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BRIEF REPORT

# Production techniques of glass beads imitating banded agate during the Iron Age in Thailand

Siwen Xu[1,2] · Yemao Hou[2] · Xiaoyu Yang[3] · Thanik Lertcharnrit[4] · Yimin Yang[1]

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**Abstract**
Black-and-white glass beads, designed to imitate banded agate beads, offer valuable insight into the history of ancient glass beadmaking. However, efforts to reconstruct ancient glass production techniques are hindered by a limited understanding of their chemical and physical properties. This study investigated several glass beads from the Phromthin Tai site, Central Thailand during the Iron Age (~2000 BP). Two different glass types were utilized (m-mixed-Ca-Al and m-Na-Ca-Al). Tin oxide, a relatively uncommon opacifier in contemporary Southeast Asian glass, was responsible for white coloration. The black hue was caused by the presence of Fe-S chromophores and $Mn^{4+}$. The evidence of both winding and drawing shaping methods challenges previous assumptions regarding the exclusive use of folding methods. The manufacture and popularity of these banded glass beads were closely connected to the intensified maritime trade networks extending to South India and Sri Lanka, which served to satisfy the Southeast Asian demand for South Asian banded agate.

**Keywords** Banded glass beads · Central Thailand · South Asia · Glass exchange network

## Introduction

Some natural gemstones, such as agate, have long served ornamental and symbolic purposes. Significantly, certain artificial glass artifacts exhibit deliberate morphological and chromatic simulations of agate, underscoring intentional replication practices. Reconstructing the pyrotechnological and chemical methodologies underlying agate-simulated glass production is thus critical for elucidating ancient vitreous industries and transregional ornament trade networks.

The artificial application of colors on stone beads, such as colored agate beads with red, orange, black, and white hues, was practiced and gained popularity from Neolithic Asia (Carter and Dussubieux 2016; Francis 1994; Hirsch et al. 2024; Kenoyer 2003, 2017; Kenoyer et al. 2021; Mackay 1933). A refined stone bead is meticulously crafted through a series of processes, including mining, drying, flaking, drilling, polishing, and dyeing (Kenoyer 2003). The white color originated from either the inherent coloration of the agate or was generated through etching processes (Glover and Bellina 2001). The red hue of the beads resulted from heat treatment, whereas the black color was achieved through carbon infiltration, enhancing their unique aesthetic appeal (Li et al. 2023). The beauty of banded beads is accentuated by the contrasting black and white bands. Black-and-white banded agate beads are widely prevalent in South and Southeast Asia (Glover and Bellina 2001). Their production and circulation hold both cultural and economic significance.

In addition to agate, glass was widely used for ornamental and symbolic purposes in South and Southeast Asia during the Iron Age (approximately 2000 BP). Common glass types of mineral soda-alumina glass (m-Na-Al) and mineral potash (m-K) glass were worked into Indo-Pacific beads and bracelets (Carter 2010; Dussubieux et al. 2010, 2020). Interestingly, glass was also fashioned to imitate banded agate.

✉ Thanik Lertcharnrit
thanik@su.ac.th

✉ Yimin Yang
yiminyang@ucas.ac.cn

1 Department of Archaeology and Anthropology, University of Chinese Academy of Sciences, Beijing, China

2 Key Laboratory of Vertebrate Evolution and Human Origins, Institute of Vertebrate Paleontology and Paleoanthropology, Chinese Academy of Sciences, Beijing, China

3 Schools of Arts, Chongqing University, Chongqing, China

4 International Program in Architectural Heritage, Creative Industries, and Tourism Management, Faculty of Architecture, Silpakorn University, Bangkok, Thailand

In Pattanam, South India, elongated banded black and white beads are considered to imitate the appearance of banded agate beads (Abraham 2021). Similarly, several banded glass beads excavated in Central Thailand have unique chemical compositions suggesting ties to India (Carter et al. 2022). The folding method is commonly regarded as the preferred shaping technique, which yields a longitudinal seam on the surface of the glass bead (Francis Jr 2002). However, the seamless surface of banded glass beads in Thailand raises questions regarding the shaping technique employed. Therefore, although previous studies have conducted compositional analyses of black-and-white banded glass beads, manufacturing techniques, including coloring and shaping techniques, require further in-depth investigations.

In this study, we focused on the analysis of several black-and-white banded glass beads from Central Thailand during the later prehistoric period or the Iron Age (Lertcharnrit 2014). The aim of this work is to disclose manufacturing techniques, providing a fresh perspective on South and Southeast Asian glass beadmaking. This study contributes to reevaluating how ancient people understood and utilized various materials and techniques in bead production.

## Materials and methods

### Sample description

All samples for this study are associated as grave goods with a human burial labeled as Burial 20 from excavations directed by Thanik Lertcharnrit at the archaeological site of Phromthin Tai (PTT, 14°99′55″ N, 100°62′39″ E) in Lopburi Province, Central Thailand (Fig. 1a), where a number of human burials (over 60 burials) were unearthed. Burial 20 dates from 200 BCE to 100 CE, is among the other burials interred in the same area of the site. The burial occupier is a young female individual aged between 20 and 25 years and is interred in an extended supine posture with grave goods consisting of a variety of beads including agate, carnelian, green stone beads, and glass beads (Lertcharnrit et al. 2024). All the beads were found in situ around the neck and ear areas of the skull (Fig. 1b), suggesting that they were potentially used as necklaces or earrings. In this study, we analyzed one intact black-and-white banded glass bead (PTT-1) and two sherds (PTT-2&3). PTT-1 features four black bands and three white bands (Fig. 1c).

### Analytical methods

The beads were observed and measured by a digital microscope (HiROX-01). The chemical composition of the glass beads was analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at Beijing Createch

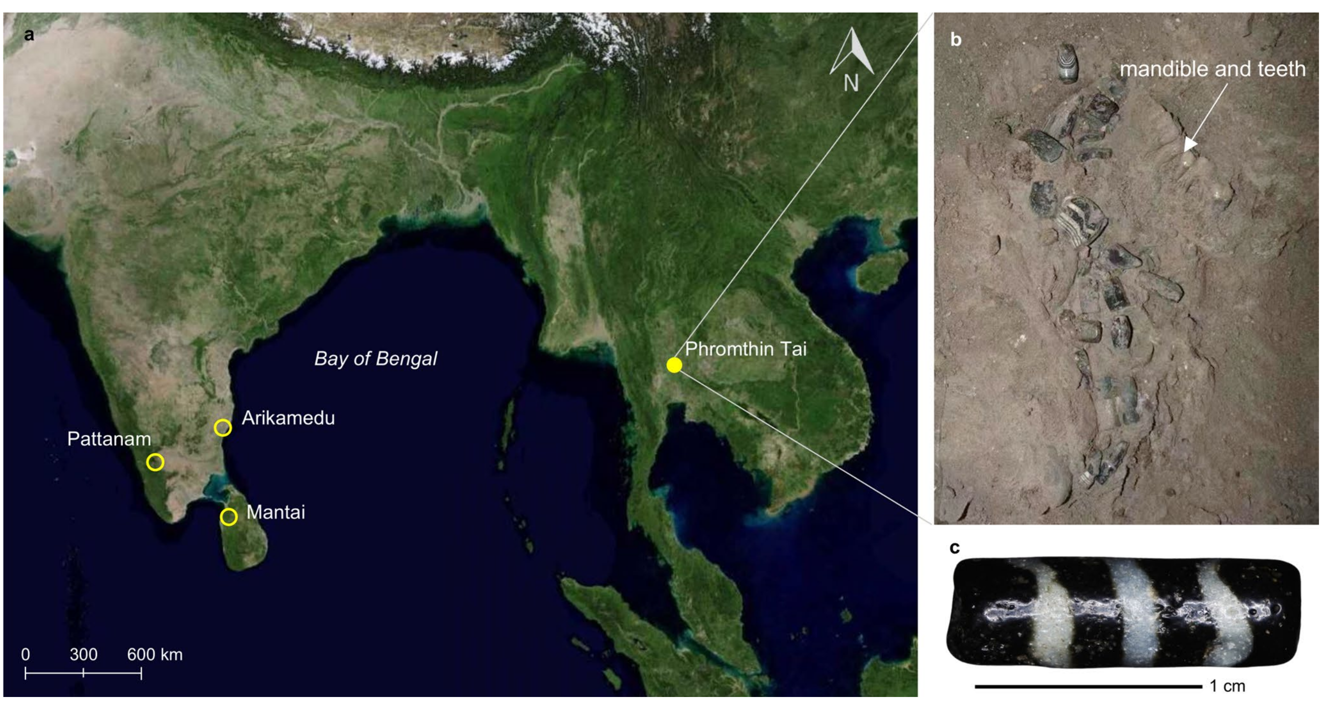


**Fig. 1** (a) Schematic diagram of the location of the Phromthin Tai site. (b) Photo of Burial 20, where numerous agate and glass beads were unearthed. (c) Photo of the intact sample of PTT-1

Testing Technology Co., Ltd. It is composed of an ICP-MS (AnalytikJena PQMS) and a matching RESOlution 193 nm laser ablation system. The laser ablation was set with a spot beam diameter of 38 μm, frequency of 5 Hz, and energy density of 5 J/cm$^2$. High-purity helium was used as the carrier gas. The analysis process consisted of 3 s preablation to remove the corrosion layer, 15 s background, 45 s ablation time, and 25 s purging time. Five standard reference materials were used to calculate the chosen elements: NIST 610, NIST 612, and Corning reference glasses A, B and D. We referred to the data from Pearce et al. (1997) to determine the concentrations of minor and trace elements. The relative standard deviation of major elements is mostly lower than 3%, while that of trace elements is mostly lower than 9%. The relative error of major elements is mainly ± 5%, and that of trace element ranges mainly ± 10%. The standard reference materials and accuracy used for calibration are nearly identical to those from the analysis in the Field Museum of Natural History in Chicago, USA (Dussubieux and Bellina 2018; Then-Obłuska and Dussubieux 2023), thereby ensuring the comparability of the compositional data.

X-ray computed tomography (μ-CT) scans were recorded by Phoenix V|tome|x M, GE, USA. The sample was scanned at a high voltage of 140 kV, a current of 100 μA, and the resolution of each voxel was 4.603 μm.

Raman spectra were acquired using an alphaCART (WITec GMBH, Germany) mobile Raman system. A diode-pumped solid-state laser (532 nm, cobalt Laser) was focused on the sample with a 20x objective (NA = 0.90). The collected Raman signals were dispersed by DUHTS spectrometer and detected using a back-illuminated charge-coupled-device thermoelectrically cooled to −60 °C. The Raman data analysis was performed with WITec Project 6.1 software.

Surface chemical compositions were analyzed using an X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, ThermoFisher Scientific Inc., USA). Al Kα X ray was used as source. All binding energies were referenced to the carbon 1 s component set to 284.8 eV. The Avantage v5.979 XPS program was employed to fit the XPS peaks.

## Results and discussion

### Shape

In order to study beads, analyzing their morphological characteristics is essential. Since the other two samples were merely sherds and their exact shapes could not be determined, only PTT-1 bead was analyzed. It is a very long cylinder bead, with an outer diameter of 5.19 mm and a length of 15.25 mm. According to the criteria established by Beck (1928), this sample is classified as Type I.D.2.b. The alternating black and white bands are parallel, exhibit minimal undulations, and are oriented perpendicularly to the perforation direction.

### Elemental composition

The composition data for black and white portions of the samples are presented in Table S1, revealing two distinct compositional types. The white portion has high contents of $Na_2O$ (11.62–12.16 wt%) but rather low contents of MgO (0.51–0.63 wt%) and $K_2O$ (2.37–2.73 wt%), suggesting the soda flux taken from a mineral source (Sayre and Smith 1961). The CaO (5.44–6.32 wt%) and $Al_2O_3$ (5.29–5.76 wt%) concentrations exhibit negligible disparity. Hence, white glass is classified under the m-Na-Ca-Al type. In particular, white glass portions have relatively high uranium concentrations (14.28–15.47 ppm), matching the chemical signature of this glass type (Dussubieux and Gratuze 2013; Dussubieux et al. 2012). The m-Na-Ca-Al glass is regarded as produced in South and Southeast Asia, and specific regions can be distinguished based on the concentrations of Cr and V (Dussubieux et al. 2025). The white portions of sample PTT-1 contain Cr and V concentrations of 29.88 ppm and 65.64 ppm, respectively, indicative of a Southeast Indian provenance (Dussubieux 2001; Dussubieux et al. 2025). Conversely, samples PTT-2 and PTT-3 display relatively low Cr and V levels, which complicates the determination of their origin.

The black portions exhibit inconsistent composition characteristics, with a high level of $K_2O$ and a potash-to-total alkali ratio of about 50%. Another banded glass bead from the PTT site, of which the black portion has a similar composition (Carter et al. 2022). Based on their major composition, we call them the m-mixed-Ca-Al type, which was also identified at Arikamedu site in India and Khao Sam Kaeo site in Thailand (Lankton 2013; Lankton and Dussubieux n.d.). Regarding the type of black glass, there are two hypotheses: one advocates employing a mixture of soda glass and potash glass, while the other suggests incorporating pigments and fluxes into primary m-Na-Ca-Al glass to elevate $K_2O$ concentrations. The significantly high cobalt levels (> 1000 ppm) in black samples provide compelling evidence that primary glass contains cobalt materials. The cobalt materials in Southeast Asian glass can be classified into two types: Co-As and Co-Mn-Ba (Dussubieux 2016). The former was found at Ban Don Ta Phet and Khao Sam Kaeo in Thailand during the 4th-2nd centuries BCE. The latter, however, exhibited broader temporal and spatial distributions. The black glass samples have high Mn and Ba concentrations but low As concentrations. Compared to the cobalt blue glass from Southeast and South Asia, black samples were suggested to have undergone remelting with cobalt blue glass with Co-Mn-Ba type (Fig. S1). While it remains difficult to determine whether cobalt materials were introduced via soda glass, potash glass, or both, the contemporary m-Na-Al 1 glass can be excluded as the raw cobalt blue glass, as it contains no cobalt blue (Dussubieux et al. 2008, 2010). Moreover, the average composition of m-Na-Al 1 is $Na_2O$ 15.5%, $Al_2O_3$ 9.8%, $K_2O$ 2.3%, and CaO 3.0% (Dussubieux et al. 2010). The $Al_2O_3/Na_2O$ ratio of m-Na-Al-1 glass exceeds 0.6, and during this period potash glass was mainly of the m-K-Al and m-K-Ca-Al types. A mixture of m-Na-Al-1 and potash glass would therefore be expected to further increase the $Al_2O_3/Na_2O$ ratio. However, the $Al_2O_3/Na_2O$ ratio of the black glass is approximately 0.5, suggesting that the use of m-Na-Al-1 glass as a raw material is relatively unlikely. Therefore, we suggest that the black glass was mixed by m-Na-Ca-Al and/or m-K types.

Additionally, one black-and-white banded glass bead reported by Carter et al. (2022) was made of glass of an unknown type. The presence of multiple glass types may suggest an instability in the production chain of raw glass.

## Color

### White hue

In the white portion, many air bubbles in microns are responsible for opacification due to the Mie scattering (Nassau 2001). Additionally, tin oxide was identified as the opacifying agent detected, as indicated by Raman bands at 637 and 782 $cm^{-1}$ (Fig. 2a). This aligns with findings from other black-and-white banded glass beads at the PTT site, where tin oxide was also used as an opacifier, evidenced by their high tin concentrations (Carter et al. 2022).

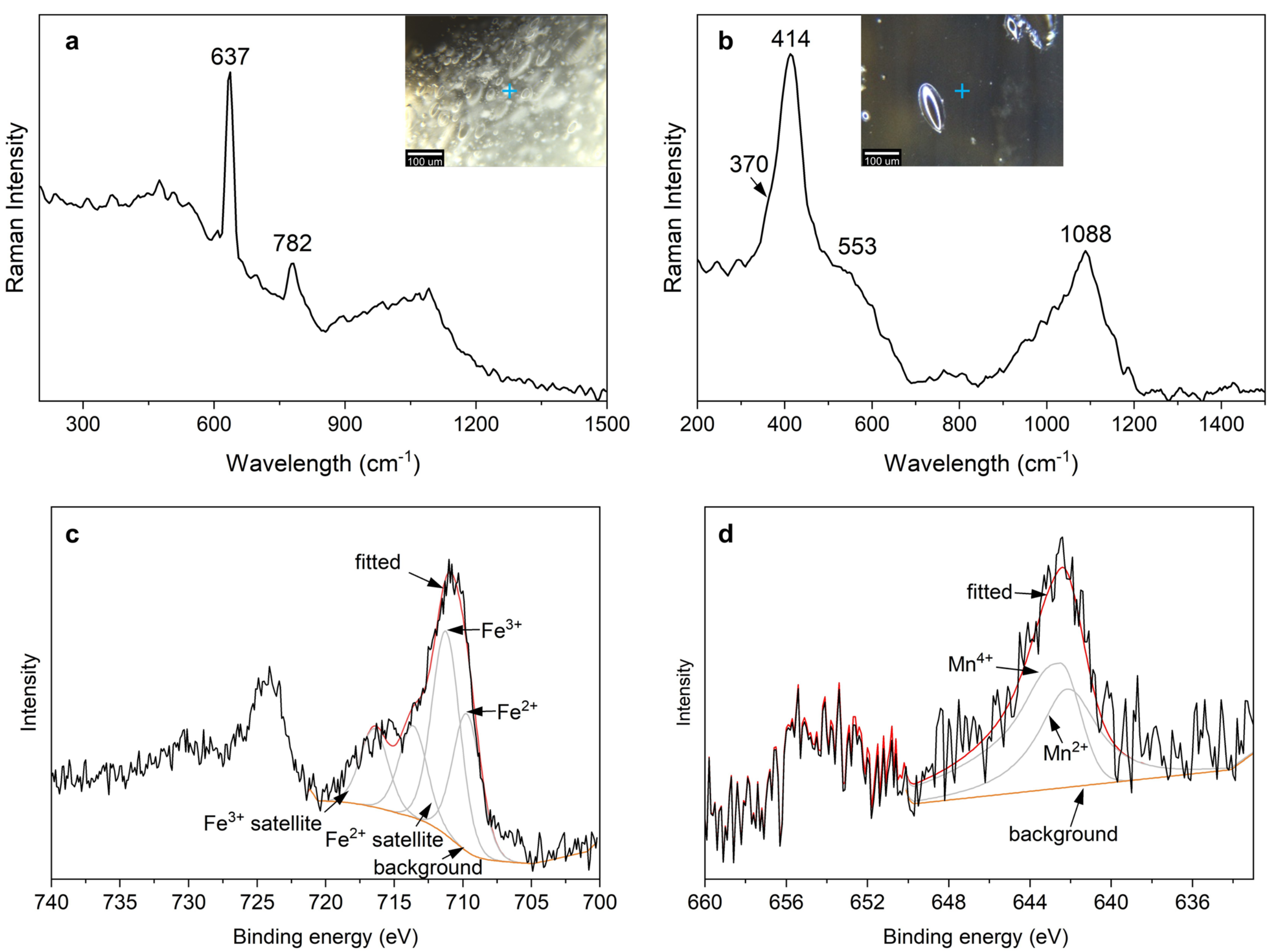


**Fig. 2** Chromogenic analysis of black and white hues. (**a**) the raman spectrum of the white portion in PTT-3 showing the presence of cassiterite, (**b**) the raman spectrum of the black portion in PTT-3 showing the presence of Fe-S chromophore, (**c**) the XPS spectrum of Fe 2p showing the presence of $Fe^{2+}$ and $Fe^{3+}$ of the black portion in PTT-2. (**d**) the XPS spectrum of Mn 2p showing the presence of $Mn^{2+}$ and $Mn^{4+}$ of the black portion in PTT-2

Tin oxide has a long history as an opacifier in glass production. The popularity of tin-based opacifiers in the Mediterranean region mainly occurred after the 4th century CE (Neri et al. 2016), whereas earlier tin-based opacified glass has also been identified in parts of Eurasia (Tite et al. 2008; Xu et al. 2025). Carter (2015) summarized the correlation between color and glass type in South and Southeast Asia. Tin oxide was used in a glass bead with the m-K-Ca-Al type, combined with copper to produce an opaque blue hue (Li et al. 2014). It is important to note that white glass was predominantly associated with m-Na-Al glass during the first millennium CE. This implies that the tin white technique was already being applied in those regions. The transition from antimony-based to tin-based opacifiers in the Mediterranean region during the 4th century CE was likely influenced by multiple factors, such as resource availability or trade connections with South Asia (Tite et al. 2008). In addition to tin-oxide white, another type of tin-based opacifier is lead-tin yellow. Although yellow glass beads are also present in m-K glass (Dussubieux and Bellina 2018; Xu et al. 2022a), which is widely prevalent in Southeast Asia, white potash glass is lacking. Similarly, lead-tin yellow is identified in yellow m-Na-Ca-Al glass from Myanmar (Dussubieux et al. 2020) and Cambodia (Dussubieux 2001), but white m-Na-Ca-Al glass remains rare among Southeast Asian glass. Although white glass remained relatively uncommon in South and Southeast Asia during the early Iron Age, the presence of white portions in black-and-white beads suggests that such glass was deliberately produced.

### Black hue

The black color is rare in the m-mixed-Ca-Al glass type. Optical microscopic observations revealed no crystals within the black portions. The black hue is likely to be related to the presence of Fe ($Fe_2O_3$ 1.71–2.09 wt%) and Mn (MnO 2.03–2.36 wt%) ions. Raman spectroscopy detected Fe-S chromophores (Fig. 2b), characterized by the bands at 370 and 414 $cm^{-1}$ (Koleini et al. 2019; Prinsloo and Colomban 2008) and silicate glass, with the broad bands centered at 553 and 1088 $cm^{-1}$.

To further reveal the electronic state information of Mn and Fe, XPS analysis was employed to examine the surface characteristics of sample PTT-2. The high-resolution Fe 2p spin-orbit doublet spectrum is shown in Fig. 2c. The Fe $2p_{3/2}$ peak observed at 711.2 eV corresponds to the contribution from $Fe^{3+}$ ions and a satellite peak of $Fe^{3+}$ at 716.5 eV is detected. The presence of peaks at 709.7 and 713.6 eV is in agreement with $Fe^{2+}$. The $Fe^{3+}$-$S^{2-}$ chromophores formed by $Fe^{3+}$ ions primarily attribute to the black color. Moreover, the Mn 2p spectrum (Fig. 2d) reveals the characteristic peaks of $Mn^{4+}$ and $Mn^{2+}$ at 642.5 and 642.1 eV, respectively, whereas mostly $Mn^{4+}$ ions are present. The black hue is also likely attributed to the presence of $Mn^{4+}$.

The introduction of Mn occurred concurrently with Co (Fig. S1a); however, after the remelting process, the influence of cobalt blue appeared to be diminished. Although cobalt blue glass in Southeast Asia also contains Fe, its concentration is not stable. In the black portions of the black-and-white beads from the PTT site, the Co-Fe correlation is weak (Fig. S1c), suggesting that Fe was not introduced simultaneously with Co and Mn.

Glass with black or amber coloration related to the Fe-S chromophore exhibits a broad temporal and geographical span. Comparable examples are evident from Europe and North Africa in the 2nd millennium BCE (Bettineschi et al. 2025; Shortland and Eremin 2006). Although iron-rich black glass appeared in the first millennium BCE (Conte et al. 2018), the continued use of the Fe-S chromophore is further attested by finds in Roman Europe (Barroso-Solares et al. 2024; Caggiani et al. 2017), as well as in contemporary Southeast Asia (Dussubieux et al. 2020, 2024). A black glass beads dating to the 8th century CE in our previous paper has also been discovered in Xinjiang, China (Xu et al. 2022b). Comparable beads are documented in Africa as early as the late 1 st and the 2nd millennium CE (Koleini et al. 2019; Prinsloo and Colomban 2008), which are possibly linked to long-distance trade networks in the Indian Ocean. The detection of Fe-S chromophores in Southeast Asian glass beads dating to approximately two thousand years ago is consistent with this broader archaeological context.

## Manufacturing methods

Glass beads imitating agate were documented as early as the mid-2nd millennium BCE, with examples found in Nuzi, Northeast Iraq (Vandiver 1983). They were produced by wrapping a glass strip around a glass bead body, resulting in a spiral pattern. Some of the wound beads produced by this method were also unearthed in Pakistan (Francis Jr 2002). The folding method is hypothesized as a common method for producing black-and-white banded beads. Originating in the Mediterranean world by the 3rd century BCE, this method was later adopted in South and Southeast Asia, where it gained widespread use (Francis Jr 2002). Archaeological evidence includes folded and segmented glass beads from Mantai, Sri Lanka and multicolored folded glass beads from Vijaya, Indonesia (Francis Jr 2002). A defining feature of this method is a longitudinal seam parallel to the perforation (Fig. S2). Furthermore, rod-piercing method was employed with the folding method to produce banded glass beads, as observed in Indonesian beads (Francis Jr 2002). The rod-pierced bead has a tapered perforation due to the tapered mandrel. This method was also employed in the

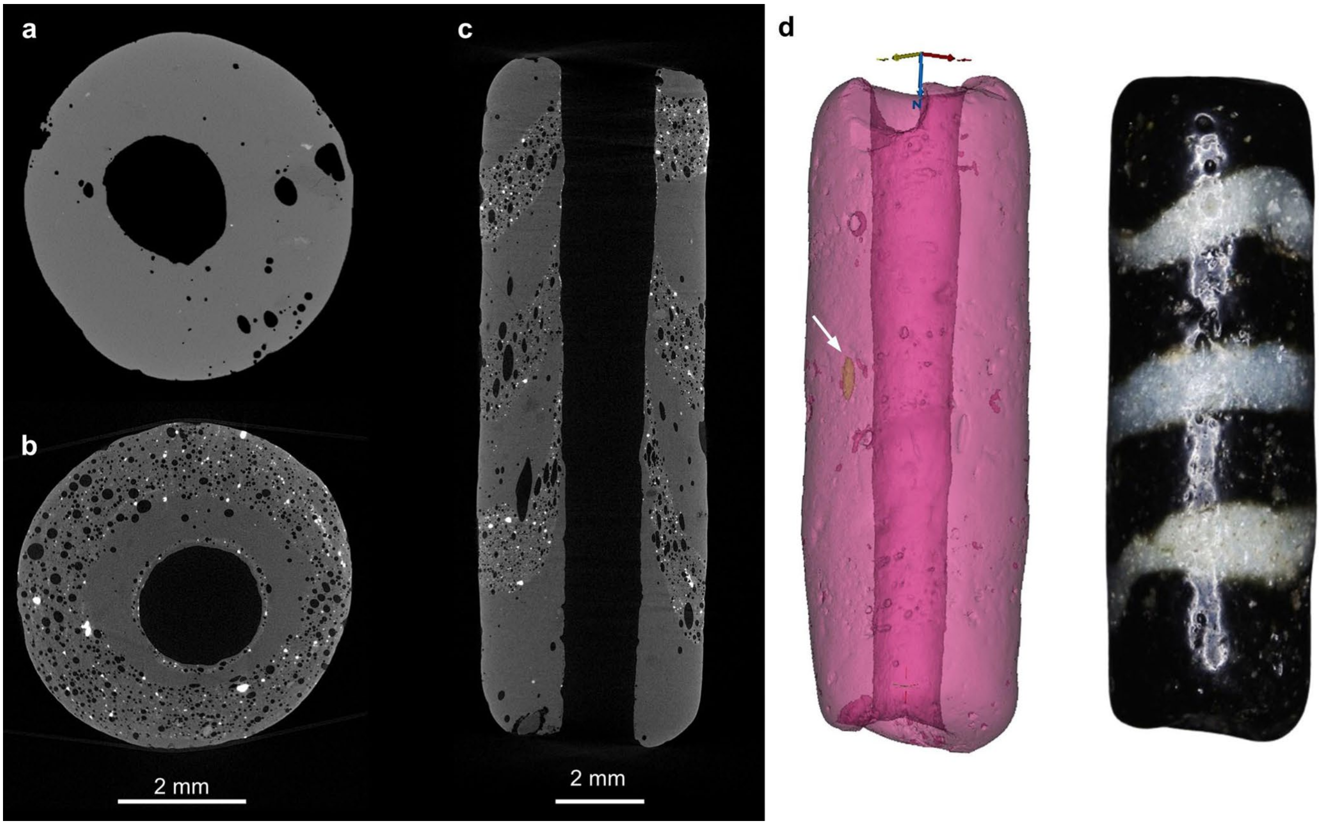


**Fig. 3** Micro-CT slices of PTT-1. (**a**-**b**) axial slices at different positions on the Z axis. (**c**) longitudinal slice. (**d**) elongated bubble (yellow) in 3D projection

beads of regions such as Egypt and Syria (Francis Jr 2002; Then-Obłuska 2016), and it was likely introduced from the Middle East to Southeast Asia.

CT scanning is valuable for visualizing the structure of a bead and reconstructing its texture. Figure 3 shows representative slices in both the longitudinal and axial directions. First, the stratification of black and white portions is evident: the black portion exhibits a high density, while the white portion contains lots of tin oxide crystals (white) and bubbles (black). The introduction of tin oxide appears to be responsible for the formation of tiny bubbles, whereas larger bubbles are attributed to the stitching of black and white glasses (Bertini et al. 2014). Notably, the white glass is not only confined to the surface of the bead, but also extends to its interior, suggesting that it is not wrapped around the exterior of the black glass.

While it has previously been hypothesized that black-and-white banded beads were produced using the folding method (Carter 2013), neither microscopic examination nor CT-reconstructed 3D models reveal the seam formed by two-edge meeting in the analyzed sample (Figs. 1c and 3). The diameters of the two ends present no obvious difference, indicating that this bead was not shaped by the rod-piercing method (Francis Jr 2002). Instead, it is inferred that the winding method was applied for layering molten glass with different colors onto a metal rod. The glass assembly was subsequently rolled on a smooth surface for polishing. The black and white glass rings are not as regular as doughnuts, with the white glass (the porous area) observed to envelop the black glass (the dense area) around the perforation (Fig. 3c). The deformation of the white glass ring may be attributed to incomplete solidification of the glass bead during the detachment from the metal rod. Elongated bubbles (e.g. the yellow bubble in Fig. 3d) parallel to the perforation provide additional evidence that this glass bead was drawn. Thus, it is first reported that the drawing method was used in the production of the banded glass bead.

## Exchange network of agate and glass

In terms of composition, opacifier, or drawing method, the banded glass beads in this study all exhibit certain South Asian characteristics. In the Iron Age, Central Thailand participated in complex exchange networks within South Asia and Southeast Asia, with abundant evidence of the trade of agate and other types of glass beads. For example, many agate/carnelian beads in Phromthin Tai are considered Indian sources (Carter and Dussubieux 2016). Among the glass artifacts unearthed at this site, m-Na-Al-1 glass, which clearly originated from South Asia, predominates (Carter 2015). In particular, Carter et al. (2022) argued that Burial 20 at Phromthin Tai met the transition from the South China Sea bead exchange (focused on m-K glass) to the Mekong Interaction Sphere (focused on m-Na-Al glass).

Interactions between Southeast Asia and South Asia are classified into two distinct phases (Bellina and Glover 2004; Dussubieux et al. 2025). Phase I (the second half of the first millennium BCE) pointed to the exchange network with Northeast South Asia. Compositional and isotopic analyses of glass artifacts from the sites in South Thailand and Myanmar suggest an Indian origin (Dussubieux and Bellina 2017, 2018; Dussubieux and Pryce 2016). However, Phase II (the 2nd-4th centuries CE) showed intense connections from South India and Sri Lanka to the Mekong Delta region. The introduction of black-and-white banded glass beads is probably a moment following the transformation of exchange networks. Our analysis further supports the intensifying trade network with South India and Sri Lanka, which includes not only common monochrome glass beads and agate beads of various shapes, but also glass beads imitating agate.

## Conclusions

This study highlights the manufacturing technique of black-and-white banded glass beads. In particular, some unique techniques are first applied to imitate agate beads. First, two distinct glass types of m-mixed-Ca-Al (black) and m-Na-Ca-Al (white), owing to their rarity, are likely produced specially for making such imitating agate banded glass beads. Second, tin oxide served as the white opacifier, while Fe-S chromophores and manganese contributed to the black coloration. Third, both winding and drawing methods were used to shape the long cylindrical banded glass bead. The drawing method is first reported for the production of banded glass beads. Therefore, our comprehensive analysis confirms the glass type combination and techniques which is a crucial step in advancing our understanding of glass beadmaking. This study opens a new perspective on glass and stone exchange from South Asia to Southeast Asia, since its presence confirms the imitation of artificial glass for natural stones.

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s12520-025-02341-0.

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**Author contributions** S. X. wrote the main manuscript text; S. X., Y. H., and X. Y. analyzed the samples; T. L. obtained samples and provided archaeological information; Y. Y. conceptualized the research and edited the paper. All authors reviewed the manuscript.

**Data availability** No datasets were generated or analysed during the current study.

## Declarations

**Competing interests** The authors declare no competing interests.

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