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An archaeometallurgical study of Ming Dynasty (1368–1644 AD) coins from the North Reef, South China Sea

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The prosperity of trade along the Maritime Silk Road during the Ming Dynasty facilitated the use of Chinese copper coins as primary or secondary coins in East Asian and Southeast Asian countries. However, there are few studies on Ming Dynasty overseas trade coins in medieval maritime history and numismatics. This study investigated the alloy compositions and lead isotope characteristics of Ming Dynasty coin samples unearthed from the North Reef in the South China Sea via X-ray fluorescence (XRF) and lead isotope (MC-ICP-MS) analyses. The experimental study revealed that most samples are Cu–Pb–Sn ternary alloys. The Pb isotopes of the samples are consistent with the Pb isotopic signatures of some mines in the SE China region. By combining archaeological background and historical documents, it can be inferred that the raw metal materials of the coin samples came from southeast China, and the coins minted entered the overseas trade network.

The ‘Maritime Silk Road’ refers to the sea routes through which ancient China exchanged envoys with overseas countries to trade silk and other goods for cultural exchange[1].

At the beginning of the Ming Dynasty, to prevent Japanese attacks, Emperor Taizu ordered a strict maritime prohibition policy, allowing only tribute trade and forbidding private trade. The tribute trade system of the Ming Dynasty was an essential way for ancient China to address its relations with neighbouring countries and regions, i.e., the dual content of ‘paying tribute’ on the tributary side and ‘rewarding’ on the suzerainty side. The official document of the Ming Dynasty, ‘the Daming Huidian大明會典 (1576 AD)’, Volume 108, records that foreign countries paid tribute with various goods, including their country’s specialties, as well as common tribute incense, gold and silver utensils, exotic birds and animals, and ivory. In return, China mainly rewarded them coins, silk, ceramics, and tea[2,3].

During the Yongle period, the Ming Emperor Chengzu rebuilt the city Hublot departments of Quanzhou, Mingzhou, and Guangzhou. At the same time, he sent Zheng He (1371–1433 AD), a famous early Ming Dynasty eunuch, to lead a massive fleet on seven ocean voyages. Zheng He’s fleet reached more than 30 countries in 29 years, the farthest region being Africa, which was the largest scale and longest distance of Chinese navigation at that time. Zheng He’s fleet carried many copper coins for trade and reward, and Ma Huan, a navigator who had followed Zheng He to the West many times, recorded in ‘Yingya Shenglan 瀛涯勝覽 (1451 AD)’ that many rich people in foreign countries used Chinese coins for buying and selling transactions[4,5].

In recent years, underwater archaeology has flourished, with the Underwater Archaeology Center of the National Museum of China and other units conducting large-scale surveys and excavations of underwater cultural relic sites along the coast. Copper coins left in the waters along the Maritime Silk Road in the Ming Dynasty are physical evidence of the prosperous maritime trade from the 14th to 17th centuries A.D. Therefore, studying Ming Dynasty coins left behind by shipwrecked vessels from the relevant waters has become an integral part of understanding this maritime trade network. Using the underwater archaeological survey report by the National Museum of China and other organisations, this paper counts the Maritime Silk Road coins left behind by shipwrecked vessels from the relevant waters[6].

Table 1 shows that the total number of coins from the Maritime Silk Road in all age groups is 160,307, including 73,755 coins from Yongle Tongbao and 20,173 coins from Hongwu Tongbao from the Ming Dynasty. The number of coins from the Ming Dynasty accounted for 59% of the total number of coins, which suggests the prosperity of the Ming Dynasty Maritime Silk Road trade. The coins used for overseas trade are two kinds: Hongwu Tongbao and Yongle Tongbao[7].

As shown in Fig. 1, the North Reef of the South China Sea is located in the southeastern waters of Hainan Province. Canton (Guangzhou) was an important overseas trading port on the South China Sea route during the Ming Dynasty. The area where some mines are located in southeastern China is known as ‘the hometown of nonferrous metals’[8]. The figure shows a few locations where Ming Dynasty coins were excavated (Fig. 2).

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Table 1 | Statistics of coins excavated from the Maritime Silk Road over the years

Age	Coin type	Quantity (pieces)	Explanatory note
Tang Dynasty (618–907)	KaiyuanTongbao, QianyuanZhongbao, etc.	3248	Among them, 3085 pieces are Kaiyuan Tongbao.
Song Dynasty (960–1279)	HuangSongTongBao and 25 other coins.	63,022	
Yuan Dynasty (1279–1368)	ZhizhengTongbao, etc.	109	
Ming Dynasty (1368–1644)	HongwuTongbao, YongleTongbao.	93,928	Among them: Hongwu Tongbao's 20,173 pieces, YongleTongbao 73,755 pieces, totalling 93,928 pieces.
		Total: 160,307.	

The data in Table 1 are from refs. [10–12].

Fig. 1 | Coins circulation map of the Ming Dynasty Maritime Silk Road. ▲Coins excavated from the ocean and ▲coins excavated from the land[39–42].

Materials and methods

Materials

North Reef, located in the sea near southeastern Hainan Island, the northernmost part of the Xisha Islands, north of the Yongle Islands, and approximately 30 nautical miles south of Coral Island, is a type of reef, and the sedimentary zone consists of a prereef phase, reef flat phase, lagoon phase, point reef zone, intrareef reefs, etc. This dangerous sea area with many reefs has also become a place of frequent shipwrecks because of its location at the critical point of the Maritime Silk Road route. According to a survey, there are 12 shipwreck sites at North Reef and as many as 22 underwater cultural relic sites[9].

The Ming Dynasty overseas trade coins Hongwu Tongbao and Yongle Tongbao are mostly from the underwater site of North Reef in the South China Sea.

In the first year of Hongwu (1368 AD), Zhu Yuanzhang, the Great Ancestor of the Ming Dynasty, ordered the Baoyuan Bureau in the capital and Baoquan Bureaus in the provinces to mint Hongwu Tongbao. There were five types of coins, but those used for overseas trade and bounties were mainly Xiao Pingqian (小平錢), which is ~2.45 cm in diameter and weighs ~3.5 g.

In the fourth year of the Jianwen period of the Ming Dynasty (1402 AD), after the accession of Emperor Zhu Di, the Emperor Chengzu of the Ming Dynasty, the state policy of 'Friendship with Foreign Countries' was diplomatically implemented. In the sixth year of Yongle (1408 AD), the coins of Yongle Tongbao began to be minted for foreign trade and rewards. Yongle Tongbao coins were minted in Guangdong, Nanjing, and the other four money bureaus, all of which were Xiao Pingqian (小平錢), with a coin diameter of 2.5 cm and a weight of ~4 g.

The Hainan Provincial Museum provided 17 representative samples of Ming Dynasty coins from different batches, including 7 Hongwu Tongbao and 10 Yongle Tongbao coins. Two of the fragments are from coins inscribed with numismatic characters.

Seventeen coin samples were excavated from the North Reef No. 19 Underwater Cultural Relics Site in the South China Sea.

Named by the National Museum of China, the North Reef No. 19 Underwater Cultural Relics Site (XSBS19) in the South China Sea is an underwater area containing many cultural relics from Chinese dynasties. Since the 1920s, Hainan Island fishermen have salvaged many ancient copper coins, copper ingots, ceramics, and other cultural relics in the waters of the site. In 1974, Hainan Qionghai County fishermen salvaged 403.2 kg agglutinated blocks of copper coins. In 1975, Guangdong Provincial Museum and other organisations conducted archaeological investigations in the area, collecting some of the copper money and other relics[10–12].

In 2007 and 2010, the National Museum of China Underwater Archaeology Centre and the Hainan Provincial Cultural Relics Bureau carried out two archaeological investigations at the North Reef No. 19 cultural relics site. Archaeologists unearthed 605 copper coins from all dynasties, the earliest being the Tang Dynasty Kaiyuan Tongbao copper coins and the latest being the early Ming Dynasty Yongle Tongbao copper coins. Among these coins, 205 are Ming Dynasty Hongwu Tongbao, 215 are Yongle Tongbao, and nearly 70% are Ming Dynasty copper coins[12].

Analysis of the constituent elements of coins (XRF)

Coins removed from the water are usually covered with a rusty layer formed by marine life and corrosion. Therefore, it is necessary to carry out a pretest treatment before XRF analysis to protect the artifacts as much as possible. Therefore, a nondestructive technique has been used. Provided that a sufficiently large metal surface (~1–3 mm) is exposed to the light spot of the instrument, it is possible to obtain reliable data on the nature and approximate concentration of the main components in copper-based alloys such as tin and lead[13].

According to the different conditions of the rusty layer of the samples, surfaces of about 10–25 mm^2 were selected and the metal layer of the coins was polished with fine sandpaper. According to their specific conditions, 2–6 points were selected for testing, and the average value is taken as the test result.

Fig. 2 | Ming Dynasty coin samples from the North Reef. Sample Hongwu Tongbao was cast for the 1368–1398 (AD) period, and the average size and weight were as follows: 24.3 mm outer diameter, inner diameter of 6.7 mm, thickness of 1.4 mm, and weight of 3.8 g. Sample Yongle Tongbao were minted from 1408–1424 (AD), and the average size and weight were as follows: 24.8 mm outer diameter, inner diameter of 6.3 mm, thickness of 1.5 mm, and weight of 3.9 g.

The elements of the sample coins were determined via a Shimadzu EDX-8000 fluorescence analyser from Japan, which was used in the Laboratory of Scientific and Technological Archaeology of the University of Science and Technology of China. The range of elements analysed by the instrument is C(6)---U(92); the range of content analysed is 1 ppm, --99.99%; the energy resolution is less than 140 eV; and the repeatability is better than 0.12%. The instrument was set in metal analysis mode, the spot size was 1 mm, the constant test voltage was 50 kV, the current was more than 1000 μA, the test atmosphere was standard air, and the X-ray target was Rhodium (Rh). The sensitivity factor is corrected according to the built-in curve for old copper alloys[14].

Lead isotope analysis

The Solid Isotope Laboratory of the School of Earth and Space Sciences, University of Science and Technology of China used Neptune Plus MC-ICP-MS to analyse the lead isotopes of the coin samples. The following steps were used to purify the Pb samples: 1) An appropriate amount of the coin matrix was taken, the samples were cleaned with acetone and deionized water, dried, approximately 50 mg was dissolved in dilute nitric acid, and then the Pb was extracted via the ion exchange resin method; 2) the concentration of the purified Pb solution was checked by ICP-MS, then diluted to 200 ppb, and analysed by MC-ICP-MS. Analytical accuracy, ppm, was determined. During the analysis of each sample, a calibration test was performed on the NBS-981 lead standard material. The standard error of the 2σ lead isotope ratios was better than +0.001[15].

Results

Elemental composition

The elemental compositions used in this study are presented in Table 2. The content ranges from 37.84% to 83.83%, 2.49% to 48.75%, and 0% to 12.16% for copper, lead, and tin, respectively.

According to records of the 'Daming Huidian 大明會典 (1576 AD)' Volume 194, the Ming Dynasty stipulated that the copper content of cast money should be more than 70%. The lead and tin contents are not specified, but the lead content is

usually less than 20%, and the tin content is <10%[16,17].

The results of the elemental composition analyses of the coin samples fluctuate relatively widely. The lower copper content and higher lead content of some samples may result from the surface corrosion enrichment[13].

The Database of Alloy Composition of Ancient Chinese Coins contains alloy composition data of 10 Hongwu Tongbao and 6 Yongle Tongbao coins. These 16 coins are strictly identified as copper coins minted according to the official standards of the Ming Dynasty[16].

The alloy composition data of the 17 North Reef coin samples in Table 2 and the alloy composition data of the 16 coins in the Ancient Chinese Coin Alloy Composition Database were plotted together to form a comparative Cu–Pb–Sn ternary composition diagram as follows:

Results of lead isotope ratio analysis

The lead isotope ratios of the ten coins range from 18.2353 to 18.6487 for 206Pb/204Pb, 15.6612 to 15.7705 for 207Pb/204Pb, and 38.6747 to 39.1275 for 208Pb/204Pb (Table 3). Different perspectives concerning the introduction of lead have been expressed by Western scholars[18–20], but the conventional threshold is considered to be 2% in most published studies of ancient Chinese metallic artifacts[21]. In this regard, the overall lead contents of the coins in this study are not lower than 15.27%, suggesting that the lead was added intentionally and that the lead isotopes can indicate the source of lead ores.

Discussion

The alloy compositions of the samples are shown in Table 2 and Fig. 3. The contents for Hongwu Tongbao coins range from 39.52–83.83% for Cu, 7.23–44.37% for Pb, and 1.36–6.75% for Sn. The contents for Yongle Tongbao coins range from 37.84 to 82.15% for Cu, 2.49 to 48.75% for Pb, and 0 to 12.16% for Sn.

Fourteen of the seventeen coins in the sample are made of a ternary alloy containing more than 2% copper, lead, and tin. Among the remaining

Table 2 | Results of the chemical composition analysis of the Ming Dynasty coin samples

Sample number	Coin Name	Elements of Coin Composition (wt%)							
		Cu	Pb	Sn	Fe	As	Zn	Bi	Ni
ZY-NH-47	Hongwu Tongbao	77.33	15.27	6.30	0.11	0.13	0.07	0.06	0.04
ZY-NH-48	Hongwu Tongbao	70.08	24.24	3.89	0.13	0.26	0.06	0.08	0.04
ZY-NH-49	Hongwu Tongbao	59.59	31.95	6.68	0.08	0.27	0.05	0.17	0.03
ZY-NH-50	Yongle Tongbao	40.15	31.97	12.16	13.89	0.34	0.12	0.17	0.04
ZY-NH-51	Yongle Tongbao	71.62	18.03	7.13	1.21	0.20	0.08	0.07	0.03
ZY-NH-52	Yongle Tongbao	39.28	45.74	11.06	2.63	0.33	0.02	0.21	0.02
ZY-NH-53	Hongwu Tongbao	80.95	7.23	3.47	0.188	0.232	0.084	0.061	0.025
ZY-NH-54	Hongwu Tongbao	83.83	9.313	6.75	0.069	bd	bd	bd	bd
ZY-NH-55	Hongwu Tongbao	39.52	38.00	1.36	13.33	6.50	bd	bd	bd
ZY-NH-56	Yongle Tongbao	82.15	2.49	8.29	0.085	0.085	0.072	0.016	0.039
ZY-NH-57	Yongle Tongbao	73.59	18.37	7.48	bd	bd	bd	bd	bd
ZY-NH-58	Yongle Tongbao	73.69	21.13	4.32	0.059	bd	0.064	bd	bd
ZY-NH-59	Yongle Tongbao	82.10	15.91	bd	0.008	bd	0.46	bd	0.058
ZY-NH-60	Yongle Tongbao	65.33	25.03	0.446	3.108	3.368	0.419	bd	bd
ZY-NH-62	Hongwu Tongbao	45.67	44.37	5.13	0.74	0.85	bd	bd	0.02
ZY-NH-63	Yongle Tongbao	70.81	23.44	3.74	1.03	bd	0.05	0.07	bd
ZY-NH-64	Yongle Tongbao	37.84	48.75	8.98	0.93	0.75	bd	bd	0.05

bd below the detection limit.

Table 3 | Results of lead isotope analysis of the Ming Dynasty coin samples

No.	Sample number	Sample name	^{206}pb/^{204}pb	$\pm 2\sigma_m$	^{207}pb/^{204}pb	$\pm 2\sigma_m$	^{208}pb/^{204}pb	$\pm 2\sigma_m$
1	ZY-NH-50	Yongle Tongbao	18.3434	0.0008	15.6923	0.0007	38.8506	0.0018
2	ZY-NH-51	Yongle Tongbao	18.3498	0.0006	15.6915	0.0006	38.8345	0.0015
3	ZY-NH-57	Yongle Tongbao	18.2992	0.0007	15.6935	0.0006	38.8433	0.0017
4	ZY-NH-47	Hongwu Tongbao	18.5067	0.0007	15.7315	0.0006	38.8506	0.0016
5	ZY-NH-55	Hongwu Tongbao	18.3525	0.0009	15.6939	0.0007	38.8508	0.0019
6	ZY-NH-49	Hongwu Tongbao	18.2449	0.0005	15.6728	0.0005	38.7137	0.0016
7	ZY-NH-58	Yongle Tongbao	18.2353	0.0008	15.6612	0.0007	38.6747	0.0018
8	ZY-NH-62	Hongwu Tongbao	18.6009	0.0007	15.7585	0.0005	39.0812	0.0014
9	ZY-NH-63	Yongle Tongbao	18.6487	0.0007	15.7705	0.0007	39.1275	0.0015
10	ZY-NH-64	Yongle Tongbao	18.6406	0.0010	15.7666	0.0009	39.1134	0.0023

three coins, two Yongle Tongbao (ZY-NH-59, 60) have tin content less than 1%, with copper content of 82.1% and 65.3% and lead content of 15.9% and 25%, respectively. One of the Hongwu Tongbao samples (ZY-NH-55) has a tin content of 1.36% but a copper content of 39.5%, a lead content of 38.0%, and an iron content greater than 13%, making it a severely corroded sample. The other two Yongle Tongbao samples (ZY-NH-50 and 52) had copper content of about 40%, lead content of 32.0% and 45.7%, and tin content of 12.16% and 11.1%, respectively, and high-lead bronzes. The former also has an iron content of more than 13%. Among the samples with iron content exceeding 1%, four Yongle Tongbao (ZY-NH-51, 52, 60, and 63) and one Hongwu Tongbao and one Yongle Tongbao had iron content exceeding 13%, of which ZY-NH-51, 52, and 63 were high-lead bronze wares. The six samples with abnormal iron contents, one from Hongwu Tongbao and five from Yongle Tongbao, may be attributed to the wet copper refining process. Wet copper refining is the principle of using iron to replace copper in the solution of the ore material, but this process often results in the copper material being adulterated with Fe[8,22]. Some heavily corroded coins may also cause iron enrichment, resulting in high iron contents[13]. This may also be related to the characteristics of the ore source[8].

No zinc or nickel was found in this batch of samples in excess of 1%, i.e., no zinc-brass or nickel–copper alloy coins were found. For the arsenic–copper alloys, two samples with arsenic content over 3% (ZY-NH-55, 60) are noteworthy for their tin content less than 2%, lead content greater than 25%, and iron content greater than 3%.

Scholars generally agree that bronze coins were mainly minted in the early Ming Dynasty and that after the Jiajing period of the Ming Dynasty (1522–1566 AD), the alloy composition of the coins underwent a significant change, gradually transforming from a copper-lead-tin ternary alloy to a copper-lead-tin-zinc tetragonal alloy; finally, brass, an alloy of copper and zinc, was completely used to mint copper coins[17]. The results of this paper show there are no brass coins in this group of early Ming Dynasty coins.

Trace elements such as Ag, Co, and Sb are usually impurities introduced into bronze coins through metals such as Cu and Pb, and their contents are usually relatively low. As ancient Chinese metallurgical processes improved, the values of these trace elements often fell below experimental detection limits[16].

In the article 'Database of Alloy Composition of Ancient Chinese Coins' by Zhou Weirong[16], the alloy composition data of 16 Ming Dynasty coins are given, which agrees with the official Ming Dynasty data. The comparison of the Figure-Ternary Composition Chart (Fig. 3) shows the compositional differences between the South China Sea North Reef samples and the database samples in the ternary representation of copper–lead–tin. Some samples from the South China Sea North Reef show a decrease in copper and an increase in lead. Nevertheless, the reasons for the differences in the compositional data need to be investigated and explored further.

Recently, A.M. Pollard and Liu Ruiliang published the average values of the elemental compositions of 35 Hongwu Tongbao and 19 Yongle Tongbao coins in the Journal of Archaeological Science; for Hongwu Tongbao: 70.3% Cu, 18.1% Pb, 7.9% Sn, and 0.2% Zn; Yongle Tongbao: 70.3% Cu, 19.9% Pb, 7.9% Sn, 0.1% Zn. These data are in general agreement with the official Ming standard described in this paper[17].

Notably, the elemental composition data for the Hongwu Tongbao and Yongle Tongbao copper coins were published by MJNF de Melo[23] and Lin et al.[24], as shown in the table below:

As shown in the Table 4, among the elemental composition data of 6 Hongwu Tongbao and 2 Yongle Tongbao, 5 Hongwu Tongbao and 2 Yongle Tongbao contain less than 70% copper, while their lead content is higher than 20%. This is inconsistent with the official minting standard of the Ming Dynasty, but is similar to the data of the bronze coins of the Northern Reef, with reduced copper and increased lead (Table 2), which are studied in this paper.

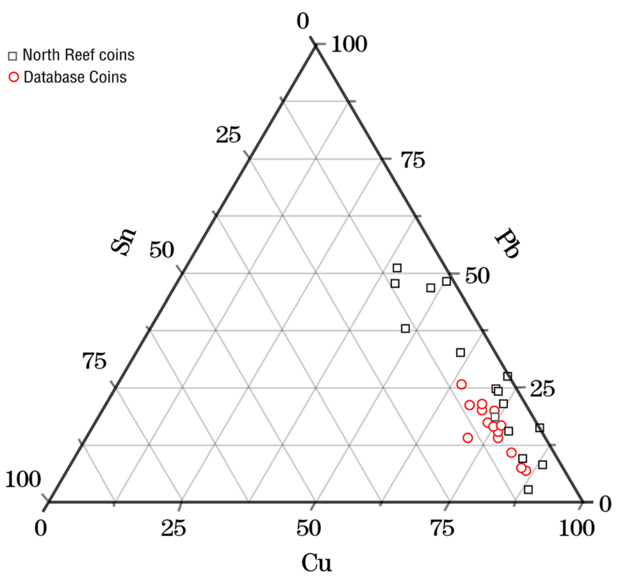

Fig. 3 | Ternary component charts (weight percent) of the North Reef coin sample and coins from the 'Database of Alloy Composition of Ancient Chinese Coins'.

In her paper, MJNF de Melo suggested that lead corrosion leaching, which precipitates on the surface of the coin's matrix, may be responsible for the high lead content in bronze coins. In addition, as shown in Table 4, three bronze coins presented abnormally high iron contents, which were 2.09%, 2.08%, and 1.97%, respectively. This finding mirrors the data in this study, further supporting the idea that anomalous iron values may also be related to factors such as wet refining and corrosion of iron[13,22,23].

The data of this study (Table 3, Table 5) are plotted in Fig. 4. On the basis of the theory of geochemical provinces in China[25–27], the whole dataset is distributed in three different ranges: northern China, Yangtze, and southern China. More importantly, the data used in this study are located in China's southern provinces.

On the basis of lead isotope studies of galena mines in various provinces of China and lead isotope studies of ancient Chinese copper alloy artifacts, and in combination with historical documents and archaeological contexts[8,28–34], during the Song and Ming dynasties, the main lead-producing areas in China were the neighbouring southern provinces of Guangdong, Jiangxi, and Guangxi. These inferences also coincide with the historical document 'Song Huiyaojigao 宋會要輯稿(1809 AD)' foodstuffs and goods articles 27 to 33, that is, 'Lead 7943350 catty in the Song Dynasty, Guangnan Donglu (Guangdong) lead 4642736 catty, i.e., Guangdong lead production accounted for nearly 60% of the country.' 'Song Huiyaojigao 宋會要輯稿' 23 to 25 also records that the Southern Song Dynasty, Jiangxi, and Guangxi production of lead is quite abundant. Volume 50 of the official Ming Dynasty historical document 'Daming Yitongzhi 大明一統誌' (1461 AD) records that, during the Ming Dynasty, lead was produced in Renhua County in Shaozhou Prefecture, Guangdong Province (the site of the Guangdong Fankou lead–zinc mine)[8].

According to 'The Compendium of Materia Medica (本草纲目)', Volume VIII (1596 AD), 'Goldstone and Lead', lead was produced in Shaozhou, Guangdong Province during the Ming Dynasty. In addition to being used as a metal, lead produced in Shaozhou was also made into lead powder, for use in cosmetics and medicinal applications. Song Yingxing, a Ming Dynasty scientist, recorded in the document 'Tiangongkaiwu' (Heavenly Workers' Works), Volume 1 and Volume 2 (1637 AD) that, during the Ming Dynasty, lead was produced in Shangrao and Leping County in Jiangxi Province (Shangrao and Leping Counties are adjacent to the Jiujiang lead and zinc mines in Jiangxi Province). The Ming Dynasty historical

Table 5 | Pb isotope data for Yongle Tongbao coin samples from Japan

sample number	Sample name	206Pb/204Pb	207Pb/204Pb	208Pb/204Pb
C-21	Yongle Tongbao	18.288	15.644	38.664

Table 5 Data are cited from the article 'Lead Isotope Ratios of Ancient East Asian Copper Coins' by Hisao Mabuchi[38].

Table 4 | Hongwu Tongbao and Yongle Tongbao Elemental Composition Data (wt%)

Sample name	Cu	Pb	Sn	Zn	Fe	Ni	As	Data sources
Hong Wu Tong Bao	49.6	36.7	11.0	0.35	2.09	<q.l.	-	23
Hong Wu Tong Bao	80.9	11.8	6.20	0.29	0.56	0.11	-	
Hong Wu Tong Bao	61.6	28.1	7.86	<q.l.	2.08	<q.l.	-	
Hong Wu Tong Bao	45.6	46.0	6.08	<q.l.	1.97	<q.l.	-	
Hong Wu Tong Bao	62.2	26.6	10.5	<0.1	<0.06	<0.06		24
Hong Wu Tong Bao	69.8	23.7	5.5	<0.3	<0.2	0.06		
Yong le Tong Bao	58.2	34.4	6.18	0.13	0.03	0.07	0.11	
Yong le Tong Bao	59.9	21.7	7.45	0.25	0.2	<0.06	<0.03	

(- below the detection limit).

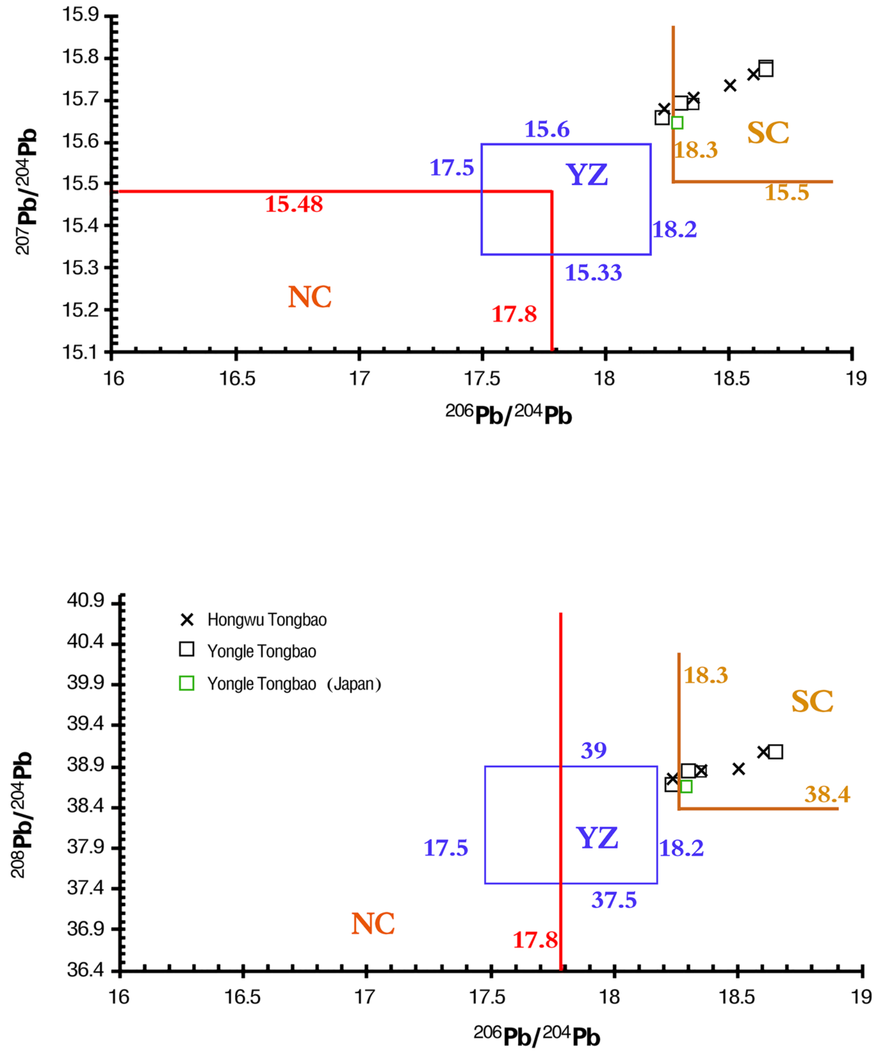

Fig. 4 | Distribution of lead isotopes in coins from North Reef in the South China Sea in the geochemical province of China (NC Northern China, YZ Yangtze, SC Southern China).

document 'Ming Shi ■ Geography Zhi Jiangxi (2)' recorded that lead was produced in Lead County, Shangrao, Jiangxi Province, during the Ming Dynasty[8,28–30].

Specifically, we selected lead isotope data from galena mines in southeastern China as a reference[28–32]. These include the Fankou Pb–Zn mine in Guangdong, the Dabaoshan polymetallic mine and the Zhaoqing area in Guangdong, the Sidingshan Pb–Zn mine and the Dachang polymetallic mine in Guangxi, and the Jiujiang Pb–Zn mine in Jiangxi.

As shown in Fig. 5, the data of the North Reef Ming Dynasty samples are completely within the data range of the Guangdong Fankou Pb-Zn mine, and they are in perfect agreement with the data of the Guangdong Fankou Pb-Zn mine. The data of the samples match better with the data of the Guangdong Dabaoshan polymetallic mine. The Guangdong Fankou Pb-Zn mine was a famous lead-producing mine during the Song and Ming dynasties. The data from the Guangdong Zhaoqing mine are different from the sample data.

The Jiangxi Jiujiang Pb–Zn mine has three data points that are in general agreement with the sample data.

The data from the Guangxi Sidingshan Pb-Zn mine are relatively far from the range of the sample data, and only two pieces of data are similar to the sample data. The data from the Guangxi Dachang polymetallic mine also include 3 pieces that are similar to the sample data.

In summary, the data from the North Reef samples in the South China Sea match the lead isotope data signatures of some lead mines in southeastern China. The mining of the coin samples may have used lead material from this region, which is also consistent with the archaeological context and historical documents.

During the Song and Ming Dynasties, Guangdong and Jiangxi Provinces were important copper-producing regions in China, and 'Song Huiyaojigao 宋會要輯稿' 33 recorded the production of copper in the first year of the Yuanfeng era (1078 AD), with the output of one state, Guangdong's Shaozhou, accounting for approximately four-fifths of the entire Song output. The document also recorded the end of the Southern Song Dynasty Shaoxing (1162 AD) copper production, with an annual output of 263,169 catty of copper, while Jiangxi Xinzhou and Raozhou, Guangdong Shaozhou, produced 219,206 catty of copper, accounting for as much as 83% of the country's copper production.

Historical document 'Yuan Shi 元史 (1370 AD)' Volume 92 Hundred Officials Zhi records: 'Zhizheng 12 years in March (1352 AD), set the copper smelting field in Jiangxi Raozhou Dexing County, Xinzhou Qianshan County and Guangdong Shaozhou.'

The official historical document of the Ming Dynasty, 'Daming Yitongzhi, 大明一统志 Volume 50 (1461 AD), also records that copper was produced in Qujiang County, Shaozhou, Guangdong Province (the site of the Guangdong Dabao Mountain Polymetallic Mine) during the Ming Dynasty. From 1958 to March 1961, the 705 Geological Team of Guangdong Province conducted an exploration survey of the ancient mining site of Dabaoshan. According to the Summary Report on the Geological Exploration of Dabao Mountain Mine compiled by the Guangdong 705 Geological Team, more than 500 abandoned mine shafts can be seen at the

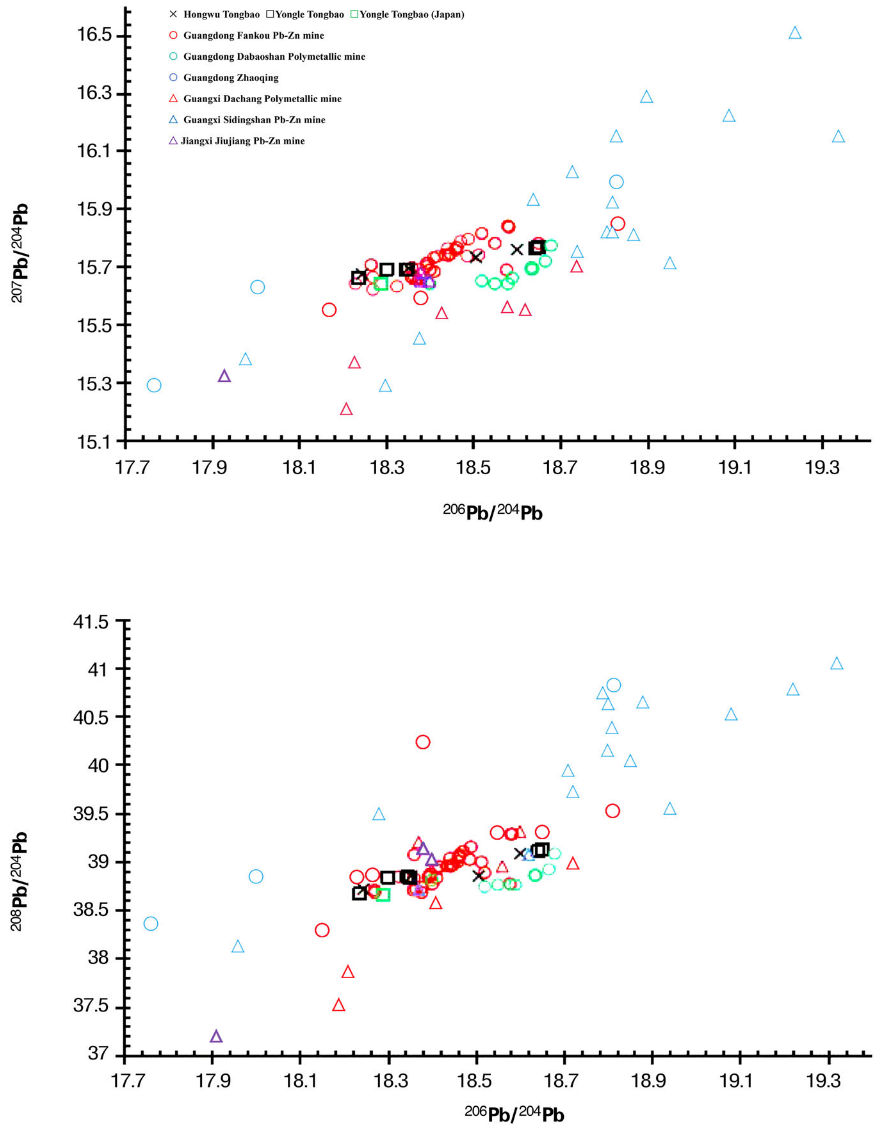

Fig. 5 | Lead isotope ratios of North Reef samples from the South China Sea and lead ores from southeastern China.

mine site. Refining slag scattered across the mining area weighed ~1.5 million tonnes. Analysis of the slag confirmed that mining focused on copper, lead, and other metals. Mining may have started in the Tang and Song dynasties, but mining has continued for a long time, and there is no doubt that the scale of mining is enormous. The ancient official document 'Qujiang County Records' (1687 AD) also records the situation of wet copper refining in the Dabao Mountain copper mine in Qujiang County, Guangdong Province, in the Ming Dynasty[8,22,35,36,37].

Song Yingxing, a Ming Dynasty scientist, recorded in the upper and lower volumes of Tian Gong Kai Wu (1637 AD) that copper deposits in Dexing County, Raozhou, Jiangxi Province, were abundant and easy to mine during the Ming Dynasty. The Ming Dynasty historical document 'Ming Shi ■ Jiangxi Geography (II)' recorded that the Ming Dynasty, Jiangxi Lead County, Raozhou production of copper. During the Xuande period of the Ming Dynasty (1398–1435 AD), wet copper was refined at two copper farms in Dexing County, Lead County, Jiangxi Province, with an annual output of ~500,000 Jin (~300,000 kg). The 'Lead Book 鉛書 (1618 AD)' recorded the production of copper in Jiangxi during the Ming Dynasty[8].

The southeastern region of China, rich in nonferrous metal resources and bordering the South China Sea, enabled the export of struck copper coins overseas through the important port of Guangzhou.

Guangdong and Jiangxi are two neighbouring provinces in southeastern China, and as mentioned earlier, the coin samples may have used lead material from the southeastern region. From economic, technological, smelting and casting cost considerations, the coin samples should have used copper material from here as well. This finding is also consistent with the archaeological background and historical documents.

Regarding the origin of tin in the Ming Dynasty, Song Yingxing, a Ming Dynasty scientist, recorded in 'Tiangongkaiwu 天工開物': 'All tin, with Linhe County producing the most abundant tin and named.' Linhe County refers to Hezhou, showing that Hezhou was still an important tin-producing state during the Ming Dynasty. Hezhou is adjacent to Fankou in Shaozhou (see Fig. 1), and the Hezhou tin field and the Guangdong Fankou Pb–Zn mine in Shaozhou belong to the same ore belt. Thus, the Ming coins in the experimental sample were struck using copper–lead material from the mines in the southeastern region of China and, of course, tin material from nearby Hezhou.

Ancient China practiced 'minting money in the mountains'; i.e., to save costs, it chose to set up mints near areas with mining resources. According to the 194 volumes of the 'Daming Huidian 大明會典 (1576 AD)', the court minted Yongle Tongbao in Guangdong and Jiangxi in the ninth year of the Yongle reign (1411 AD). The historical fact that mints were established in Guangdong Province in southeastern China is also recorded in the official document 'Xinning County Records 新寧縣志' (1606 AD): 'In the early years of the Ming Dynasty, when the Hongwu Tongbao money was being struck, the imperial court established a mint in Xinning County, Guangdong, and conspired with the smelting and casting craftsmen in Xinhui County to violate the law. The mint privately struck copper coins, exchanged 1000 bad coins for 300 good coins, and mixed the bad coins with the good coins to sell them to Vietnam and the oceans.

The above historical documents not only explain that a mint was established in Guangdong during the Ming Dynasty but also indicate that the coins entered the overseas trade network.

In his article 'Lead isotope ratios of ancient East Asian copper coins', Japanese scholar Professor Hisao Mabuchi analysed the lead-containing isotope ratios of one Chinese Ming Dynasty Yongle Tongbao copper coin. The data for this coin are also within the range of the lead ore data in Fig. 5, confirming that the minting material for this overseas-traded coin also came from southeastern China.

The Ming Dynasty experienced unprecedented prosperity and unity in China, which laid the geographic foundation of China's modern territorial map and integrated various ethnic groups into an enormous multiethnic feudal empire; it was also the peak and last of the prosperous era of China's Maritime Silk Road trade. In Southeast Asian countries, through the maritime Silk Road, coins were widely spread and circulated, and most were very familiar with and relied on Chinese copper, which also laid a solid foundation for the Ming Dynasty Maritime Silk Road trade. The massive outflow of Chinese copper coins had a far-reaching impact on the cultural exchanges and economic development of both China and overseas countries.

In this work, a variety of scientific methods were used to study Ming Dynasty trade coins from the North Reef in the South China Sea. The XRF results indicate that most of these coins are Cu–Pb–Sn ternary alloys. The Pb isotope data indicate that the coins' Pb source is located in the South China Geochemical Province. Combining the scientific results with the archaeological context and the historical record, it can be deduced that these coins were minted in southeastern China via local metallic raw materials and also used for foreign trade.

Data availability

Data are provided within the manuscript or supplementary information files.

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Author contributions

D.L. and Z.J. wrote the main manuscript text and selected the samples. F.H. directed and assisted with the experiments. H.J. and D.L. pretreated the samples and performed the experiments. All the authors read and approved the final manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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