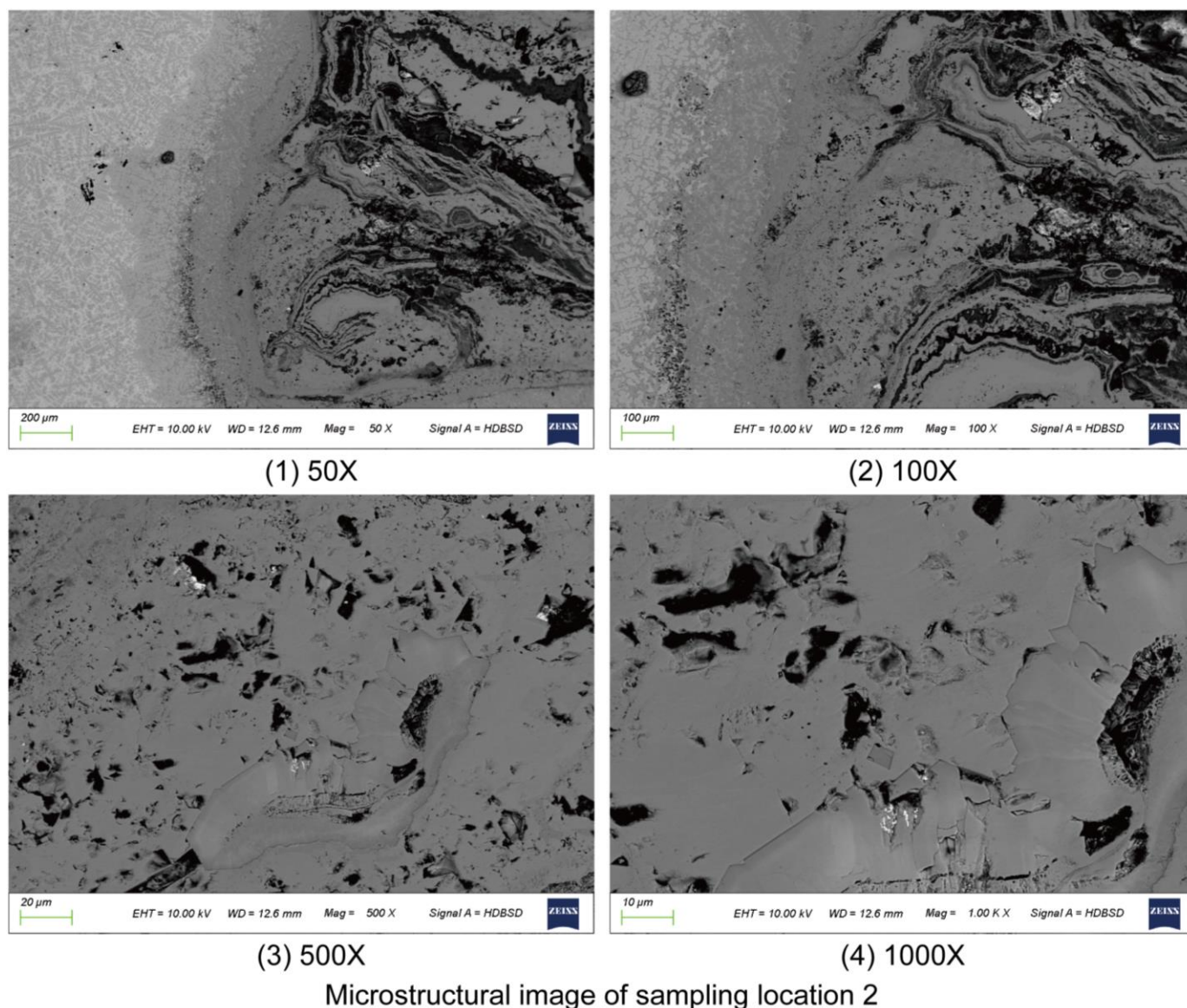


Figure 7. Microstructural image from sampling location 2: (1) 50×. (2) 100×. (3) 500×. (4) 1000×. (Image source: photographed and annotated by the author.)

In the distribution diagram of lead (Pb) elements, it can be seen that lead (Pb) is mainly concentrated in the local area of the corrosion layer and is distributed in a granular form. This phenomenon indicates that lead (Pb) may exist in the original alloy composition of the bronze material in a small amount, and, during the corrosion process, it remains in the corrosion product due to its relatively high stability. Lead (Pb) particles play an important role in improving the casting properties and corrosion resistance of bronze.

Tin (Sn) is evenly and widely distributed, and it is mainly concentrated in the inner area of the corrosion layer. Tin (Sn) is a key component of bronze, and its presence in the corrosion products indicates that the composition of the original bronze alloy is partially retained during the corrosion process. At the same time, the formation of tin oxides (such as SnO_2) may form a protective oxide layer to a certain extent, delaying further corrosion.

The distribution of oxygen (O) is dense and covers the entire corrosion layer, indicating that oxidation reactions dominate the corrosion process. The high distribution of oxygen (O) elements indicates that the corrosion products are mainly composed of oxides (such as Cu_2O , CuO , and SnO_2) and carbonates (such as $\text{Cu}_2(\text{OH})_2\text{CO}_3$).

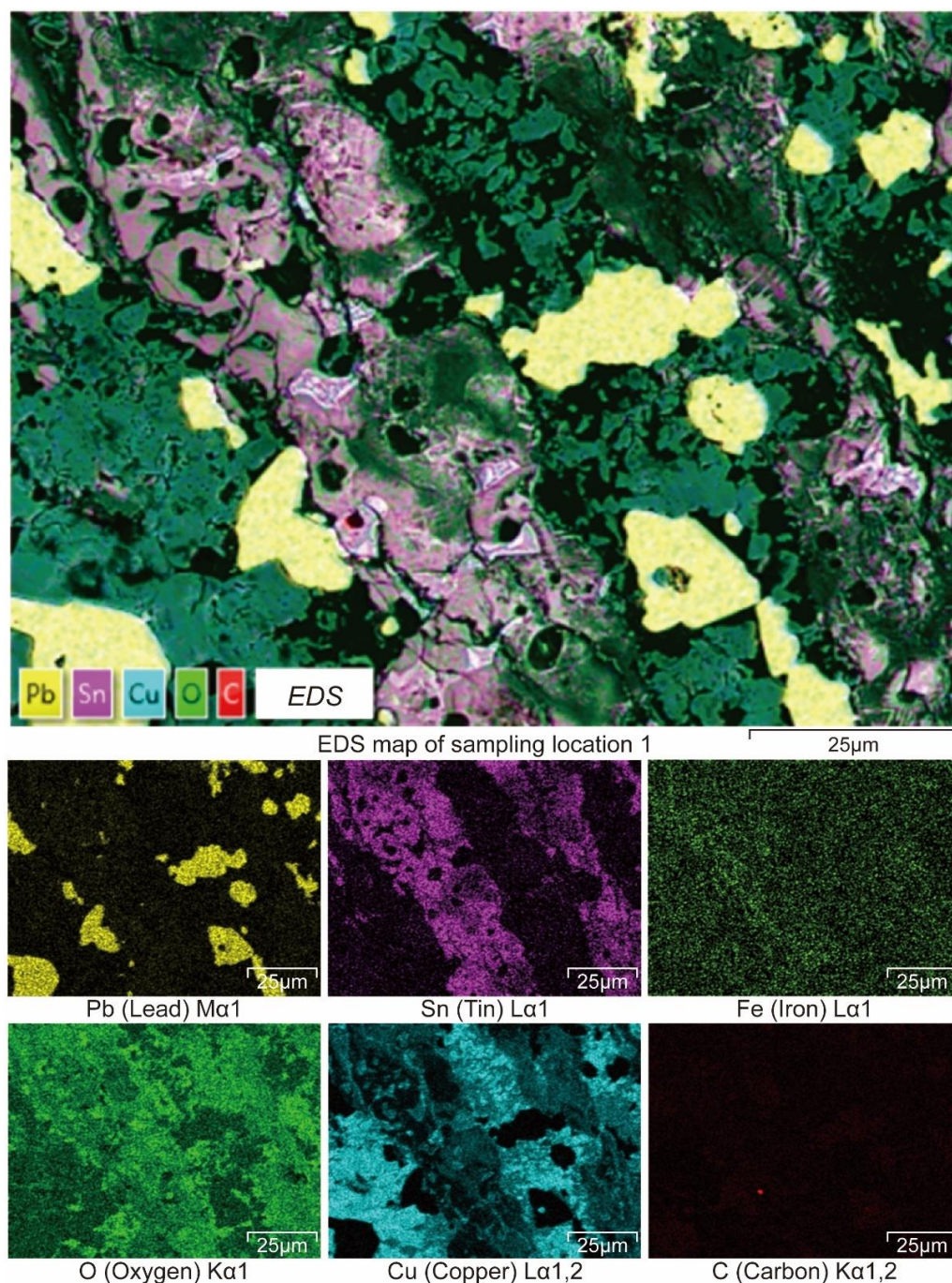


Figure 8. Element superposition and distribution results for sampling location 1 (image source: photographed and annotated by the author).

Copper (Cu), as a matrix element of bronze, is distributed relatively evenly in the corrosion layer and highly overlaps with the distribution of oxygen (O). This indicates that copper (Cu) is mainly involved in the corrosion reaction, generating copper (Cu) oxides or salt compounds, such as copper oxide (Cu_2O and CuO) and basic copper carbonate (copper (II) carbonate hydroxide). The porous nature of these products is an important cause of further corrosion.

The distribution of iron (Fe) is relatively sparse and only appears in a small number of areas. This may be due to the infiltration of iron (Fe) pollutants in the environment around the sampling point or trace iron elements included in the original bronze material. At the same time, iron oxides may catalyze local corrosion.

In addition, the distribution of carbon (C) is very limited, and only a small amount is detected in individual areas. This may be due to trace carbon introduced by contact with organic matter during corrosion or contaminants in the underground environment. The low content of carbon (C) indicates that its participation in the corrosion products is limited.

Combining these characteristics, it can be inferred that, during the corrosion process of these bronze arrowheads, the formation of oxides and carbonates is the dominant chemical reaction. The distribution characteristics of lead (Pb) and tin (Sn) show that they have strong corrosion resistance, while the oxidation of copper (Cu) and the formation of porous corrosion products reflect serious matrix degradation.

Figure 9 shows the element distribution spectrum at sampling location 1 according to EDS, showing the main elements and their relative abundance in the area. Table 1 shows the results of the energy-dispersive spectrometer component analysis of sampling location 1. It can be seen from the spectrum that copper (Cu) and oxygen (O) are the main elements, and their signal peaks are significantly higher than those of other elements, indicating that the corrosion products are mainly composed of copper oxides (such as Cu_2O and CuO) and basic salts of copper (such as $\text{Cu}_2(\text{OH})_2\text{CO}_3$). This is consistent with the previous elemental distribution map, further confirming that copper (Cu) oxidation and corrosion dominate the entire reaction.

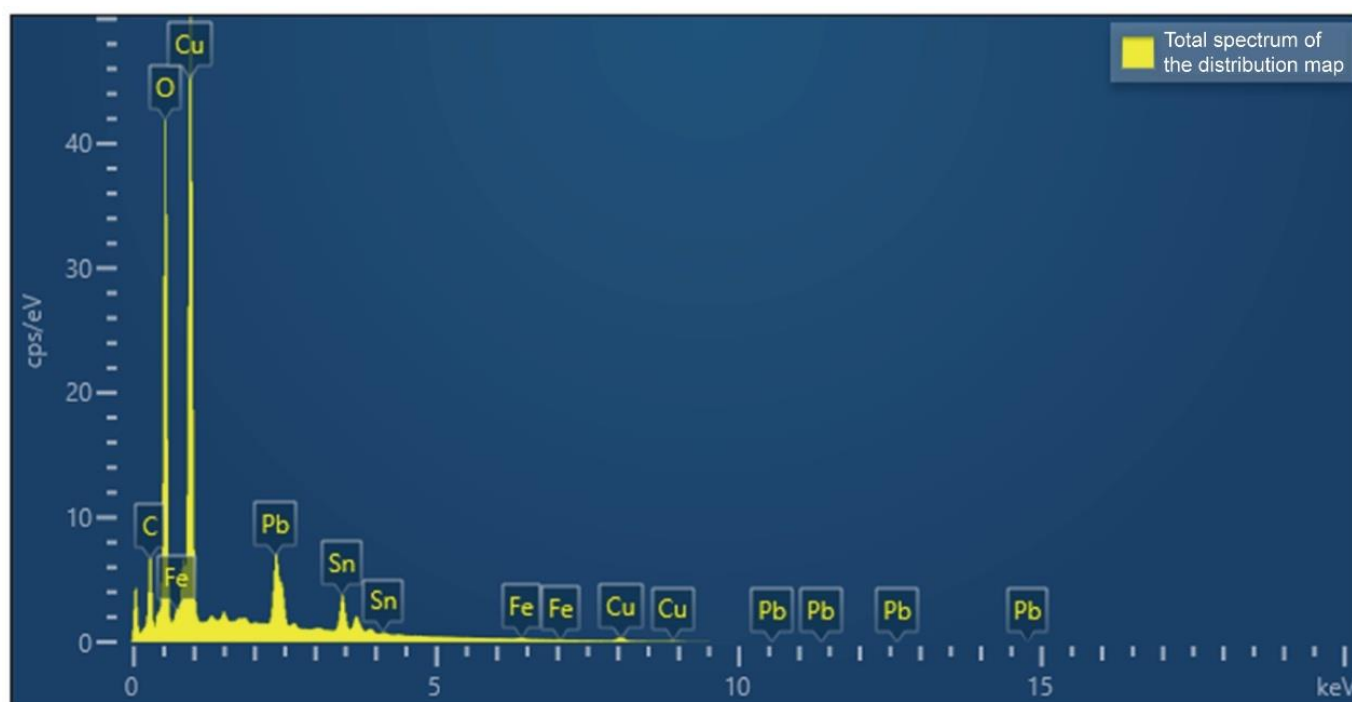


Figure 9. Element distribution at sampling location 1 (image source: annotated by the author; the author changed the annotation in the upper-right corner of the original picture, and the original language was Chinese).

In combination with the data in Table 1, the following was found:

- (1) Oxygen (O) dominates with an atomic percentage of 59.95% and a mass percentage of 23.17%, reflecting a large number of oxidation reactions in the corrosion layer. The high content of oxygen indicates that the corrosion of the bronze arrowhead is mainly oxidative corrosion. These oxides may form a protective rust layer to a certain extent, slowing down the further oxidation of the internal matrix, but their porous structure may also provide a channel for further corrosion.

- (2) Copper (Cu) is the main component of bronze, with a mass percentage of 45.81% and an atomic percentage of 29.84%. This indicates that a large amount of incompletely oxidized copper matrix is still retained in the corrosion layer and that the main body of the bronze arrowhead is still copper-based. Combined with the background of ancient Chinese bronze technology, copper (Cu) is usually the main component, with appropriate amounts of tin (Sn) and lead (Pb) to improve the hardness and casting performance. This alloy ratio is particularly common in bronze arrowheads from the Warring States Period (475 B.C. to 221 B.C.) to the Han Dynasty. The EDS data further showed that the oxidation reaction of copper dominated the corrosion process and generated a large number of copper oxide corrosion products.
- (3) The mass percentage of tin (Sn) is 13.43% and the atomic percentage is 4.68%. This ratio is common in ancient bronzes, indicating that the alloy in the bronze arrowheads contains a high content of tin (Sn). The role of tin (Sn) in bronze alloys is to improve the hardness and casting fluidity. At the same time, its oxide (such as SnO_2) has strong chemical stability and can form a dense protective film, thereby effectively slowing down further corrosion. This protective effect has been confirmed many times in the study of ancient Chinese bronze materials.
- (4) The mass percentage of lead (Pb) is 15.79% and the atomic percentage is 3.16%. The addition of lead (Pb) is mainly to improve the casting performance of bronze so that arrowheads with complex shapes can be formed more finely and stably. From the lead (Pb) content of the corrosion layer, lead (Pb) is distributed in particles during the corrosion process. Its chemical stability makes it difficult to oxidize and lose, so it can be well preserved in the corrosion products. This characteristic makes lead (Pb) an important indicator for analyzing the metallurgical technology and material circulation of ancient bronze wares.
- (5) The mass percentage of iron (Fe) is 1.42% and the atomic percentage is 1.05%, which is relatively low. This suggests that the iron may have been introduced as an impurity during the original smelting process or through the infiltration of external iron contaminants in the burial environment. Iron oxides do not occupy a significant proportion of the corrosion layer, so their impact on the overall corrosion process is relatively limited.
- (6) Carbon (C) has a mass percentage of 0.38% and an atomic percentage of 1.32%. Although the content is low, it may come from organic pollutants in the burial environment or carbonated corrosion products generated during the corrosion process. The presence of carbon (C) may also be related to carbonating chemical reactions in groundwater or the surrounding soil.

Table 1. The energy-dispersive spectrometer component analysis results for sampling location 1.

Element	Wt%	Wt% Sigma	At%
C	0.38	0.00	1.32
O	23.17	0.08	59.95
Fe	1.42	0.15	1.05
Cu	45.81	0.14	29.84
Sn	13.43	0.11	4.68
Pb	15.79	0.14	3.16
Total	100.00	/	100.00

Source: Author's statistics.

3.2.2. Sampling Location 2

Figure 10 shows the SEM-EDS element superposition and distribution results for sampling location 2, depicting the spatial distribution and relative content of the main elements

in the corrosion layer in this area. These include lead (Pb), sulfur (S), oxygen (O), iron (Fe), copper (Cu), and carbon (C). In the element distribution map, it can be seen that the corrosion products at sampling location 2 are significantly different from those at sampling location 1, especially due to the appearance of sulfur (S), which provides new research clues about the corrosion environment and mechanism in this area.

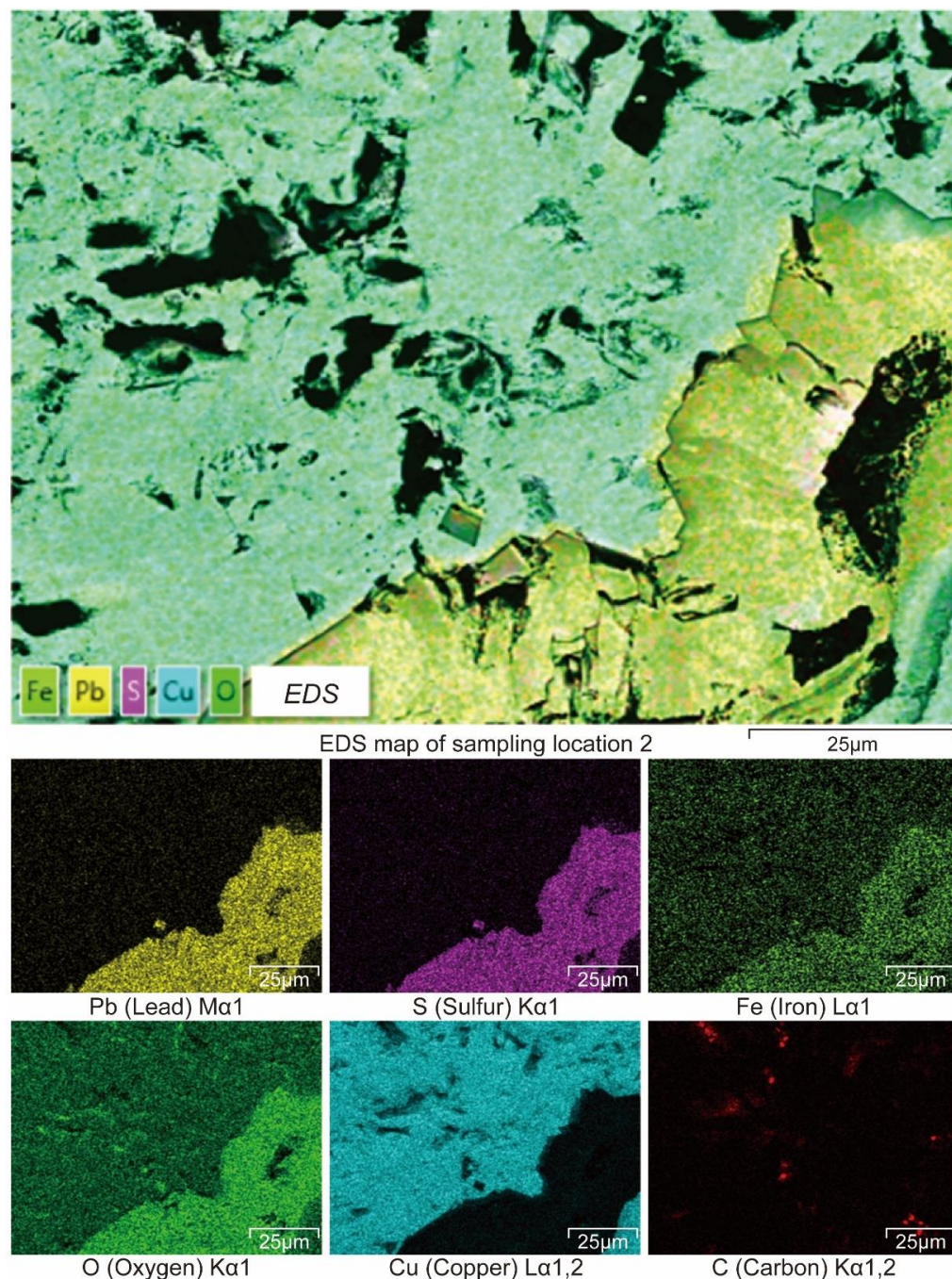


Figure 10. Element superposition and distribution results for sampling location 2 (image source: photographed and annotated by the author).

- (1) Lead (Pb) is mainly concentrated in local areas of the corrosion layer and is distributed in a point-like manner. This indicates that lead (Pb) exhibits high chemical stability during the corrosion process and can remain in the corrosion products in particulate form. The presence of lead (Pb) has a significant effect on the casting properties of

ancient bronze alloys, and its preservation from corrosion further illustrates its role in corrosion resistance.

- (2) The distribution of copper (Cu) is relatively wide, covering the entire corrosion layer and highly overlapping with the distribution of oxygen (O). This indicates that the copper matrix participates in the oxidation reaction during the corrosion process, generating corrosion products that are mainly composed of copper oxides such as Cu_2O and CuO . At the same time, this widely distributed copper oxide product may also be an important reason for the porous characteristics of the corrosion layer.
- (3) The presence of sulfur (S) is a major feature of sampling location 2. Its distribution is relatively concentrated, mainly coexisting with copper (Cu) and lead (Pb). This suggests that there may be a sulfidation reaction during the corrosion process, generating corrosion products such as copper sulfide (such as CuS) or lead sulfide (such as PbS). The source of sulfur (S) may be related to hydrogen sulfide gas produced by the decomposition of sulfide minerals or organic matter in the burial environment. These sulfide products not only have an important influence on the chemical properties of the corrosion layer but may also change the stability of the corrosion products to a certain extent.
- (4) The distribution of iron (Fe) in sampling location 2 is more obvious than that in sampling location 1, showing a larger concentrated area. This may be related to the infiltration of external iron pollutants or impurities in the raw materials for bronze. The presence of iron oxides may have a potential impact on the mechanical strength of the corrosion layer and the further corrosion process.
- (5) The distribution of carbon (C) is still sparse and is only detected in a few areas. Its source may be related to sulfate or carbonate reactions, or it may be a product of the decomposition of organic pollutants in the environment.
- (6) Oxygen (O) is still the most important element in the corrosion layer, and its distribution covers the entire area, indicating that oxidation reactions dominate the corrosion process. This feature, combined with the distribution of copper (Cu) and lead (Pb), further proves that copper oxide and lead oxide are two of the main corrosion products in this area.

Based on the above analysis, Figure 10 reveals that sampling location 2 has element distribution characteristics different from those of sampling location 1 during the corrosion process. The introduction of sulfur (S) and the possible generation of sulfides are a major feature of sampling location 2, indicating that this area may be affected by more complex environmental factors. Meanwhile, copper (Cu) and lead (Pb) exist in the form of stable oxides or sulfides during the corrosion process, indicating significant differences in their corrosion resistance and product characteristics.

Figure 11 shows the energy-dispersive spectrometer (EDS) element distribution spectrum for sampling location 2, which further reveals the chemical composition of the corrosion products in this area and their related characteristics. Table 2 shows the energy-dispersive spectrometer component analysis results for sampling location 2. It can be observed from the spectrum that copper (Cu) and oxygen (O) are still the main elements with significant signal intensity, which is consistent with the element distribution in Figure 10, indicating that the corrosion products are mainly oxides. In addition, the signals of lead (Pb), iron (Fe), and sulfur (S) are also obvious, reflecting the complexity of the corrosion environment at sampling location 2.

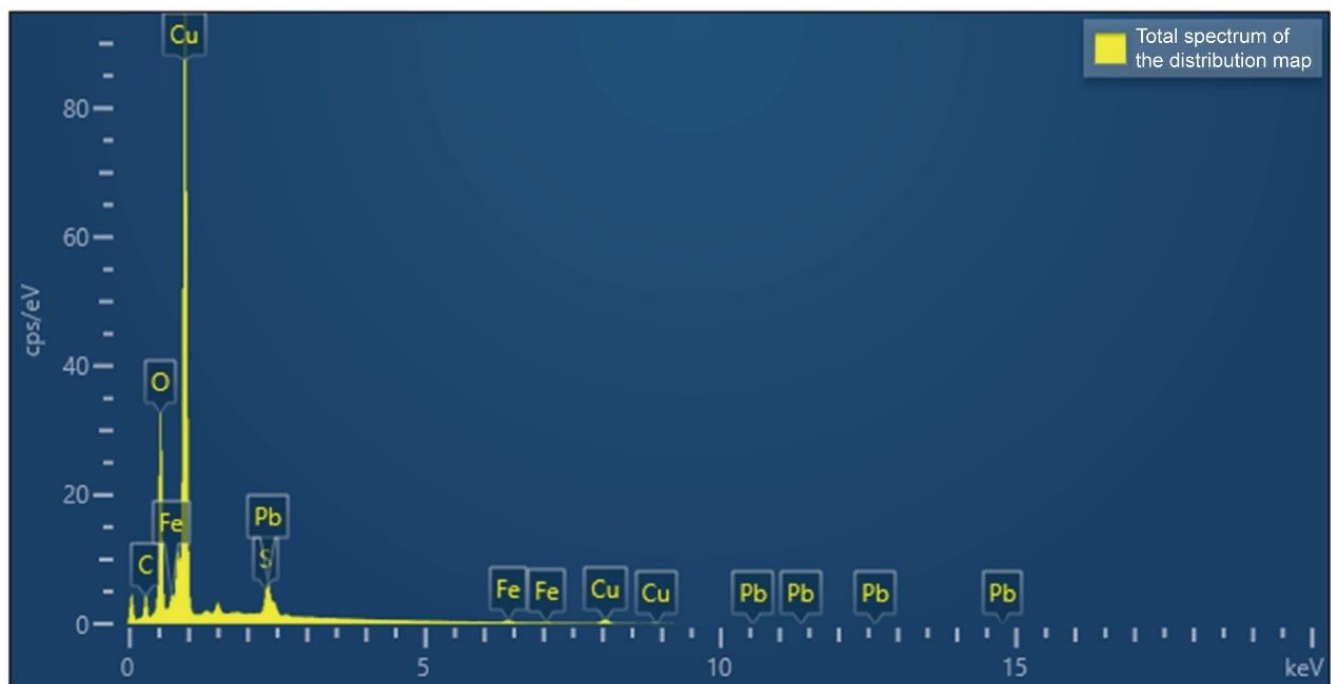


Figure 11. Element distribution in sampling location 2 (image source: annotated by the author; the author changed the annotation in the upper-right corner of the original picture, and the original language was Chinese).

Table 2. The energy-dispersive spectrometer component analysis results for sampling location 2.

Element	Wt%	Wt% Sigma	At%
C	0.30	0.00	1.12
O	14.22	0.06	40.36
S	1.94	0.04	2.75
Fe	4.05	0.18	3.30
Cu	70.76	0.19	50.57
Pb	8.73	0.17	1.92
Total	100.00	/	100.00

Source: Author's statistics.

In combination with the data in Table 2, the following is found:

- (1) Copper (Cu) is the main component of the corrosion layer, with a mass percentage of 70.76% and an atomic percentage of 50.57%, which are significantly higher than those of other elements. This result shows that the matrix material of the bronze arrowhead still has copper (Cu) as the core, and a large amount of incompletely oxidized copper is preserved in the corrosion products. This also reflects that copper oxide is the main corrosion product. According to the spectrum analysis, copper oxides (such as Cu_2O and CuO) generated by the combination of copper and oxygen (O) dominate the corrosion layer, and the porous properties of these oxides may further promote the expansion of the corrosion reaction.
- (2) The mass percentage of oxygen (O) is 14.22% and the atomic percentage is as high as 40.36%, indicating that oxidation reactions play a dominant role in the corrosion process. The oxygen content is significantly lower than that at sampling location 1, which may be related to the different environmental conditions at sampling location 2, such as the greater influence of the sulfidation environment during burial.
- (3) The mass percentage of sulfur (S) is 1.94% and the atomic percentage is 2.75%. Although the content is low, its appearance is a major feature of sampling location 2.

- The formation of sulfides (such as CuS and PbS) may be one of the main characteristics of corrosion in this area, suggesting that the sulfidic environment plays an important role in the corrosion process. This difference in the corrosion mechanism may be due to the corrosive effect of underground sulfide minerals or hydrogen sulfide gas.
- (4) The mass percentage of lead (Pb) is 8.73% and the atomic percentage is 1.92%, which is slightly lower than the lead (Pb) content at sampling location 1, but it still shows a high proportion in the corrosion products. Lead (Pb) is usually distributed in the corrosion layer in the form of particles or dots. It has high chemical stability and is not completely oxidized or lost. The presence of lead (Pb) is related to the ancient bronze alloy process, indicating that it plays an important role in improving the casting performance and corrosion resistance of bronze.
 - (5) The mass percentage of iron (Fe) is 4.05% and the atomic percentage is 3.30%, which is significantly higher than that at sampling location 1. This indicates that sampling location 2 may be more contaminated by external iron or may contain more iron impurities. The generation of iron oxides may have some influence on the structural stability of corrosion products and indicates the existence of interactions of iron materials in the burial environment.
 - (6) The mass percentage of carbon (C) is 0.30% and the atomic percentage is 1.12%. Although the content is low, it may come from organic pollution in the burial environment or a small amount of carbonate generated during the corrosion process. The trace presence of carbon (C) further illustrates the complex influence of the environment on the characteristics of corrosion products.

3.3. X-Ray Fluorescence (XRF)

When analyzing the corrosion characteristics of bronze arrowheads, it was observed that some corrosion layers had obviously eroded into the substrate layer. The XRF results for sampling location A (corrosion layer) showed that the content of copper (Cu) was 58.7%, that of lead (Pb) was 23.42%, that of tin (Sn) was 17.16%, and that of iron (Fe) was 0.71%. This result shows that a high proportion of copper-based components are still retained in the corrosion layer, but, compared with the base layer, the copper content is significantly reduced, while the proportion of lead (Pb) and tin (Sn) is increased, reflecting that these two elements are in the corrosion process. They have high chemical stability and can be enriched in the corrosion layer. In addition, the low content of iron (Fe) in the corrosion layer may be due to the trace presence of external environmental pollutants, which also indicates that iron oxides have not accumulated significantly in the corrosion layer.

On the other hand, the XRF analysis results for sampling location B (matrix layer) showed that the content of copper (Cu) increased significantly to 69.73%, the proportions of lead (Pb) and tin (Sn) were 17.79% and 8.73%, respectively, and the proportion of iron (Fe) was 3.75%. The high copper (Cu) content in the matrix layer in comparison with the corrosion layer indicates that it is still the main component of the bronze arrowheads. The lower contents of lead (Pb) and tin (Sn) indicate that these elements may migrate from the matrix to the surface during the corrosion process and form enrichments in the corrosion layer. In addition, the iron content in the matrix layer is slightly higher than that in the corrosion layer, which may be related to the impurity content of the raw materials in the metallurgical process and indicates that iron (Fe) is more retained inside the matrix.

Combining the two sets of data, it can be seen that the significant difference in element distribution between the corrosion layer and the matrix layer reflects the complex corrosion process experienced by the bronze material in a long-term burial environment. The enrichment of lead (Pb) and tin (Sn) and the reduction in the copper content in the corrosion layer indicate that these corrosion products are mainly composed of copper oxide,

tin oxide, and stable compounds of lead (Pb). The matrix layer shows typical proportions for ancient bronze alloys (Cu-Sn-Pb system).

3.4. X-Ray Diffraction (XRD)

In Figure 12, it can be seen that the two sets of XRD spectra correspond to the X-ray diffraction (XRD) analysis results for sampling location A (surface corrosion layer) and sampling location B (internal matrix), respectively.

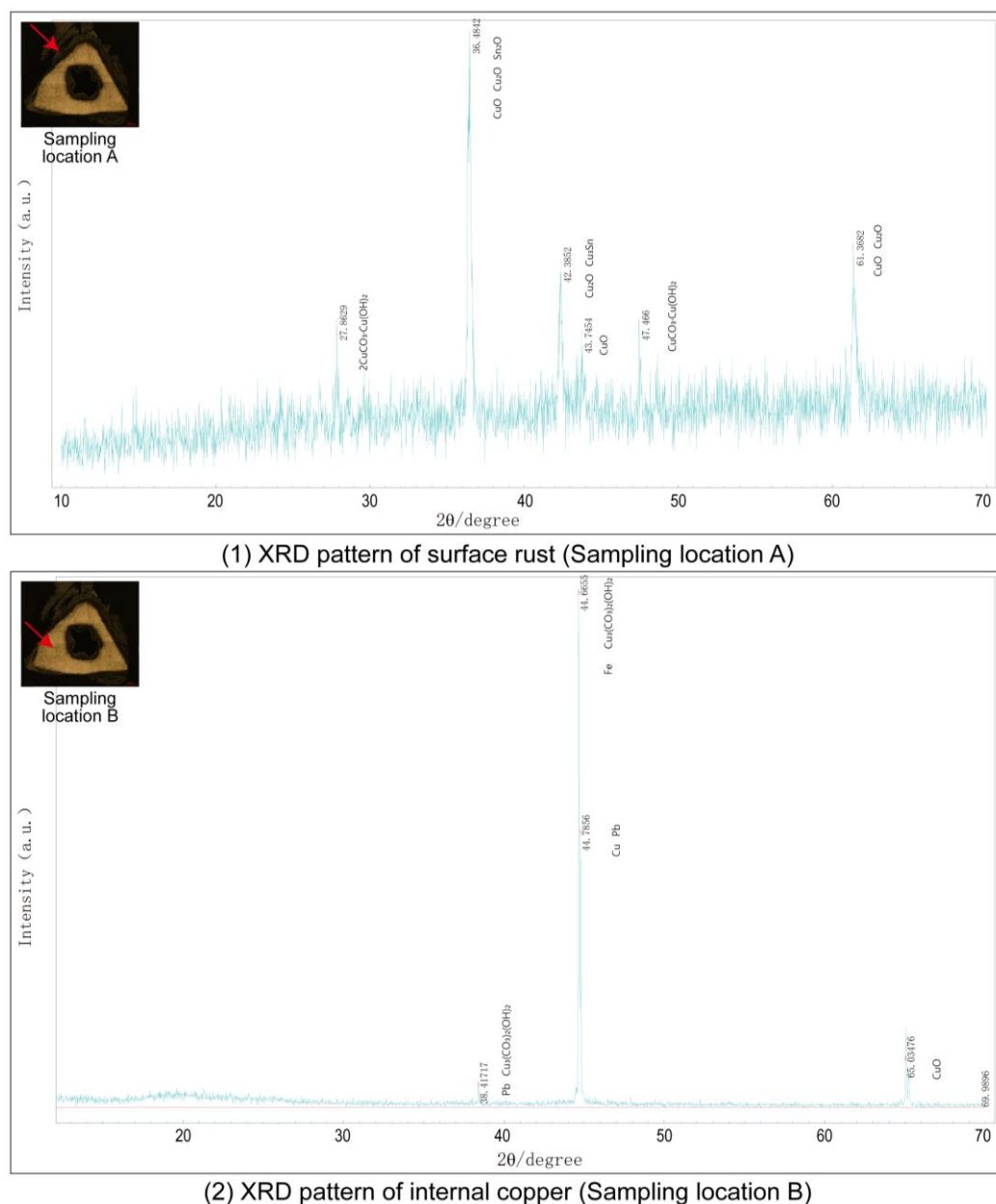


Figure 12. XRD analysis results for sampling locations of the corrosion layer and substrate layer of bronze arrowheads. (1) XRD pattern of surface rust (sampling location A). (2) XRD pattern of surface rust (sampling location B) (image source: annotated by the author).

The XRD spectrum of sampling location A shows that the main phases of the surface corrosion layer include copper oxide (CuO , Cu_2O), copper carbonate ($\text{Cu}_2(\text{OH})_2\text{CO}_3$, i.e., verdigris), and tin oxide (SnO_2). Copper oxide and copper carbonate are the most common corrosion products in the surface corrosion process of bronze artifacts. The strong diffraction peaks of CuO and Cu_2O show that they dominate the corrosion layer. The appearance

of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ indicates that the burial environment contains carbonates or carbonate ions in groundwater. These ions react with copper oxide to form stable verdigris-like corrosion products. This layer of corrosion products may provide a protective effect to a certain extent. It is worth noting that the diffraction peak of SnO_2 was also detected in the XRD spectrum, indicating that tin (Sn) mainly formed tin oxide products during the corrosion process. Tin oxide is chemically stable and can form a dense protective film in the corrosion layer, thereby slowing down the further development of corrosion.

In contrast, the XRD spectrum of sampling location B reflects the main phase characteristics of the internal matrix, and its diffraction peaks clearly show copper (Cu), lead (Pb), and a small amount of iron (Fe). The matrix is mainly composed of metallic copper, and the strong copper (Cu) diffraction peak indicates that copper (Cu) has a very high content in the matrix. This is consistent with the characteristics of bronze alloys. The use of copper (Cu) as the main component provides the strength and toughness of bronze.

The diffraction peak of lead (Pb) is relatively obvious, indicating that lead (Pb) exists in the matrix in the form of metal and has high chemical stability, which is why it can be well preserved in long-term burial environments. The weak diffraction peak of iron (Fe) may originate from impurities in the bronze alloy or trace amounts of iron introduced during the casting process. It is worth noting that no obvious diffraction peaks of oxide or carbonate corrosion products were observed in sampling location B, indicating that the matrix has not undergone significant corrosion and mainly retains the original metallic properties of the bronze arrowhead.

In summary, the main difference between sampling location A and sampling location B lies in the generation of oxide and salt corrosion products in the corrosion layer, while the base layer is mainly composed of metallic copper (Cu) and lead (Pb) and is hardly corroded. The generation of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ in sampling location A indicates that there is a certain amount of carbonate in the underground environment, and these chemical components significantly affect the phase structure and characteristics of the corrosion layer. At the same time, the appearance of SnO_2 further proves the important role of tin in corrosion products, and its protective effect may delay the expansion of matrix corrosion.

3.5. Raman Spectroscopy

The Raman spectroscopy analysis results in Figure 13 show the chemical composition and structural characteristics of sampling location A (surface corrosion layer) and sampling location B (internal matrix layer). The microscopic image of the surface corrosion layer in Figure 13(1) shows a complex microstructure with obvious granular and porous distribution, demonstrating typical morphologies of oxidation products during the corrosion process. The corresponding Raman spectrum in Figure 13(2) shows that the characteristic Cu-O peak at 283.19 cm^{-1} indicates that copper oxide (Cu_2O) is one of the main products of the corrosion layer, indicating that the reaction of copper (Cu) with oxygen (O) is the dominant process of corrosion in this area. The peak at 612.36 cm^{-1} clearly points to tin oxide (SnO_2), which indicates that tin (Sn) is oxidized in the surface corrosion layer to form a stable oxide, which usually has high chemical stability and can form a protective oxide layer to delay further corrosion. The peaks at 964.27 cm^{-1} and 1346.48 cm^{-1} correspond to $\text{Cu}_2(\text{OH})_2$ and $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (copper green substances). Their appearance indicates the presence of carbonate ions in the burial environment. The formation of green copper further confirms that the reaction between carbonate and copper oxide plays an important role in the corrosion layer. The characteristic peak of CO_3^{2-} at 1068.26 cm^{-1} further shows that the chemical activity of carbonate has a key influence on the formation of the corrosion layer.

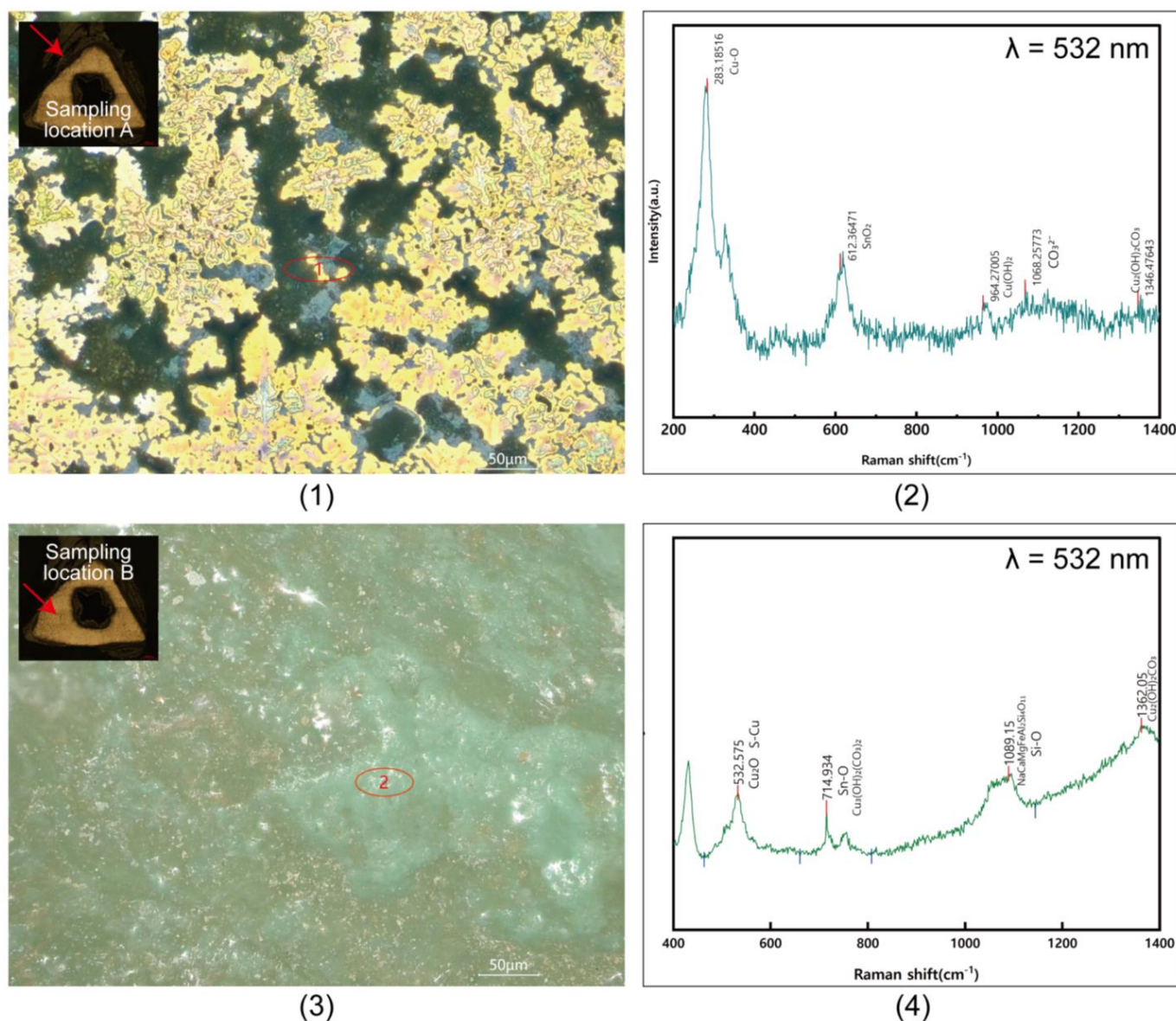


Figure 13. Raman spectroscopic analysis of the corrosion layer and matrix layer of bronze arrowheads. (1) Surface rust image (sampling location A). (2) Raman spectrum (sampling location A). (3) Internal copper image (sampling location B). (4) Raman spectrum (sampling location B). (Image source: annotated by the author.)

Figure 13(3) shows a microscopic image of the inner matrix layer, which has a smooth surface and lacks obvious pores and a granular structure, indicating that this area has not been significantly corroded. The Raman spectrum in Figure 13(4) shows that, at 532.58 cm^{-1} , the coexistence of Cu_2O and S-Cu indicates that, although the internal matrix layer is relatively intact, it is slightly affected by oxidation and sulfidation reactions. The characteristic Sn-O peak at 714.93 cm^{-1} shows that a relatively high metallic tin content is still retained in the matrix layer, further reflecting the typical proportions of ancient bronze alloys. In addition, the characteristic Si-O peak at 1089.15 cm^{-1} indicates the possible presence of siliceous contaminants in the burial environment, which may come from soil particles or sediments and come into physical or chemical contact with the internal metal surfaces. The appearance of the $\text{Cu}_2(\text{OH})_2\text{CO}_3$ peak at 1362.05 cm^{-1} indicates that a small number of patina corrosion products are also formed on the substrate surface, but

the intensity is significantly lower than that at sampling location A, indicating that the corrosion degree of the substrate layer is relatively light.

Therefore, the Raman spectrum of sampling location A reflects the complex mineral composition of the surface corrosion layer, which mainly includes Cu_2O , SnO_2 , $\text{Cu}_2(\text{OH})_2$, and $\text{Cu}_2(\text{OH})_2\text{CO}_3$, indicating that oxidation and carbonation reactions in the burial environment play a dominant role in the formation of the corrosion layer. The Raman spectrum of sampling location B shows the relative integrity of the internal matrix, with only small amounts of traces of Cu_2O and $\text{Cu}_2(\text{OH})_2\text{CO}_3$, as well as the characteristic peaks of Si-O and S-Cu, indicating that the internal environment is less corroded by the outside world, but it is also slightly affected by sulfides and siliceous materials. In summary, the complex mineral composition of the surface corrosion layer of the bronze arrowheads reflects that they have undergone long-term chemical reactions in the underground burial environment, including multiple processes such as oxidation and carbonation. The internal matrix layer is mainly composed of metallic copper (Cu) and tin (Sn), and it only shows limited traces of corrosion.

3.6. Matrix Porosity Analysis

In the study of bronze arrowheads, the microstructure of the matrix layer plays a key role in determining the stability and durability of the overall material. Through the determination of porosity, we can have a deeper understanding of the impact of ancient metallurgical processes on material properties and how these microscopic features play a role in the corrosion process. In combination with the previous analysis of the corrosion layer and the overall corrosion state of the arrowhead, Section 3.6 focuses on the porosity distribution characteristics of the matrix layer and their potential impact on the material properties.

As shown in Figure 14, the red marks in the image are pores. Through measurement, it is found that the porosity of the matrix layer is 11.92%, and there are approximately 0.0048 holes per μm^2 . The area of the holes ranges from $0.09 \mu\text{m}^2$ to $498.60 \mu\text{m}^2$. This high porosity and uneven distribution suggest that, in the ancient bronze smelting process, there were significant limitations in the alloy melting and pouring process, such as uneven cooling rates or the precipitation of impurities. The large pores may have originated from the retention of bubbles during the casting process, while the small pores may have been caused by grain boundary inhomogeneity or alloy element segregation. The presence of pores not only reduces the mechanical strength of the matrix but also provides channels for external corrosive media (such as oxygen and moisture) to penetrate into the interior, significantly accelerating the expansion of the corrosion reaction.

This phenomenon is closely related to the formation mechanism of the corrosion layer of bronze arrowheads. The previous analysis showed that the corrosion layer is enriched with copper oxide and copper carbonate products, and the pores in the matrix layer provide the necessary pathways for the formation of these corrosion products. In addition, the presence of pores may also lead to a decrease in the adhesion between the corrosion layer and the matrix, thereby increasing the risk of peeling of the surface corrosion layer.

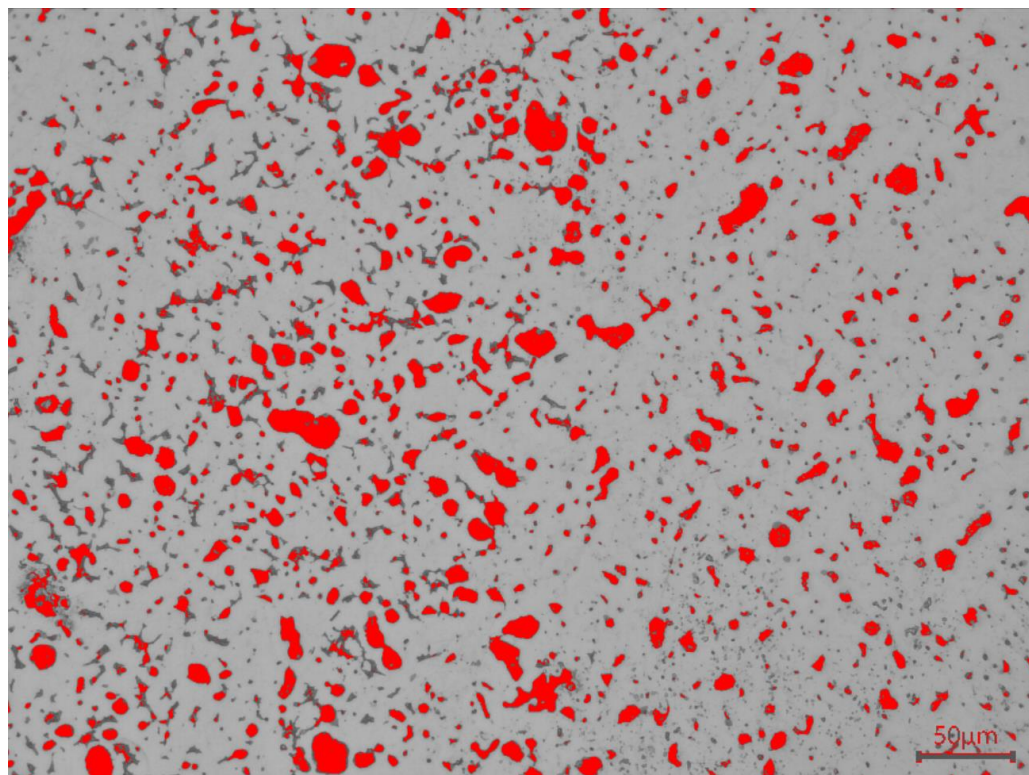


Figure 14. Microstructure of pores in the bronze arrowhead matrix (image source: photographed and annotated by the author).

4. Discussion

4.1. Material Characteristics

The material of this study is a bronze arrowhead unearthed from the Ruins of the Imperial City of the Minyue Kingdom. It is mainly composed of copper (Cu), tin (Sn), and lead (Pb) alloys, and it has formed a distinct multi-layer structure under the long-term action of its burial environment, including a surface corrosion layer, a matrix layer, and an inner cavity area. Through material truncation processing, corrosion powder extraction, and microstructural and chemical composition analyses, the uniqueness of the bronze arrowhead in terms of its material and corrosion behavior is revealed.

The microstructural analysis of the surface corrosion layer shows that the area is mainly composed of copper oxide (Cu_2O), tin oxide (SnO_2), and carbonate corrosion products (such as $\text{Cu}_2(\text{OH})_2$ and $\text{Cu}_2(\text{OH})_2\text{CO}_3$). These corrosion products reflect the chemical reactions that bronze arrowheads have undergone in burial environments for a long time, including oxidation and carbonation. The Cu-O characteristic peak of 283.18516 cm^{-1} in the Raman spectrum shows that copper oxide is the main component of the corrosion layer, while the characteristic SnO_2 peak of 612.36471 cm^{-1} shows that tin generates a stable oxide during the corrosion process. This oxide is chemically inert and can delay the further development of corrosion to a certain extent. In addition, the characteristic carbonate peaks ($\text{Cu}_2(\text{OH})_2$ and $\text{Cu}_2(\text{OH})_2\text{CO}_3$) at 964.27005 cm^{-1} and $1346.47643\text{ cm}^{-1}$ indicate that carbonate ions in the environment further reacted with copper oxide to form stable green copper products. The presence of carbonate corrosion products not only has a certain protective effect but also provides clues for understanding the underground burial environment.

The metallographic analysis of the matrix layer revealed that its structure was mainly composed of metallic copper (Cu), supplemented by tin (Sn) and lead (Pb), showing typical characteristics of ancient bronze alloys. The XRF and EDS analyses showed that the mass percentage of matrix copper was as high as 70.76%, while the proportions of tin and lead

were 8.73% and 8.72%, respectively. The presence of tin significantly increased the material's hardness and casting fluidity, while lead improved the casting properties, enabling complex bronze arrowhead designs to be realized. In addition, the characteristic peaks of Raman spectroscopy in the matrix layer showed that Cu_2O and copper sulfide (S-Cu) were detected at 532.575 cm^{-1} , which indicates that, although the matrix is well preserved, it has also been affected by oxidation and sulfidation to a certain extent. This sulfidation characteristic may be related to the presence of sulfides in the burial environment.

The porosity of the matrix layer is 11.92%, which shows the inhomogeneity of the ancient metallurgical process during smelting and casting. These pores may come from residual bubbles or impurity separation during the casting process. The presence of pores not only reduces the mechanical strength of the matrix but also provides channels for the penetration of external media (such as oxygen and moisture), accelerating the expansion of the corrosion layer. In addition, the porous characteristics are closely related to the generation of corrosion products, such as the porous morphology of copper carbonate and copper oxide, which further indicates that pores are an important feature of the active area of corrosion reactions.

The material characteristics of the bronze arrowheads show that the material design achieved excellent mechanical properties and casting complexity through a reasonable ratio of copper (Cu), tin (Sn), and lead (Pb). However, the limitations of the metallurgical process led to a high porosity in the matrix layer, which posed a hidden danger for later corrosion. The composition of the corrosion layer reflects the oxidation and carbonate chemical reactions in the burial environment, while the high copper content of the matrix layer and the stability of tin oxides indicate that it retained the original characteristics of the bronze alloy to a large extent. In addition, no copper chloride corrosion products were detected, further indicating that the influence of chloride ions in the burial environment was low.

4.2. Metallurgical Process

The production process of bronze arrowheads reflects that the bronze metallurgy of the Minyue Kingdom was influenced by both the Central Plains culture and the local casting tradition. The material composition and microstructure of the arrowheads reflect the craftsmen's mastery of metallurgical technology at that time, especially the high technical level in the proportioning of multi-alloy systems and mold casting. This technology played an important role in improving the lethality, accuracy, and service life of arrowheads. In addition, the metallurgical characteristics of the bronze arrowheads show that the production technology achieved a certain scale, but the smelting and casting processes could not completely avoid defects, indicating that there was a trade-off between production efficiency and quality.

According to the microstructural and chemical composition analyses, it is speculated that the bronze arrowheads of the Minyue Kingdom were prepared using the melt casting method. This process may include the initial smelting of copper ore, the addition of tin (Sn) and lead (Pb), the high-temperature mixing of the melt, mold casting, and cooling molding. From the observation of the cross-section, it can be seen that the arrowhead has a complex geometry, indicating that the mold design and precision are high, which may be related to multiple trial castings and the accumulation of experience. In addition, the high content of copper (Cu) ensures the mechanical strength of the matrix, while the proportion of tin (Sn) and lead (Pb) is adjusted to balance the hardness, toughness, and castability.

However, the porosity analysis reveals the limitations of ancient metallurgical processes. The porosity of the matrix layer is 11.92%, with approximately 0.0048 pores per square micron. The pore sizes range from $0.09\text{ }\mu\text{m}^2$ to $498.60\text{ }\mu\text{m}^2$, and the distribution

is dense and uneven. This porosity may be caused by problems such as uneven cooling, residual bubbles, or the separation of alloy elements during smelting and casting, reflecting that ancient metallurgical technology did not yet achieve densification casting in the modern sense. Although a high proportion of lead (Pb) helps to improve the casting fluidity, the generation of bubbles and impurities is still an inevitable result. In addition, the limited purity of raw materials in ancient metallurgical processes and local temperature fluctuations during processing further lead to the unevenness of the internal structure of the material.

4.3. Corrosion Phenomena and Mechanisms

Bronze is the earliest alloy in the history of human metal smelting. Adding tin or lead to pure copper or red copper often forms a copper–tin alloy. During the Han Dynasty, iron wares gradually replaced Chinese bronze wares, which first appeared in 5000 B.C. China's Bronze Age spanned a long history of about three thousand years. Bronze alloys mainly involve copper–tin–lead as the main raw materials. Compared with pure copper and red copper, bronze has high strength, a low melting point, good castability, wear resistance, and stable chemical properties.

Bronze corrosion usually starts from the local part of the bronze surface and gradually forms a mineral surface layer, which is commonly known as a “patina”. Common bronze corrosion products include copper (II) oxide (CuO) or cupric oxide, copper (I) oxide or cuprous oxide (Cu₂O), copper (II) sulfide (CuS), copper (I) sulfide (Cu₂S), copper (II) sulfate (CuSO₄), basic copper sulfate (CuSO₄·3Cu(OH)₂·H₂O), basic copper carbonate (Cu₂(OH)₂CO₃), copper (I) chloride (CuCl), dicopper chloride trihydroxide (Cu₂(OH)₃Cl), and stannic oxide (SnO₂).

When this mineral surface is in a stable state, the rust is called harmless rust. Under a microscope, the bronze interface displays numerous impurities and undissolved mineral particles due to the limitations of ancient metallurgy. These defects create stress and lattice defects in the bronze, resulting in distinct potentials for different parts of the metal. There are soluble salts in the unearthed bronzes, and their rate of electrochemical corrosion far exceeds that of pure chemical corrosion. Harmless rust can produce different colors, such as emerald green, turquoise, lake green, gray-green, reddish brown, black, and silver-gray, on the surface of bronze. It is magnificent and colorful. It has esthetic value and adds to the artistic effect of bronzes. Simultaneously, it serves as a testament to a specific historical era. The most important thing is that the mineral surface that it forms does not change the shape of the bronze, which can protect the internal metal from corrosion.

Harmful rust refers to an unstable state of the mineral surface. The corrosion product of harmful rust is light-green powdery rust, so it is also called “bronze disease” and “powdery rust”. This corrosion will continue to spread, penetrate into the bronze matrix, and repeat this process in the bronze body, causing the bronze to be deformed, the patterns to peel off, the inscriptions to be blurred, the object to be penetrated, and even the entire object to be powdered, broken, and made brittle until it is completely damaged, causing harm to the bronze matrix. This rust will also disperse among various bronzes, thereby posing a threat to entire storage spaces.

The results of the analysis and test of harmful rust confirmed that the light-green powder is dicopper chloride trihydroxide (Cu₂(OH)₃Cl), also known as chlortacorite. Dicopper chloride trihydroxide (Cu₂(OH)₃Cl) primarily produces basic cupric chloride when it reacts with bronze to form copper (I) chloride (CuCl). Copper (I) chloride (CuCl) reacts with water to produce copper (I) oxide (Cu₂O) and hydrochloric acid. Hydrochloric acid can continue to react with copper, copper (I) oxide (Cu₂O), and basic copper carbonate (Cu₂(OH)₂CO₃) to produce dicopper chloride trihydroxide (Cu₂(OH)₃Cl). This series of

reactions is repeated on bronze. Without human intervention, the reaction will continue until it completely transforms into dicopper chloride trihydroxide ($\text{Cu}_2(\text{OH})_3\text{Cl}$), resulting in the object becoming completely powdered and damaged.

The corrosion phenomena of bronze arrowheads are mainly reflected in the formation of a surface corrosion layer and the local degradation of the matrix layer. Through cross-sectional observation, it can be seen that obvious layered corrosion products are formed on the surface of the arrowhead, including compounds such as copper oxide (Cu_2O), tin oxide (SnO_2), and copper carbonate ($\text{Cu}_2(\text{OH})_2$ and $\text{Cu}_2(\text{OH})_2\text{CO}_3$). These corrosion products show a porous structure in their microstructure, with an uneven pore distribution accompanied by cracks, indicating that there is a high degree of heterogeneity in the corrosion layer. In particular, the cracks and granular products at sampling location 1 (surface corrosion layer) indicate that the chemical reactions of oxidation and carbonation are mainly concentrated in the surface layer, and the corrosion products are accumulated layer by layer. Sampling location 2 (the inner cavity corrosion layer) shows deeper corrugated textures and penetrating cracks, indicating that this area may be corroded by stronger humidity and chemical media.

The corrosion phenomenon of the matrix layer is relatively mild, but small amounts of oxidation products and sulfide generation are observed on its surface. The higher porosity in the matrix layer makes it more susceptible to the penetration and local reaction of the corrosive medium. These pores provide channels for oxygen, moisture, and other reactants, further accelerating the development of the corrosion process.

The underground burial environment plays a decisive role in the corrosion of bronze arrowheads. Oxygen, carbonate, and sulfide ions in groundwater are important media that cause corrosion. The generation of oxidation products and copper carbonate compounds indicates that the concentrations of oxygen and carbonate ions in the underground environment are high, and the presence of sulfides at sampling location 2 further reflects the role of hydrogen sulfide or sulfide minerals in the local environment. In addition, the humidity and temperature fluctuations in the burial environment may further accelerate the rate of corrosion reactions; especially under the action of cracks and pores, the corrosive medium can quickly penetrate into the matrix layer, leading to deeper corrosion.

4.4. Recommendations for Protective Coatings

Based on the systematic analysis of the material properties, metallurgical processes, and corrosion mechanisms of bronze arrowheads unearthed from the Ruins of the Imperial City of the Minyue Kingdom in this study, combined with in-depth research on the microstructure and chemical composition of the corrosion layer and the substrate layer, targeted recommendations can be made from the perspective of coating protection to achieve the long-term protection of bronze arrowheads. The following are specific recommendations.

- (1) Physical isolation and chemically inert coatings: The main corrosion mechanisms of bronze arrowheads include oxidation, carbonation, and sulfidation. The cracks and porous structures in the corrosion layer provide penetration channels for corrosive media (such as oxygen, moisture, and sulfide ions). Therefore, the protective coating should have excellent physical isolation properties and be able to form a dense coating to effectively block the invasion of external corrosion factors. At the same time, the coating itself must be chemically inert and not react with the bronze matrix or corrosion products to avoid inducing new chemical changes. For example, silicone resin coatings and polyvinylidene fluoride (PVDF) coatings have good chemical stability and environmental corrosion resistance and are potentially preferred materials.

- (2) Optimization of the coating formula based on material compatibility: Studies have shown that the bronze arrowhead matrix is mainly composed of copper (Cu) (70.76%), tin (Sn) (8.73%), and lead (Pb) (8.72%). Tin and lead have higher stability and can form a certain amount of protective oxide film, while copper (Cu) has a more active oxidation reaction and is prone to generate porous oxide or carbonate corrosion products. Therefore, the coating should give priority to compatibility with copper-based materials to reduce the interfacial stress and shedding risk between the coating and the substrate. In addition, active ingredients with a corrosion inhibition function, such as nitrite or benzotriazole (BTA), can be added to form a protective molecular film at the coating interface to inhibit copper oxidation and carbonation reactions.
- (3) Coating filling and crack repair for pores: The porosity of the substrate layer is as high as 11.92%, and the size of cracks and holes ranges from $0.09 \mu\text{m}^2$ to $498.60 \mu\text{m}^2$, which provides an important channel for the penetration of corrosive media. Therefore, before coating, nanoparticles or microparticle fillers should be used to repair and fill pores and cracks. Silica (SiO_2) nanoparticles or zirconium oxide (ZrO_2) microparticles have excellent corrosion resistance and good interface adhesion, and they can be used as filler materials to synergize with the coating to further enhance the density of the coating.
- (4) Multi-layer coating design and functional differentiation: In view of the complex influence of different corrosive media, a multi-layer coating design strategy can be adopted to optimize the protective function in layers. The first layer can use a primer with high adhesion, such as an epoxy resin primer, to form a stable bond with the bronze substrate. The second layer is a functional intermediate coating to which corrosion inhibitors (such as benzotriazole) and nanofillers can be added to further enhance the coating's anti-oxidation and anti-sulfurization properties. The outermost layer should use a transparent protective coating with excellent weather resistance (such as acrylic or fluoride coating) to resist long-term erosion by ultraviolet rays, moisture, and air pollutants. In addition, the use of a transparent coating can also preserve the original texture and color of the bronze arrowhead surface, meeting the dual needs of the display and protection of cultural relics.
- (5) Development and application of reversible coatings: For the long-term sustainability of cultural relic protection, reversible coating systems should be preferred so that, when necessary, the coating can be completely removed by gentle means without damaging the bronze substrate. The development of reversible coatings can refer to polymer systems with good swelling properties (such as polyvinyl butyral, PVB) or water-soluble resins, which can be removed using solvents or water. This design concept can meet contemporary conservation needs while providing flexibility for future research and conservation.

In summary, coating protection is only part of the protection of bronze cultural relics, and it must also be combined with environmental control measures to achieve more comprehensive protection. Bronze arrowheads should be stored in an environment with stable temperature and humidity as much as possible to avoid high humidity (>60% RH) and acidic gases (such as SO_2 and H_2S) from corroding the coating and the cultural relics. For example, equipment for dehumidification and adsorption of pollutants can be installed in museum display cabinets, and environmental parameters can be monitored in real time.

5. Conclusions

This study has shown that the main alloy components of bronze arrowheads are Cu-Sn-Pb systems, in which the high proportion of copper (70.76% in the matrix) provides structural strength, while the addition of tin and lead optimizes the material's hardness,

toughness, and casting fluidity. Microscopic analysis reveals a high porosity (11.92%) in the matrix of bronze arrowheads, showing the limitations of ancient metallurgical processes in casting control and impurity separation. These microstructural defects not only affect the mechanical properties of the material but also provide channels for later corrosion reactions. The main products of the corrosion layer are copper oxide (Cu_2O and CuO), tin oxide (SnO_2), and copper carbonate ($\text{Cu}_2(\text{OH})_2\text{CO}_3$), among which tin oxide exhibits strong chemical stability and can provide a certain degree of protection in the corrosion layer.

Studies on the corrosion mechanism found that oxidation reactions and carbonation are the main driving forces for the corrosion of bronze arrowheads, while humidity, carbonate ions, and sulfides in the burial environment also play a key role in the corrosion process. The surface corrosion layer exhibits significant stratification characteristics, and the cracks and porous structures enable the corrosive media to penetrate into the matrix layer, accelerating the expansion of local corrosion. The matrix layer is mainly characterized by slight oxidation and sulfidation reactions, indicating that it is relatively well preserved. The research results further reveal the influence of environmental factors (such as carbonate ions and sulfides in groundwater) on the generation and distribution of corrosion products.

Although this study used comprehensive analytical techniques, the following limitations should be considered: (1) Sample representativeness: The study samples were limited to the Ruins of the Imperial City of the Minyue Kingdom, and the results may not be generalized to all bronze artifacts from the Minyue Kingdom or even the Fujian region. (2) Impact of environmental changes: The burial environment of bronze arrowheads may change over time, thus affecting the corrosion process. Future experiments with controlled variables can be conducted to further verify the influence of environmental factors. (3) Instrument detection sensitivity: Some trace elements (such as chlorine) may not be accurately identified due to instrument detection limits. (4) Non-destructive analysis limitations: Although non-destructive analysis (such as XRF and Raman spectroscopy) was used as much as possible in this study, a small amount of sampling is still required for high-resolution imaging and phase identification.

Given the cultural value of the bronze arrowheads, all of the analyses in this study were conducted under the supervision of cultural relic conservation experts to ensure minimal impact on the artifacts. After the analysis, the samples were stored in a controlled humidity environment to prevent further degradation. The findings of this study will help develop long-term conservation strategies for bronze artifacts and provide practical guidance in museums and field archaeological research. In conclusion, this study provides an important basis for understanding the material properties, corrosion mechanisms, and metallurgical processes of ancient bronze arrowheads. Future research needs to further combine multidisciplinary methods such as archeology, materials science, and environmental chemistry to promote the sustainable development of bronze cultural relic research and protection.

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