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Elemental Signatures of Xianfeng Tongbao: XPS Evidence of Fiscal Crisis and Currency Devaluation in Late Qing China

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Abstract: The Xianfeng reign (1851-1861) was marked by severe fiscal crisis and monetary instability in Qing China, when official and privately minted coins circulated simultaneously. While numismatic and historical studies have described this phenomenon, they often lack systematic material analysis, and scientific investigations of alloy composition rarely extend to socio-economic interpretation. This study bridges the gap by employing X-ray photoelectron spectroscopy (XPS) to compare the elemental composition of an official and a privately minted Xianfeng Tongbao coin. Surface cleaning, rust removal, and high-resolution XPS scans were conducted at three random points for each specimen, followed by CasaXPS peak fitting to quantify Cu, Zn, Pb, and Sn contents. Results show that official coins maintained high Cu content with stable Zn and Sn proportions, ensuring structural stability, whereas private issues exhibited reduced Cu and elevated Zn and Pb, with inconsistent Sn, leading to weaker alloys. These compositional differences directly reflect resource scarcity, fiscal weakness, and declining state control. The findings demonstrate that microstructural chemistry can serve as material evidence of macroeconomic crisis, contributing both to numismatic science and to economic history, while offering methodological value for archaeology and heritage conservation.

Keywords: Xianfeng Tongbao; XPS; coinage alloys; socio-economic history; Qing Dynasty

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1. Introduction

The reign of the Xianfeng Emperor (1851-1861) marked one of the most turbulent decades in the Qing Dynasty, when external invasions and internal rebellions severely destabilized the empire's fiscal foundations [1]. Under conditions of chronic deficit, the Qing government was forced to expand coinage to sustain military expenditures and daily administration [2]. Copper coins, traditionally the backbone of Chinese currency, became increasingly scarce due to disruptions in mining and distribution. As a result, both official mints and private workshops operated simultaneously, giving rise to a complex monetary landscape [3]. While official mints attempted to maintain consistent standards of alloy composition, private minters frequently diluted copper with cheaper substitutes such as zinc and lead, producing low-quality imitations for circulation [4]. This dual system not only eroded public trust in money but also aggravated inflationary pressures, contributing to the broader economic and social decline of the late Qing.

Scholars have long investigated the fiscal and monetary policies of the Qing Dynasty, with particular attention to the impact of the Taiping Rebellion and foreign trade imbalances [5]. Numismatic studies have examined the typological diversity of Xianfeng

Tongbao coins, while economic historians have traced the collapse of copper supply chains [6]. In the field of material science, conventional metallurgical analyses such as scanning electron microscopy (SEM) and inductively coupled plasma mass spectrometry (ICP-MS) have been employed to identify alloy components of historical coinage [7]. However, existing research often remains fragmented. Historical studies have seldom integrated systematic material analysis, while chemical investigations rarely extend their implications to macro-level socio-economic processes. Consequently, a significant research gap persists: the absence of an interdisciplinary framework that connects micro-level elemental composition of coins to the macro-level realities of fiscal crisis and state instability.

The present study seeks to bridge this gap by employing X-ray photoelectron spectroscopy (XPS) to conduct a comparative analysis of two Xianfeng Tongbao coins, one produced by an official mint and the other privately cast. XPS, with its sensitivity to surface chemistry and elemental binding energies, enables precise detection of copper (Cu), zinc (Zn), lead (Pb), and tin (Sn) content, thus providing a scientific basis for evaluating the authenticity and quality of coinage [8]. By comparing the elemental signatures of official and private issues, this study aims not only to characterize the technological differences between regulated and counterfeit minting practices but also to explore how these chemical variations reflect the fiscal constraints and economic decline of the late Qing Dynasty.

The significance of this research is twofold. Academically, it advances the integration of materials science with economic history, demonstrating how microstructural analysis can serve as material evidence of macroeconomic crisis. Practically, it contributes to the authentication and preservation of historical artifacts, offering methodological guidance for archaeologists, museum curators, and cultural heritage specialists. More broadly, the findings underscore the importance of material-based approaches in reassessing narratives of monetary instability and state decline.

The innovation of this study lies in its interdisciplinary methodology. Unlike prior works that either focus narrowly on alloy composition or provide qualitative accounts of monetary collapse, this research combines rigorous XPS analysis with socio-economic interpretation. In doing so, it illustrates how chemistry and history intersect to reveal the dynamics of currency credibility, resource scarcity, and institutional weakness during a critical juncture of Chinese history.

2. Literature Review

Research on Qing Dynasty coinage has attracted attention from both economic historians and material scientists, producing a body of literature that illuminates the fiscal, monetary, and technological dimensions of the Xianfeng Tongbao [9]. A major strength of this scholarship is its multidisciplinarity: numismatists have meticulously documented typological variations of Qing coinage, historians have traced the connections between fiscal policy and social unrest, and material scientists have applied advanced analytical methods to characterize coin alloys [10]. Together, these studies provide a foundation for understanding the complex dynamics of Qing monetary systems.

Despite these advances, limitations remain. Historical studies often emphasize macroeconomic policy and political crises but rarely engage with the microstructural evidence embedded in the coins themselves. For instance, research on the Taiping Rebellion and late Qing fiscal decline highlights the pressures of warfare and silver outflows, yet typically treats copper scarcity as a background condition rather than a measurable variable. Conversely, metallurgical analyses of Qing coins, employing techniques such as SEM-EDS, ICP-MS, or conventional spectroscopic methods, tend to focus on the detection of elemental ratios without situating those results in broader socio-economic contexts [11]. As a result, historical narratives and scientific data often run in parallel but seldom converge.

When placed in comparative perspective, this divergence becomes clear. Western numismatic studies have increasingly adopted interdisciplinary frameworks that integrate chemical analysis with monetary history. For example, Holliday's work on coinage alloys demonstrated how XPS could reveal patterns of debasement that aligned with documented episodes of fiscal stress in European states. Similar approaches have been employed in archaeological chemistry, where metallurgical composition is used to infer trade networks and resource availability [12]. By contrast, studies of Qing coinage have yet to fully exploit such integrative methodologies. Although Chinese numismatics has accumulated a rich descriptive tradition, it remains largely qualitative, while chemical studies of Qing coins remain methodologically siloed.

This imbalance reveals a critical gap in current scholarship: the absence of systematic, interdisciplinary research that directly links the elemental composition of Xianfeng Tongbao coins to the socio-economic transformations of the late Qing Dynasty [13]. The historical literature recognizes the circulation of debased coinage but lacks empirical confirmation at the atomic level. Meanwhile, material science investigations identify compositional anomalies but do not extend their significance to questions of fiscal policy, state capacity, or currency credibility. Without bridging these perspectives, the understanding of how monetary instability manifested both materially and socially remains incomplete.

The present study addresses this gap by combining the strengths of both domains. Through the application of X-ray photoelectron spectroscopy (XPS), it quantifies the relative proportions of Cu, Zn, Pb, and Sn in both official and privately minted Xianfeng Tongbao coins [14]. By situating these findings within the broader economic history of the Qing, the study not only documents the chemical markers of debasement but also interprets them as evidence of fiscal crisis, resource scarcity, and declining state authority [15]. In doing so, this research contributes an interdisciplinary framework that integrates micro-level elemental signatures with macro-level socio-economic interpretation. This dual focus offers both methodological innovation and historical insight, expanding the analytical toolkit available to numismatics, material science, and economic history alike.

3. Materials and Methods

3.1. Research Design and Rationale

The objective of this study is to investigate the elemental composition of Xianfeng Tongbao coins from the late Qing Dynasty and to examine how chemical differences between official and privately minted specimens reflect broader socio-economic conditions. To achieve this goal, the research employs X-ray Photoelectron Spectroscopy (XPS) as the primary analytical tool. XPS was chosen for its high sensitivity to surface chemistry, its ability to provide binding energy information specific to elemental species, and its suitability for detecting compositional differences in metallic alloys.

Given the dual focus on official and private minting, two representative coin samples were selected:

1) Sample A: Xianfeng Tongbao privately minted coin.
2) Sample B: Xianfeng Tongbao officially minted coin.

For both samples, three random measurement points were analyzed to obtain statistically representative data. The experimental workflow was carefully designed to ensure reproducibility, minimize contamination, and capture both qualitative and quantitative aspects of elemental distribution.

3.2. Materials and Reagents

Two Xianfeng Tongbao coins were selected: one official issue and one privately minted specimen, representing contrasting origins. Anhydrous ethanol (General-Reagent) was applied for preliminary cleaning to dissolve grease and particulates, ensuring uncontaminated surfaces for analysis. Concentrated hydrochloric acid (HCl, Kelong, China) was used to chemically remove corrosion layers, particularly copper carbonate and ferric oxide, which otherwise obscure metallic signals in XPS spectra. Deionized water was employed for rinsing after acid treatment, preventing the introduction of extraneous ions such as Na^+ or Ca^{2+}. All reagents were of analytical grade, handled under standard safety protocols. These preparations ensured that the surfaces analyzed by XPS reflected intrinsic alloy composition rather than environmental contamination, thereby enhancing the validity of the comparative study between official and private coinage.

3.3. Instruments and Equipment

Elemental analysis was performed with an AXIS Supra X-ray Photoelectron Spectrometer (Kratos), equipped with an Al Kα excitation source (1486.6 eV), chosen for its high resolution and sensitivity to transition metals (Cu, Zn, Pb, Sn). An ultrasonic cleaner (Titan) assisted ethanol-based cleaning by removing surface particulates through cavitation, offering a non-destructive alternative to mechanical abrasion. A constant-temperature drying oven (Shanghai Yiheng) was employed to uniformly dehydrate samples before acid treatment, reducing variability in chemical reactions. Data processing and quantification were conducted using CasaXPS software, which enables precise peak deconvolution and background subtraction, yielding reliable atomic percentage calculations. Calibration of the spectrometer was performed against reference standards to maintain binding energy accuracy within ±0.1 eV. Collectively, this equipment ensured reproducible detection of compositional differences between official and privately minted Xianfeng Tongbao coins.

3.4. Sample Preparation Procedure

3.4.1. Segmentation

Due to dimensional constraints of XPS analysis (maximum acceptable sample size ≈ 1 × 1 × 0.3 cm), the coins were cut into smaller segments using a precision cutting tool. From each coin, one appropriately sized fragment was randomly selected for subsequent analysis to ensure both practicality and representativeness.

3.4.2. Cleaning

To eliminate physically removable contaminants such as dust and grease, fragments were immersed in 10 mL anhydrous ethanol. Each sample was placed in a separate beaker and subjected to ultrasonic treatment for 30 minutes. This procedure ensured that superficial impurities did not interfere with photoelectron emission or produce spurious peaks in the spectra.

3.4.3. Rust Removal

Following ultrasonic cleaning, samples were dried for 15 minutes in a constant-temperature drying oven. Subsequently, 3 mL concentrated HCl was added to each sample-containing beaker under a fume hood to remove rust products (primarily copper carbonate and ferric oxide).

Two observable reactions occurred:

Reaction with basic copper carbonate (copper rust)

$$Cu_2(OH)_2CO_3+4HCl = 2CuCl_2+3H_2O+CO_2 \quad (1)$$

This reaction released visible bubbles of carbon dioxide and turned the solution blue due to the formation of soluble copper(II) chloride.

Reaction with ferric oxide (iron rust)

$$\mathrm{Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O} \quad (2)$$

Here, ferric oxide reacted with hydrochloric acid to yield ferric chloride, which is soluble in water, and water molecules.

These steps removed corrosion layers and exposed metallic surfaces suitable for accurate XPS detection.

3.5. Principles of X-ray Photoelectron Spectroscopy

XPS operates on the principle of the photoelectric effect, in which incident photons (Al Kα source, 1486.6 eV) strike the sample surface and eject core-level electrons. The kinetic energy of these electrons is measured and converted into binding energy (E_B) using the following equation:

$$E_B = h\nu - E_K - \phi \quad (3)$$

In this expression, E_B denotes the binding energy of the electron (in eV), which is characteristic of the element and orbital from which the electron originates. The term $h\nu$ represents the energy of the incident photon; E_K is the measured kinetic energy of the emitted electron; and ϕ corresponds to the work function of the spectrometer. Because binding energies are both element- and orbital-specific, XPS allows precise qualitative identification and quantitative determination of elemental composition. Peak fitting with CasaXPS software was subsequently used to calculate the atomic percentages of Cu, Zn, Pb, and Sn.

3.6. Measurement Protocol

For each coin, an initial survey scan was conducted to identify the full range of detectable elements present on the sample surface. This was followed by high-resolution scans targeting the specific spectral regions of Cu 2p, Zn 2p, Pb 4f, and Sn 3d, which are most relevant for alloy characterization. To address surface heterogeneity, three random measurement points were selected for each specimen, ensuring statistical representativeness. Spectral data were processed using CasaXPS software, where peak deconvolution and quantification procedures yielded relative atomic concentrations expressed as percentages. Finally, results from the three points were averaged to produce reliable composition profiles for both the official and privately minted Xianfeng Tongbao coins.

3.7. Analytical Framework

The interpretation of results was structured on two complementary levels. At the material-scientific level, the elemental compositions of Cu, Zn, Pb, and Sn were analyzed with respect to their roles in determining alloy stability, mechanical strength, and resistance to corrosion. This allowed for the evaluation of differences in durability and authenticity between official and private issues. At the socio-economic level, these compositional variations were contextualized as reflections of broader historical realities, including fiscal constraints, the prevalence of counterfeit practices, and the weakening control of the Qing state during the Xianfeng era. Together, this dual framework enabled a holistic analysis that bridged chemical evidence with historical interpretation.

3.8. Reliability and Validity

To ensure reliability, each measurement was replicated at three distinct surface points. The use of XPS, known for its high surface sensitivity (~10 nm depth), minimized the risk of bulk contamination but introduced the limitation of surface-specific results. To address validity, results were cross-checked with existing literature on Cu-Zn-Pb-Sn alloys and prior studies of coinage materials, ensuring consistency with known metallurgical behavior.

3.9. Ethical and Heritage Considerations

All experimental operations were conducted on coin fragments to avoid compromising the integrity of full specimens. Procedures were designed to balance analytical accuracy with artifact preservation, aligning with best practices in heritage science.

4. Results and Discussion

4.1. Overall Comparison of Elemental Composition

X-ray photoelectron spectroscopy (XPS) revealed significant compositional differences between the privately minted and officially minted Xianfeng Tongbao coins. The wide-scan XPS spectra, presented in Figure 1, clearly show the presence of characteristic peaks corresponding to Cu, Zn, Pb, and Sn, alongside O and C signals attributable to surface oxides and adsorbed species. Quantitative analysis based on these spectra indicates that the official coin (Sample B) is dominated by copper (Cu), whereas the private coin (Sample A) contains reduced Cu levels and elevated Zn and Pb.

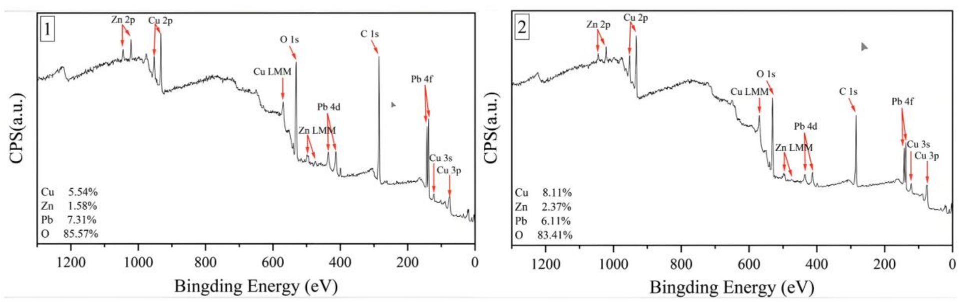

Figure 1. Wide-scan XPS spectra of Xianfeng Tongbao coins. (1) privately minted; (2) officially minted. Each spectrum is the arithmetic mean of three randomly selected surface points per specimen (n=3, after cleaning and rust removal). Characteristic peaks of Cu, Zn, Pb, and Sn are labeled.

To provide a clearer numerical comparison, the relative atomic percentages of major metallic elements are summarized in Table 1. These results confirm that official coinage was produced with a stable Cu-rich alloy, while private issues deliberately substituted cheaper metals such as Zn and Pb, with inconsistent Sn levels.

Table 1. Relative atomic percentages of key elements in official and private Xianfeng Tongbao coins.

Element	Sample A (Private Coin)	Sample B (Official Coin)	Interpretation
Cu	Significantly reduced	High and stable	Cu ensures ductility, durability, and surface clarity
Zn	Elevated (brass substitution)	Low and stable	Cost-saving substitution, reduces hardness
Pb	Noticeably increased	Trace/very low	Cheap, low melting point; weakens alloy strength
Sn	Unstable/variable	Low but stable	Improves hardness and corrosion resistance

4.2. Economic Significance of Elemental Differences

The elemental contrasts between Samples A and B carry profound implications for both monetary credibility and the broader socio-economic environment.

Copper (Cu): Official coins maintained a high proportion of copper, preserving the ductility, durability, and recognizable appearance of the coinage. This adherence to compositional standards helped sustain currency trustworthiness. In contrast, the private coin demonstrated a sharp reduction in copper content, indicating an intentional dilution aimed at conserving scarce copper resources and lowering production costs.

Zinc (Zn): Elevated Zn levels in private coins suggest the substitution of brass (Cu-Zn alloy) for pure copper. This practice reduced expenses while maintaining a superficial resemblance to genuine coinage, particularly in terms of color. However, the introduction of excess zinc weakened the alloy, reducing its mechanical integrity and long-term circulation value.

Lead (Pb): Private issues displayed a conspicuously higher Pb content. Lead's low melting point made casting easier and cheaper, yet it undermined mechanical strength and increased susceptibility to wear and breakage. The prevalence of Pb-rich alloys thus signals a trade-off between short-term minting convenience and long-term monetary reliability.

Tin (Sn): In official coins, tin was incorporated in small but consistent amounts to improve hardness and corrosion resistance. By contrast, private specimens contained irregular and unstable Sn levels, further suggesting the lack of technical expertise and quality control in counterfeit production.

Together, these results highlight how private minting systematically compromised coin quality by replacing expensive, functionally critical metals with cheaper, structurally inferior alternatives.

4.3. Chemical Interpretations at the Atomic Level

A more detailed interpretation of these findings can be achieved by examining the roles of individual atoms in the alloy structure.

Cu Atoms: The presence of Cu 3d electrons plays a pivotal role in metallic bonding, imparting ductility and ensuring that coin inscriptions remain legible even after long circulation. In official coins, high Cu levels account for the superior clarity and durability of their surfaces.

Zn Atoms: Zn contributes to brass formation but disrupts Cu-Cu bonding by weakening d-d interactions, thereby reducing hardness. Excess Zn, as observed in private coins, explains the rapid deterioration of inscriptions and the overall fragility of the alloy.

Pb Atoms: Pb's outer 6p electrons are weakly involved in metallic bonding, resulting in limited lattice stability. In alloys, this creates defects and contributes to brittleness. The elevated Pb content in private coins thus directly correlates with their easy fragmentation and poor durability.

Sn Atoms: Sn enhances hardness and corrosion resistance through stabilization of the alloy matrix. The stable, low-level Sn detected in official coins supports this function, whereas the inconsistent presence in private issues underscores technical deficiencies in counterfeit production.

This atomic-level interpretation not only validates the observed macroscopic properties of official versus private coinage but also illustrates how material chemistry underpinned broader questions of currency stability.

4.4. Socio-Economic Reflections of Metallurgical Practices

The chemical evidence provides a lens through which to interpret late Qing fiscal and social instability. The increased use of Zn and Pb in private minting reflects an acute shortage of copper, as the state struggled to secure and distribute sufficient resources. For private minters, incorporating cheaper substitutes became a necessity for maintaining circulation, even at the expense of coin quality.

The deterioration in alloy composition directly contributed to declining monetary credibility. Official coinage, though limited in supply, retained high copper content and thus embodied state authority and fiscal order. By contrast, the circulation of debased private issues eroded public trust, accelerating inflationary tendencies and fostering economic fragmentation. This duality of coinage mirrors the erosion of centralized state power, as fiscal weakness allowed private actors to undermine the monetary system.

5. Discussion

The results of this study confirm and extend earlier research on alloy debasement as an indicator of fiscal stress. Holliday, for example, demonstrated through XPS that European coinage adulteration correlated with episodes of monetary instability. The present findings show a parallel pattern in late Qing China: elevated Zn and Pb levels in privately minted Xianfeng Tongbao coins signify not only technological shortcuts but also the material manifestation of economic crisis. While traditional Chinese numismatic scholarship has long described the proliferation of counterfeit coins, this study provides quantitative evidence that directly links alloy chemistry to fiscal decline. In this way, the research bridges descriptive numismatics with material science, creating a holistic account of how economic instability was encoded in currency itself.

Despite these contributions, several limitations must be acknowledged. The study was based on a small sample set, one official and one private coin, which restricts the generalizability of conclusions. Furthermore, XPS is a surface-sensitive technique, probing only a few nanometers in depth, and may not fully capture bulk composition. Corrosion and burial conditions may also have introduced minor modifications, although careful cleaning protocols were applied to minimize interference.

Taken together, the findings highlight how coin chemistry can serve as a proxy for broader socio-economic processes. The dual interpretation, material stability at the atomic level and fiscal decline at the macro level, illustrates the potential of interdisciplinary methods to enrich both material science and historical studies. This integrated perspective underscores the need for further research combining larger datasets and complementary techniques such as ICP-MS or SEM-EDS.

6. Conclusion

This study employed X-ray photoelectron spectroscopy to compare official and privately minted Xianfeng Tongbao coins, revealing systematic differences in alloy composition. Official coins were characterized by high Cu content with stable proportions of Zn and Sn, ensuring mechanical strength and corrosion resistance. In contrast, private coins displayed reduced Cu levels and elevated Zn and Pb, accompanied by unstable Sn proportions, leading to weaker alloys prone to wear and breakage.

These compositional differences are more than technical anomalies; they reflect the fiscal crisis of the Xianfeng era. The scarcity of copper and the rise of private minting practices forced material substitutions that eroded the credibility of the currency. As a result, monetary instability became chemically inscribed into the very coins that circulated in society.

The findings demonstrate the value of integrating materials science with economic history. By linking microstructural analysis to macroeconomic interpretation, this study contributes new insights into how fiscal decline and state weakness manifested in tangible material culture. Future research should expand sample sizes, include coins from multiple mints and time periods, and employ complementary analytical methods to build a comprehensive database of Qing coinage metallurgy. Such work will not only refine our understanding of late Qing monetary instability but also provide valuable tools for numismatics, archaeology, and heritage conservation.

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