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Laser ablation inductively coupled plasma mass spectrometry analysis of potash and m-Na-Al glasses in China- using Kernel methods for trace element analysis

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Abstract

Monochrome drawn beads were widely circulated in South and Southeast Asia as early as the second century BC. This article aims to identify the glass beads unearthed from different sites in China and discuss their possible sources. Twenty-seven mineral soda alumina (m-Na-Al) glass and eighty-seven potash glass beads unearthed in different provinces in China were analysed by Laser Ablation Inductively Coupled Plasma Mass Spectrometry. The trace element analysis through Multivariate Kernel Density Estimation and Maximum Mean Discrepancy indicates the silica sources of m-Na-Al glass and most of the potash glass unearthed from Guangxi are identical. They were presumably produced somewhere in northeastern India or Southeast Asia and exported through the Maritime Silk Road. The silica sources of m-Na-Al glass in Henan and the rest of the potash glasses are geologically close. They were likely produced in southern India or Sri Lanka and exported through the North and Southwest Silk Roads. Future research on isotopic analysis will reveal more information about primary/secondary glass production in China, South and Southeast Asia.

Keywords: m-Na-Al glass, Potash glass, Silk Road, KDE, MMD

Introduction

The Indo-Pacific glass beads are widely distributed in different provinces in China starting from the Warring States period (475–221 BC), such as Xinjiang, Yunnan, Guangxi, Hubei, etc. [1]. Due to the lack of archaeological evidence of the primary and secondary glass production in China, there is an ongoing question, however, regarding the site of production for these early glass beads unearthed in China and whether they were produced locally or imported via the Silk Road network. In order to address this question, this paper utilizes LA-ICP-MS to analyse 114 glass beads from archaeological sites dating to the Warring States period and the Han Dynasty (202 BC–AD 220) from five provinces in China.

The Southwest and Maritime Silk Roads

The concept of 'Seidenstraße' or 'Silk Road' was first proposed by Ferdinand von Richthofen in 1877. The original definition of Silk Road is the trade route from China to India via Transoxiana from 114 BC to AD 127 [2]. Richthofen [2] believed that the beginning of the Silk Road was after *Zhang Qian's* 张骞 second journey to the Central Asian countries, as *Zhang Qian* proposed that there was no lacquer or silk in these regions. Herrmann [3] redefined the concept of the Silk Road and suggested that the Silk Road should be extended to the trade route from China to Syria in the far west, as Chinese silk was transported to the Roman Empire shortly after *Zhang Qian* reopened the trade between the Han Empire and
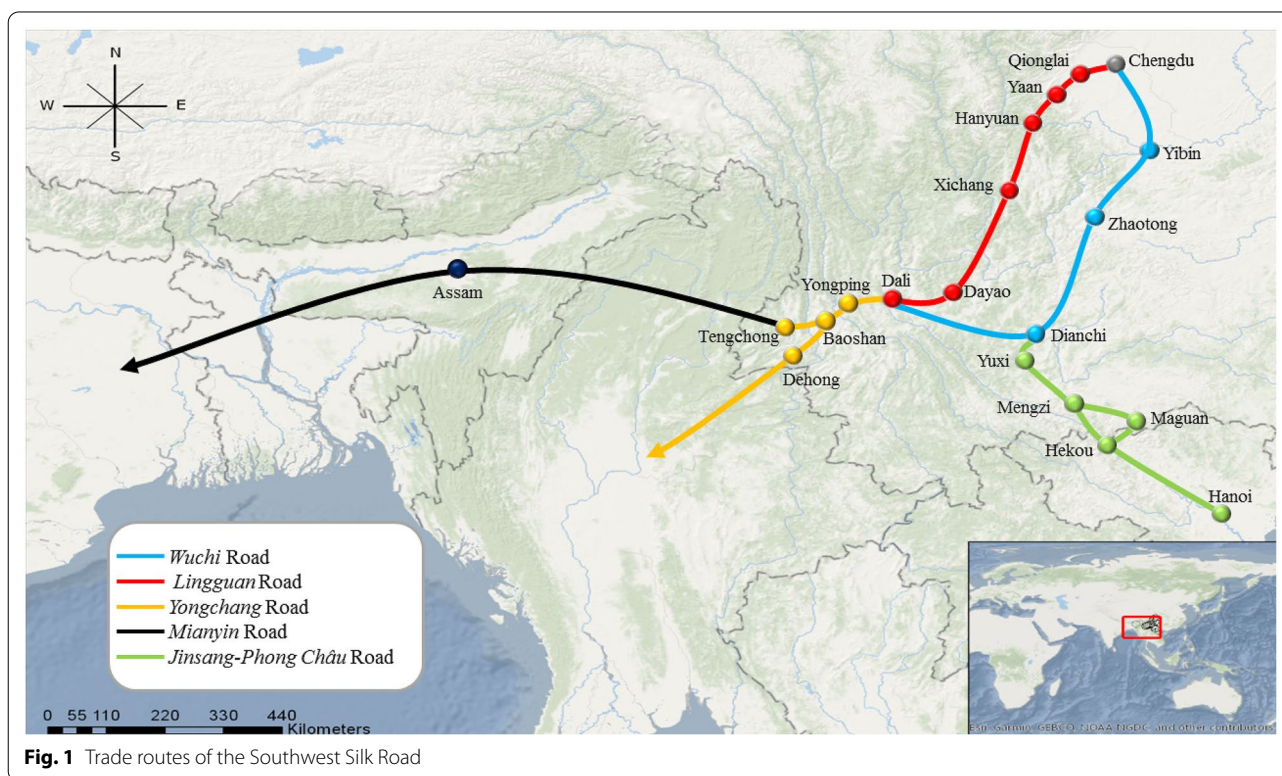
the Central Asian region. The trade between China and South/Southeast Asia was mainly through the Southwest Silk Road and the Maritime Silk Road [4]. The Southwest Silk Road originated before the Qin period (221 – 207 BC). The concept of the Southwest Silk Road is more or less influenced and inspired by the definition of the North Silk Road. However, rather than considering it as a simple trade route from China to India (Shu- Sindu Road), it is more like a trade network with various regions in South/Southeast Asia [5]. There was a trade road leading directly from Chengdu to India, but there were also indirect routes from other regions using land, river or maritime routes. Figure 1 shows trade routes from Chengdu to India, Myanmar and Vietnam. The Shu-Sindu Road can be divided into four parts: There were two routes from Sichuan Province to Yunnan Province which were named the 五尺道 *Wuchi* Road and the 零关道 *Lingguan* Road; the route from Yunnan Province to Myanmar was called the 永昌道 *Yongchang* Road; the route from Myanmar to India was called the 缅印道 *Mianyin* Road [6–8]. The 进桑麋冷道 *Jinsang-Phong Châu* Road is also part of the Southwest Silk Road from Yunnan to Vietnam [5]. What is emphasized here is that the Southwest Silk Road was a complex trade network, and no doubt it also had a strong connection with the Maritime Silk Road.

The Maritime Silk Road started from the South China Sea, passed through Southeast Asia, crossed the Indian Ocean, the Red Sea and the Nile to the Mediterranean, thus connecting Asia, Africa and Europe [4]. During the Spring and Autumn (770–476 BC) and the Warring States periods, the Qi State had already discovered the trade routes to the Liaodong peninsula (southern Liaoning Province), the Korean peninsula, the Japanese islands and the regions to Southeast Asia along the coastline [9]. During the Han Dynasty, *Fanyu* (Canton) 番禺, *Xuwen* (Canton) 徐闻 and *Hepu* (Guangxi Province) 合浦 were three important trade ports as the starting points of the Maritime Silk Road [10]. The objects unearthed from the tomb of the King of South *Yue* (Canton) reveal evidence of maritime trade between China and neighbouring regions [11]. Tens of thousands of glass beads were excavated from sites in *Hepu*, Guangxi province [4]. The sailing routes from *Hepu* (Guangxi) to Southeast Asia were documented in *Hanshu-Geography* 汉书- 地理志 (edited by *Ban Gu* 班固 in AD 105 [12]). For example, 'The distance between *Hepu* to *Duyuan State* 都元国 (inconclusive, east coast of Malay Peninsula or Isthmus of Kra in Thailand) was five months by ship; the ship could reach *Yilumei State* 邑卢没国 (inconclusive, South Thailand or Thaton in Myanmar) by sailing for another 4 months; after over twenty-days of sailing the ship could further reach *Chenli State* 谌离国 (inconclusive, South Myanmar or Prome)'.

Fig. 1 Trade routes of the Southwest Silk Road

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Indo-Pacific glass beads

The earliest imported glass found in India dates to the period of Painted Gray Culture about 12th century BC from Bhagwanpura in the Nothern state of Haryana [13]. Kopia was India's first glass-making site dating to the 5th century BC and unearthed Indian made glasses- plant ash high alumina soda glass (v-Na-Al) and potash glass [13]. Arikamedu, as one of the most famous archaeological sites located on the southeastern coast of India, is considered to be a glass-working centre from 200 BC to AD 200 and is well-known for its drawing technique for the Indo-Pacific glass bead [14]. The term 'Indo-Pacific Beads' was first proposed by Peter Francis [15], and it refers to monochrome drawn glass beads found in Indo-Pacific regions. Drawn beads are obtained by cutting thin glass tubes [16]. A mass of molten glass is gathered on the end of a hollow metal rod (a pontil or blowpipe) and then a hole was poked within the molten glass, either by blowing or by inserting a metal rod. Next, a tool which is called *lada* is attached to the molten glass to gradually draw the glass into a tube. This type of glass was not only discovered in South Asia, but throughout the Indian Ocean littoral (from the Red Sea to southern Africa to Southeast Asia and Japan: [17]). Moreover, they have also recently been identified in European Merovingian graves [18]. Francis [15] compared the glass waste debitage that resulted from various stages of modern production from Papanaidupet (India) and the glass beads from the site of Arikamedu, an Early Historic port site on the southeastern Indian coast. The Indo-Pacific glass beads from Arikamedu dating to the 1st centuries BC/AD were virtually identical to those from modern Papanaidupet village. The occurrence of glass in Southeast Asia was after 500 BC. A large number of glass beads found at Site Ban Bon Noen, Thailand are dated to the 5th century BC, and Carter [19] suggests this site was likely to be a bead trading area rather than a primary/ secondary production centre. Khao Sam Kaeo Site, Thailand dating to the 4th–2nd centuries BC was a secondary production due to the evidence of glass-working tools [19, 20]. Phu Khao Thong (200 BC–400 AD) is also regarded as the glass-working site, as two different sources of raw glasses were discovered [21]. Giong Ca Vo, Vietnam (∼400 BC) could be a primary production centre due to the presence of distinctly Sa Huynh glass ornaments [22]. The research of over 400 glass beads excavated at Iron Age Samon Valley cemeteries of Htan Ta Pin, Htan Bo, Nyaung Gon,Myo Hla, Ywa Htin, and HnawKan reveals the Samon Valley's participation in exchange networks connecting the Ganges Valley with west-central and peninsular Thailand, as well as southern Vietnam [23]. Glass unearthed at Kampong Sungei Lang in Malaysia is dated to around the 5th to second century BC; The earliest glass unearthed at

Bali and Gilimanuk in Indonesia is dated to 2020 ± 165 BP; glass unearthed at Manunggul Cave is believed as the earliest glass found in the Philippines (2140 ± 100 BP) [24]. The ^{14}C dates above were calibrated by using H. Michael's calibration tables of April 1982 [25]. Indo-Pacific Beads were also discovered in Africa, such as the mineral soda–alumina (m-Na–Al) glass excavated at sites of Unguja Ukuu and Fukuchani on Zanzibar Island dating to the 10th Century AD and Ingombe Ilede dating to the mid 15th to mid 17th centuries [26, 27].

Potash glass was commonly discovered at sites across entire India dating back to the beginning of the Christian era (e.g., northern India: Hastinapur (200 BC - AD 200 A.D); Kausambi (200 BC.- AD 200); Ter (100 BC - AD 100); Southern India: Alagankulam (300 BC - AD 300), Kodumanal (300 BC - AD 300)) [28]. Potash glass was also widely unearthed in Southeast Asia. For instance, Ban Don Ta Phet and Khao Sam Kaeo dated to the 4th century BC–1st century AD and Phu Khao Thong dated to the 2nd century BC in Thailand all yielded potash glass [20]. Lankton and Dussubieux [29] summarised three subtypes of potash glass according to concentrations of CaO and Al_2O_3. This difference reflects the change in the selection of silica, flux and stabilizer sources. Dussubieux [20] believes that there was a change of source of raw materials for producing potash glass between the 4th century BC and 2nd century BC in Thailand. However, the direct archaeological evidence of potash glass remains unknown. The primary production of mineral soda–alumina glass is relatively more clear compared with potash glass. Sri Lanka (southern India), northern India and Thailand were all possible regions for the primary production of mineral soda–alumina glass [29, 30]. Henderson et al. [31] suggest that some of the potash glass may have been produced in China, yet there is no archaeological evidence of primary production or secondary production conducted in China during the Han Dynasty. In this study, 114 m-Na-Al glass and potash glass samples unearthed at different sites in China were analysed. Since the primary production of mineral soda–alumina glass is relatively clear, the comparison of silica sources through trace element analysis for two types of glasses may reveal the potential primary production site of the potash glass. In general, this research reconstructs the network of how various types of glasses in South/ Southeast Asia were traded to different regions of China.

Materials and methods

The 114 glass beads analysed in this study are mainly from six sites in five provinces in China, including Xinjiang, Yunnan, Guangxi, Henan and Hubei (Fig. 2). Glass beads from Xinjiang, Yunnan and Guangxi were selected to understand the role of the North,

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Fig. 2 Glass beads analysed are from six sites in five different provinces in China
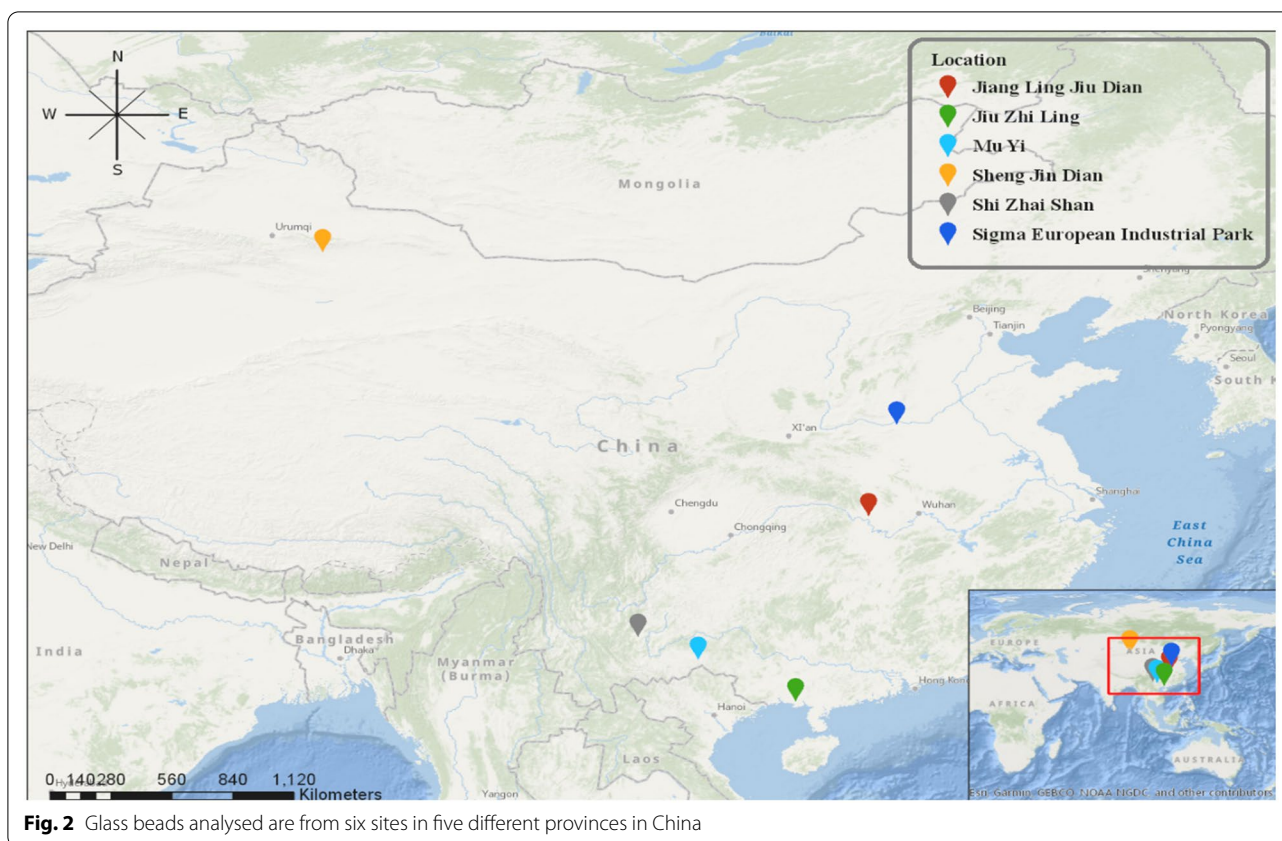
Southwest and Maritime Silk Roads for the glass trade respectively. Glass beads from Hubei and Henan were analysed to find the connection of glass beads from the borderland of China. As samples are from museums and archaeology institutes, the sample size was strictly restricted by curators accordingly. With limited options, glass beads from five provinces are sampled according to their typologies. As shown in Fig. 3, there are mainly four types of glass analysed in this case, including monochrome drawn beads from Xinjiang, Yunnan, Guangxi, Henan (Han Dynasty), a pair of glass ear pendants from Henan (Han Dynasty), eye beads and glass tubes from Hubei (Warring States period). The eyes beads and tubular beads unearthed at the noble tomb were symbols of wealth for the nobility during the Warring States period; The pair of ear pendants were clearly consumed by females. A large number of monochrome drawn beads were unearthed at Mu Yi Site and they are all relatively smaller than the other three types. They were likely used as necklaces, bracelets or ornaments on clothes. Details about the sample information and photos can be found in Additional file 1: Table A.1 and Table A.2. The background of six archaeological sites can also be found in Additional file 1: Sites background.

Fig. 3 Four types of glass objects analysed in this study
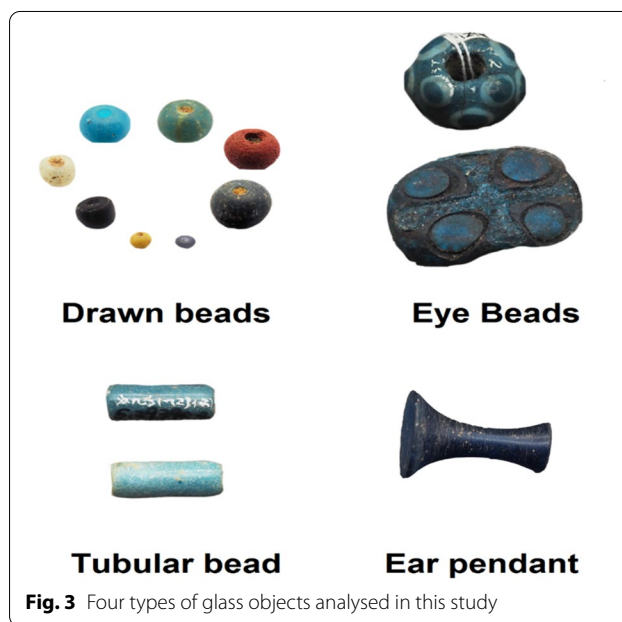
LA-ICP-MS analysis

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is a virtually non-destructive technique that has excellent sensitivity, analytical

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precision and accuracy, and is reasonably quick [32]. The high resolution of this technique allows the investigation of compositional variations in the trace and minor elements in glasses to a greater degree at the ppm level [32]. LA-ICP-MS analysis was performed at the Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China, Chinese Academy of Sciences. Analyses were carried out with a Coherent GeoLas Pro laser ablation system in conjunction with a PerkinElmer/SCIE Elan DRCIIICP-MS. Samples were directly put on the sample chamber and ablated under an atmosphere of argon. Detailed operating conditions for the laser and the ICP-MS instrument are listed Additional file 1: Table A.3.

USGS reference glasses BCR-2G, BHVO-2G and BIR-1G were used as reference materials for calibration [33]. ApplyingAblation Yield Correction Factor (AYCF) and using these three reference materials for calibration, elements can be precisely analysed in situ by LA-ICP-MS without applying internal standardization [34]. The quantitative analysis of low-mass elements would be influenced by the mass-dependent sensitivity variation [35]. By using a program *ICPMSDataCal*, all count rates were primarily normalised by Si for each analysis, and then a time-drift correction was applied using linear interpolation (with time) according to the variations of NIST SRM 610 [33], which effectively reduce the uncertainty caused by instrumental drift [34]. Additional file 1: Table A.4 shows the accuracy and precision of the data by reporting the standard deviations of major and trace elements for the reference materials. The chemical composition results of 114 glass samples by LA-ICP-MS analysis are presented in Additional file 2: Data analysed in this study.

Kernel Density Estimation and Maximum Mean Discrepancy

In this study, two statistical methods- Kernel Density Estimation (KDE) and Maximum Mean Discrepancy (MMD) were used for cluster analysis. Kernel Density Estimation (KDE) is a non-parametric estimation of the probability density function of a random variable. KDE is a fundamental data smoothing method that allows for inferences about the population to be formed from a finite data sample [36]. Maximum Mean Discrepancy (MMD) is a distance in the probability space which has found numerous applications in machine learning [37]. Detailed algorithms of KDE and MMD can be found in Additional file 1: Kernel Density Estimation and Maximum Mean Discrepancy. KDE has been used on chemical composition analysis of tephra and isotopic analysis of Chinese bronze [38, 39]. Unlike the previous application of KDE on two variables, this research used KDE to estimate the shape of distribution of three and four

variables. The use of a multi-variate KDE plot can not only estimate the distribution of one assemblage, but also allow to compare the estimated shape of distribution between each assemblage. The MMD hypothesis testing was used to test if group X and group Y come from the same distribution.
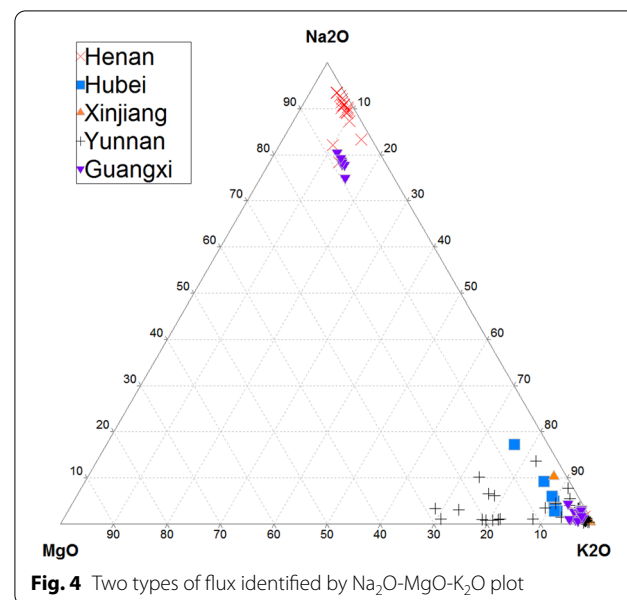
Results

The chemical composition results can be found in Additional file 2: Data analysed in this study. As shown in Fig. 4, two groups of glass beads can be classified according to their K_2O and Na_2O concentrations ($Na_2O + K_2O + MgO = 100\%$). This difference is caused by two types of flux used to produce these glass beads. Both groups show low concentrations of MgO, which suggests that both types of flux were derived from either mineral sodium or potassium sources rather than the use of plant or wood ash sources.

High sodium group

Samples identified as the first group are from two sites, Jiuzhiling Site (Guangxi) and Sigma European Industrial Park Site (Henan). Glass from Guangxi shows a turquoise colour which was contributed by Cu^{2+} ions. Two glass beads found in Henan are black with elevated MgO and FeO concentrations; The red colour of two glass beads found in Henan comes from metallic copper nanoparticles (Cu^0) [40–43], which is commonly referred to as Indian red. The rest of the Henan glass beads show a turquoise colour contributed by Cu^{2+} ions.

Mineral soda–alumina (m-Na–Al) glass has been mainly found in Africa and Asia, and appears from

Fig. 4 Two types of flux identified by Na_2O-MgO-K_2O plot

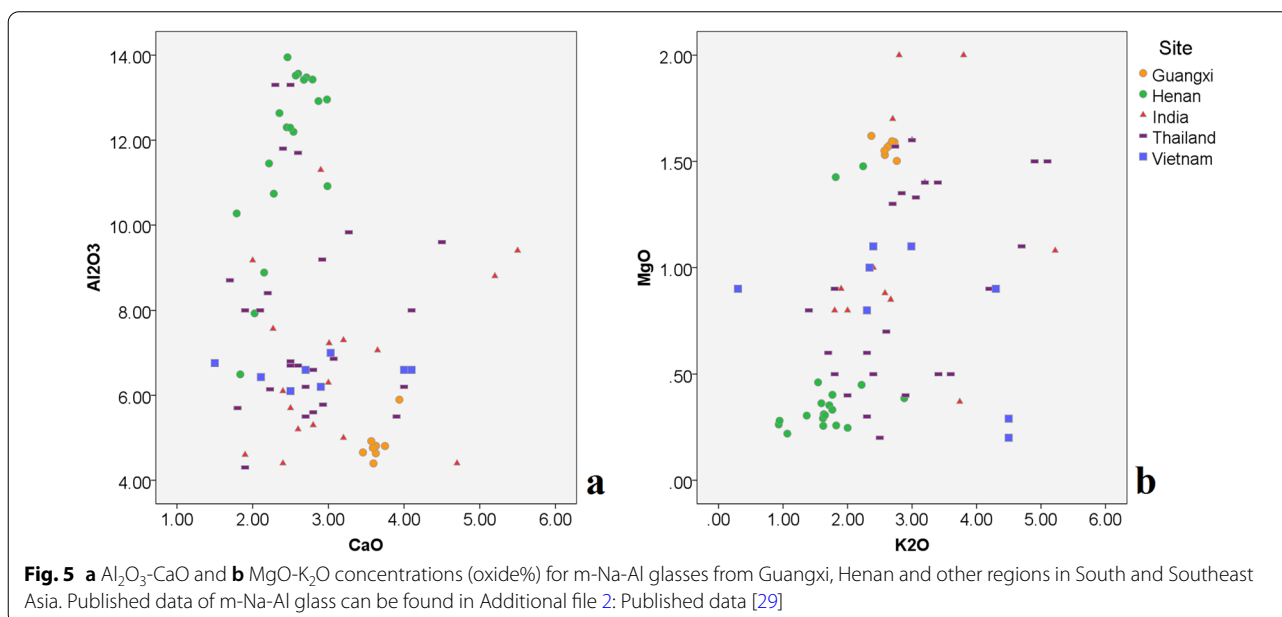Ma *et al. Heritage Science*   (2022) 10:29

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around the 5th century BC until the 19th century AD [30]. Mineral soda–alumina glass has low magnesia concentrations ($\leq 1.5\%$) and low potassium concentrations ($\leq 3\%$), suggesting the use of soda taken from a mineral source [44]. A soda-rich efflorescence similar to reh was certainly used as flux [44]. Available in India, reh is a mixture of sodium carbonate, sodium sulfate and sodium chloride with low proportions of calcium and magnesium. Alumina contents in the m-Na-Al glass vary from 5 to 15% due to the presence of reh. The relatively higher proportions of alumina and potassium, lower calcium proportions can be used to distinguish between natron glass and m-Na-Al glass.

Figures 5 show the Al_2O_3 vs CaO and MgO vs K_2O concentrations for m-Na-Al glasses from Guangxi and Henan analysed in this study and other regions in South and Southeast Asia [29]. The higher and larger variation of Al_2O_3 and lower CaO indicate that the Henan glass can be identified as m-Na-Al glass. The proportions of Al_2O_3 and CaO seem to be less dispersed than for the Guangxi glass. As for the Guangxi glass, although the Al_2O_3 concentrations are around 5% and the CaO concentrations are slightly higher than the Henan glass, their concentrations show a certain degree of overlap compared with m-Na-Al glass discovered in India and Thailand. Based on the proportions of K_2O, CaO, MgO and Al_2O_3, there seem to be two different sources of raw materials used for Guangxi and Henan glasses. The variation of Al_2O_3 and K_2O concentrations for Henan glass may indicate the use of a more variable reh source compared with that used for the Guangxi glass. Guangxi glass also shows higher

MgO concentrations which represents a different reh source to that used for the Henan glass. However, two outliers amongst the Henan glass also show higher MgO proportions, so it could either be a different selection of reh source or the influence of the colourant and opacifier, since only these two samples were opaque black. Both opaque black glass beads show higher levels of FeO and MgO, possibly derived from a source of ferromagnesian minerals (e.g., olivine, pyroxene, amphibole, and biotite). Iron and magnesium cations are essential chemical components in ferromagnesian minerals. Although both Guangxi and Henan m-Na-Al glasses show certain levels of overlap with m-Na-Al glasses discovered in India and Thailand, it is difficult to determine the origin of the m-Na-Al in Guangxi and Henan through major element analysis. The rare earth element analysis of Guangxi and Henan m-Na-Al glasses can be viewed in Additional file 1: Rare earth element analysis.

Dussubieux et al. [30] summarised 5 types of m-Na-Al by comparing the concentrations of U, Ba, Zr and Sr, but only Type 1 and Type 3 appeared since the mid first millennium BC, which matches the date of the m-Na-Al glass beads analysed in this study. Figure 6 shows that the U, Ba, Zr and Sr concentrations in Guangxi glass beads are similar to m-Na-Al-3 glass. The average Sr level in Henan m-Na-Al glass is slightly higher than the m-Na-Al-1 glass, yet a certain degree of overlap can still be observed. The variations of the other three trace elements in Henan glass are better correlated with m-Na-Al-1 glass. Considering the large variations of elemental proportions in m-Na-Al-1 glass, Henan m-Na-Al glass

Fig. 5 a Al_2O_3-CaO and **b** MgO-K_2O concentrations (oxide%) for m-Na-Al glasses from Guangxi, Henan and other regions in South and Southeast Asia. Published data of m-Na-Al glass can be found in Additional file 2: Published data [29]

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Fig. 6 a U–Zr and **b** Ba-Sr concentrations (ppm) for Guangxi and Henan glasses. Average concentrations of Sr, Zr, Ba and U (ppm) with standard deviations of m-Na-Al-1 and m-Na-Al-3 glasses are referenced from [30]
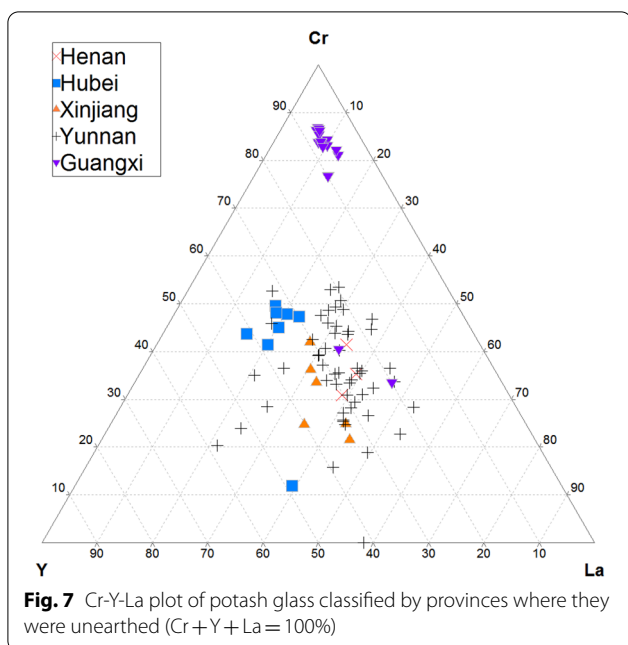
is close to m-Na-Al-1 glass. The comparison of other major and trace elements was listed in Additional file 1: Table A.6. The m-Na-Al-1 glass occurs at sites of south India and Sri Lanka dating from the 4th century BC to 5th century AD. m-Na-Al-1 glass was also found at contemporary or later Southeast Asian Sites. Furnaces with blocks of m-Na-A-1 raw glass discovered at the site of Giribawa, Sri Lanka indicates that this type of glass was likely manufactured there [30]. The m-Na-Al-3 glass is absent from south India and Sri Lanka. m-Na-Al-3 glass products have been found in Thailand, Cambodia and southern Vietnam [45]. High concentrations of raw glass and artefacts of m-Na-Al-3 glass were discovered at Khao Sam Kaeo, located in the Upper Thai-Malay Peninsula, suggesting a secondary glass producing centre located, if not at this site, then at least in the vicinity [30]. As summarized, the Ba, Zr and Sr concentrations for m-Na-Al-1 glass show large variations. The major elements such as CaO, Al_2O_3, MgO and K_2O and trace elements such as Ti, Zr, La and Cr in Henan glass also show variable concentrations. These all may indicate the less refined selection of raw materials for m-Na-Al-1 glass compared with m-Na-Al-3 glass.

High potassium group

The second group is identified as potash glass which used mineral saltpetre as the flux [46]. Eighty-seven potash glass beads were analysed in this study, including five colourless glass beads, twenty-nine blue glass beads with elevated CuO and CoO concentrations, five opaque yellow glass beads with elevated PbO and SnO_2 concentrations, fourteen purple glass beads with elevated MnO

concentration, twenty-one turquoise glass beads with elevated CuO concentration, three opaque red glass beads most likely due to the metallic copper nanoparticles (Cu^0) given the high copper, and eleven dark blue glass beads with elevated CuO and MnO concentrations. Eye bead 5.39316 shows the highest Ba concentration (> 35000 ppm), which was intentionally added rather than impurities. Barium is an opacifier commonly detected in Chinese lead-barium glass [47], but this eye bead does not contain a high level of Pb. The Barium might have been added during the secondary production to opacify this potash glass eye bead. As for glass beads with a high level of MnO, their Ba proportions range between 8000-10000 ppm. This is probably due to the use of Romanèchite ($(Ba,H_2O)_2(Mn^{4+},Mn^{3+})_5O_{10}$).

When characterizing the raw material of the sand source in glass manufacture, a combination of Ti, Zr, La, Y, and Cr shows the greatest variation between different regions [48–52]. This is due not only to their regional variability, but also to the fact that all five are refractory and non-volatile, and their inter-element ratios are unaffected by the high temperatures involved in either manufacture or subsequent reprocessing. The variation in these five trace elements is most likely due to different sand raw materials, rather than differential fractionation of the elements during glass formation. Distinct groupings of glass can be made based on combinations of elements such as Zr-Ti [53], Zr-Ti-Cr-La [54–56] and Zr-Sr-Ba [57–60]. In most cases, they are unrelated to any (de)colouring agents that may have been purposefully added to the glass batch. Figure 7 shows the Cr-Y-La plot of potash glass classified by provinces where they

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Fig. 7 Cr-Y-La plot of potash glass classified by provinces where they were unearthed (Cr + Y + La = 100%)

were unearthed. The potash glass samples can be divided into two sub-groups. Most Guangxi potash glass samples show higher concentrations of Cr, except for two Guangxi samples clustered with the rest of the potash glass beads unearthed from the other four provinces. Compared with Guangxi glass samples, the potash beads from the other four provinces show a relatively large variation of Cr, Y and La concentrations as shown in Fig. 7. Based on the Cr, Y and La concentrations, at least two different silica sources were used to produce these potash glass beads. Thus, we classified potash glasses into two

groups: Potash-1 glass from Henan, Hubei, Xinjiang and Yunnan; Potash-3 glass from Guangxi.

As the sources of m-Na-Al-1 and m-Na-Al-3 glasses are relatively clearer, it is, therefore, plausible to use the concentrations of Zr, Ti, Cr and La to test if there was any connection of the sand sources for potash glass and m-Na-Al glasses. Figure 8a presents Cr-La-Zr concentrations of two types of potash glasses and two types of m-Na-Al glasses as described above. To estimate the distribution of each group of glass, we used a multivariate Kernel Density Estimation plot as shown in Fig. 8b. Compared with Fig. 8a, four types of glass can be better differentiated by using KDE. The distribution shapes of Henan m-Na-Al-1 glass and Potash-1 glass show a linear relationship, although the overlap between the two groups is not observed. This indicates that their Zr:La:Cr ratios follow the same pattern, suggesting their silica sources are relatively close. Only eight samples from Guangxi analysed in this case were classified as m-Na-Al-3 glass. Ideally, the larger sample size will contribute to estimate a relatively accurate KDE distribution. Still, we can notice that the distribution of Guangxi m-Na-Al-3 glass is close to Guangxi Potash-3 glass. It needs to be aware that KDE is not sensitive to outliers. Two samples labelled as potash-3 glass which show similar trace element compositions as potash-1 glass were not observed in the KDE plot (same to Fig. 9).

Using ratios of trace elements can eliminate the dilution effect caused by other components in glass, such as colourant and opacifier additions. To test the similarities of the silica sources used in m-Na-Al and potash glasses, we performed 3D Kernel Density Estimation on four variables (Zr-Ti-Cr-Y and Zr-Ti-Cr-Y) in tetrahedron
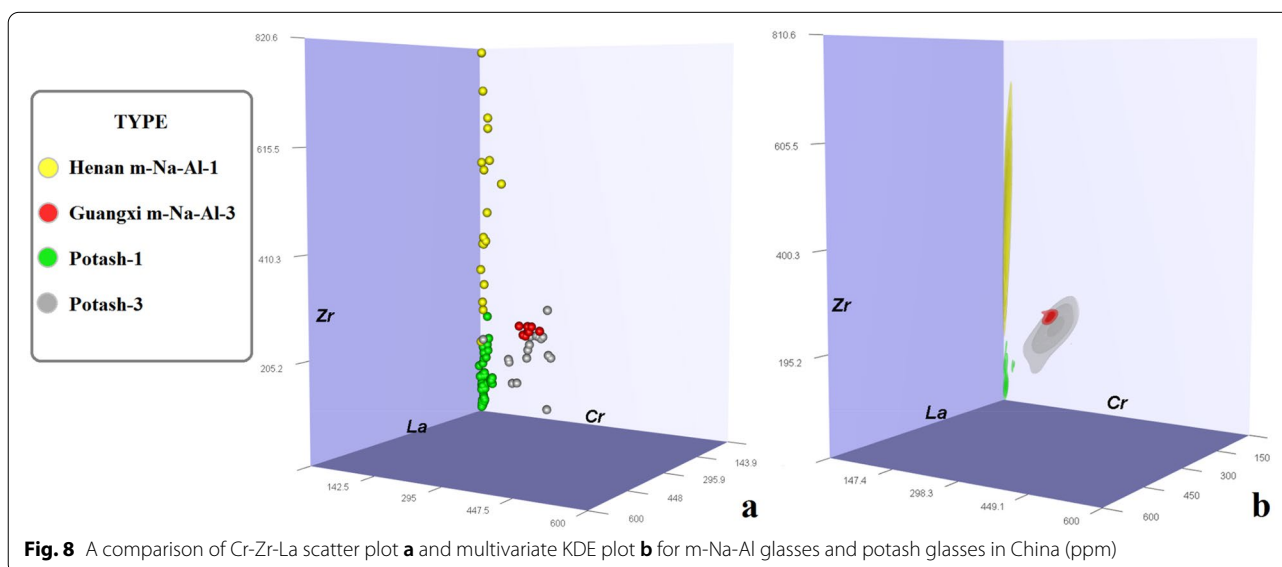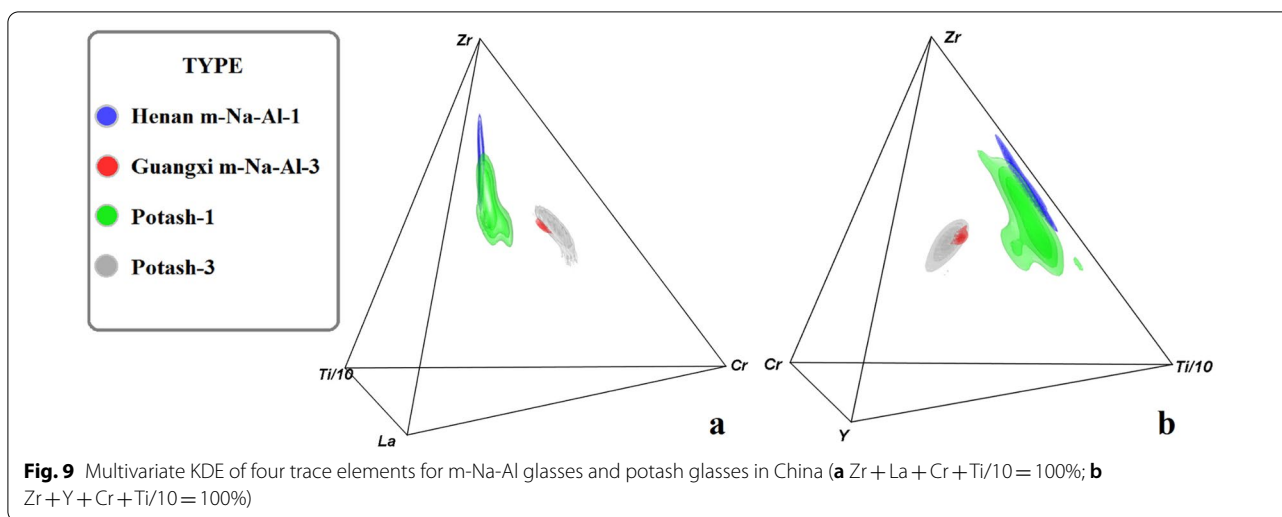

Fig. 8 A comparison of Cr-Zr-La scatter plot **a** and multivariate KDE plot **b** for m-Na-Al glasses and potash glasses in China (ppm)

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Fig. 9 Multivariate KDE of four trace elements for m-Na-Al glasses and potash glasses in China (**a** Zr + La + Cr + Ti/10 = 100%; **b** Zr + Y + Cr + Ti/10 = 100%)

plots (Fig. 9). The full codes for Fig. 8 and Fig. 9 are presented in Additional file 1: Code for KDE plot on three variables and four variables. The Ti concentration is divided by 10, as its concentration is much higher than the other three trace elements. Directly plotting Ti concentrations in the tetrahedron graph will cause the points to be biased towards the Ti axis, which makes it impossible to differentiate each assemblage. Guangxi m-Na-Al-3 and Henan m-Na-Al-1 glasses can still be successfully distinguished by using this KDE tetrahedron plot. The potash-3 glass unearthed in Guangxi shows different silica sources compared with the potash-1 glass unearthed from other regions. The relatively close variation of four trace elements in m-Na-Al-3 glass and most potash glasses unearthed in Guangxi indicates their silica sources are geologically close. This correlates with the finding that both potash and m-Na-Al-3 glasses were discovered at the site of Khao Sam Kaeo [20]. The sample size for potash-1 glass is larger than m-Na-Al-1, thus, potash-1 shows relatively bigger variations of four trace elements in this tetrahedron plot. Still, silica sources of m-Na-Al-1 glass unearthed in Henan and the rest of the potash glasses from other regions are geologically close, as a certain degree of overlap can be observed both in Ti-Cr-Zr-La and Ti-Cr-Zr-Y KDE plot. In addition, they are distributed in the same direction in the tetrahedral diagram. In this case, some glass samples from Yunnan are weathered with over 80% SiO_2 due to the flux (K_2O) loss after the data normalization. Still, ratios between Zr, Ti, Cr, Y and La are not affected and can still be plotted to trace the silica source.

In order to further estimate the similarity between different groups, Maximum Mean Discrepancy (MMD) and hypothesis testing were applied. The application of KDE allows to visualize the distribution shape of each assemblage, while MMD measure the 'mean distance' between

Table 1 Ti -Cr-Zr-La-Y Hypothesis testing results between each pair of groups (Zr + Y + La + Cr + Ti = 100%)

	1 Potash-1 glass	2 Potash-3 glass	3 m-Na-Al-1 glass
1	–	Reject	Accept
2	Reject	–	Reject
3	Accept	Reject	–

two assemblages when they are mapped to a high-dimension feature space. Table 1 shows Ti -Cr-Zr-La-Y hypothesis testing results between every two groups (full code in Additional file 1: Code for MMD hypothesis test). We did not test Guangxi m-Na-Al-3 glass due to the small sample size. The null hypothesis between Henan m-Na-Al-1 glass and potash-1 glass is accepted. The null hypotheses were rejected for potash-3 glasses with the other two groups. This further confirms what has been observed from the two KDE plots, i.e., that potash glasses from Henan, Yunnan, Hubei and Xinjiang and Henan m-Na-Al-1 glasses used similar silica sources, which were different from most potash glasses in Guangxi.

Discussion
Glass recipe and primary production
According to the previous research, potash glass gradually replaced m-Na-Al 3 glass at Khao Sam Kaeo starting from the 3rd–2nd centuries AD and extending into the 4th century AD [21]. Then, it became the dominant glass type at many sites in Southeast Asia [61, 62]. Moreover, although potash glass and m-Na-Al glass are the most frequent forms of glass in Southeast Asia, they are rarely encountered together in the same site [29, 62]. However, two sites (i.e. Jiuzhiling Site and Sigma European Industrial Park) analysed in this study both unearthed

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m-Na-Al glass and potash glass, and two sites were dated to 200 BC–200 AD. Type 1 and 3 m-Na-Al glasses were identified respectively in these two sites. According to trace element analysis, the silica sources for producing potash glasses unearthed from two sites are also close to two types of m-Na-Al glasses respectively.

There is plenty of research about the classification of glasses in South/Southeast Asia based on the major and trace element analysis. Potash glass was divided into three sub-types according to the level of CaO and Al_2O_3 [29], yet the primary production of these three types remain unknown. We suggest that three sub-types of potash glass indicate a choice of glass recipe rather than anything related to their primary production centre. In other words, three sub-types of potash glass can be produced in one primary production site, or one type of potash glass can be produced in different primary production sites. This consumption matches with the potash glass beads analysed in this case. For instance, m-K-Al glass beads were both identified at Muyi and Jiuzhiling Sites, yet their silica sources were completely different according to the trace element analysis, suggesting they were produced in different primary production sites; m-K-Al and m-K-Ca-Al glass beads were identified at Jiuzhiling Site, and their highly correlated silica sources indicate they might have been produced at the same primary production site. In this study, we notice that glasses with similar silica sources are not limited to the sub-types of potash glass, and m-Na-Al glass and potash glass might have also shared a similar silica source. It is more likely that the changes of different types of glasses at different times and exchange networks in Southeast Asia reflect changes of glass recipes over time, and they might still be produced in the same or close primary production according to their highly correlated silica sources.

Made in China?

There has long been debate whether the Chinese could have produced glass during the Warring States period and the Han Dynasty. Here, this question should be refined as to whether the Chinese could produce primary raw glass or secondary finished glass products. Various types of glass have been discovered in China, yet, no primary or secondary glass production sites have been found for any of the glass types of this period. Glass ear pendants (Fig. 4) have been commonly discovered in different regions in China during the Han Dynasty, which clearly shows uniqueness in the aesthetics and function. This provides evidence that Chinese artisans may have mastered the skill of producing secondary glass. Henderson et al. [31] argue that it is very likely that primary potash glass was made in China, and the flux saltpetre used to produce potash glass occurs in southeast China.

Saltpetre was used as a medicine during the Western Han period [63]. However, none of the other Chinese vitreous materials ever used saltpetre or reh as a flux during the Han Dynasty. The earliest documentation of using saltpetre in a glass recipe dated to the Tang Dynasty (AD 618–907). 'Liu Li'(glass) documented in 'Jin Hua Yu Ye Elixir' 金华玉液大丹 (anonymous) during the Tang Dynasty was a mixture of 250 g lead oxide (PbO), 100 g saltpetre (KNO_3) and 100 g borax ($Na_2B_4O_7 \cdot 10H_2O$). This formula fits the $PbO-Na_2O-K_2O$ glass during the Tang Dynasty. m-Na-Al glass is rare compared with potash glass unearthed in China during the Warring States and the Han period, and Henderson et al. [31] suggest the primary production for this type of glass is certainly outside China. A few clues indicate sources of m-Na-Al-1 and m-Na-Al-3 glasses based on Dussubieux [30] and Lankton et al. [45] previous research. The trace element analysis in this study surprisingly shows that potash glass can be divided into two groups and they correlate with m-Na-Al-1 and m-Na-Al-3 glasses respectively. Although we cannot fully rule out the possibility that potash glass could be produced in southeast China, it is more reasonable to believe potash glasses were produced somewhere close to where the m-Na-Al glasses were produced, as their sand sources were geochemically similar.

Transmission routes of monochrome drawn beads

As discussed in the result section, the chemical composition fingerprint of m-Na-Al glass found in Henan in this research is highly consistent with the m-Na-Al-1 raw glass at the site of Giribawa, Sri Lanka, and the potash glass beads unearthed from Xinjiang, Henan, Yunnan and Hubei show an identical silica source with the m-Na-Al glass in Henan. The isotopic composition of strontium and neodymium of the m-Na-Al 1 glass further supports the archaeological evidence that this type of glass was made in Sri Lanka and south-eastern India [64]. There is no clear archaeological evidence for the primary production of the potash glass. Yet such a correlation suggests the raw glass for these potash glasses may have been produced somewhere in southern India or close to Sri Lanka, due to their similar geochemical fingerprints. For example, the Arikamedu Site in southeastern India as a secondary production centre for monochrome drawn beads unearthed a large quantity of potash glass [14, 65–67], and potentially primary glass production may have taken place nearby. Emperor Han *Wudi* 汉武帝 (156–87 BC), the 7th emperor of the Han Dynasty, commanded officer *Zhang Qian* 张骞 to investigate the past trade routes between China, the Middle East and Europe. *Zhang Qian's* two journeys in 139 BC and 119 BC started the prosperous age of commodity circulation along the Northwest (Desert) Silk Road. Protectorate

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of the Western Regions 西域都护府 which was set up by the Han Empire in Xinjiang was to guard the border and coordinate the contradictions and disputes between the countries of the neighbouring regions, to secure the Silk Road trade. Thus, potash glass and m-Na-Al monochrome drawn glass beads in Xinjiang and Henan could have been traded from Sri Lanka or southern India along the North Silk Road during the West Han period.

As documented in *Shiji- Biographies of Dayuan*史记-大宛列传, when *Zhang Qian* arrived in Bactria (current Afghanistan) in 122 BC, he noticed that Shu Cloth (made by bamboo fibre) and Bamboo stick produced in Shu State (current Sichuan) were circulated here. The local people told him that these products were traded by merchants from Sindu, and Sindu merchants imported these products from Shu merchants. There was a potential trade route from Sichuan to India via Yunnan controlled by minorities in Yunnan (i.e. *Dian*, *Gouding*, *Ailao*, etc.), and *Zhang Qian* persuaded Emperor *Wudi* to conquer these minorities, to take control of the Shu-Sindu road (Southwest Silk Road). Yet, after over ten years of the battle between the Han Empire and minorities in Yunnan, *Wudi* only conquered the *Dian* people. Potash glass samples in Yunnan were unearthed from *Dian* (Shi Zhai Shan) and *Gouding* (Mu Yi) burial sites as introduced, and they were likely traded from Sri Lanka or southern India along the Southwest Silk Road. It needs to be reemphasized that the Southwest Silk Road was a complex trade network when compared to the North Silk Road, with a strong link to the Maritime Silk Road. Potash glass either could be traded from Sindu to Yunnan via Myanmar or primarily shipped to Southeast Asia along the Maritime Silk Road and then traded to Yunnan through *Jinsang-Phong Châu* Road or *Yongchang-Thande River* Road. Potash glass samples from Jiang Ling Jiu Dian Site, including two glass tubes and two eye beads, are dated to the Warring States period. There are limited historical records that we can use to deduce how these glasses were traded from Sri Lanka or southern India to the Chu State. As the Chu State was close to the Shu State, these glasses may have been traded through the Shu-Sindu Road.

The chemical composition of m-Na-Al glass in Guangxi is close to the m-Na-Al-3 glass found in Khao Sam Kaeo. Except for two potash glass beads that show a southern Indian origin, the rest of the m-Na-Al and potash glass in Guangxi show close silica sources. However, Khao Sam Kaeo might not be the primary glass production centre for m-Na-Al-3 glass and potash glass. The unearthed raw glass and finished products without any archaeological evidence of primary glass furnace suggest Khao Sam Kaeo might be a port as an exchange network along the Maritime Silk Road. Lankton et al. [45] and Dussubieux [20] suggested that m-Na-Al-3 glass was quite likely manufactured in northeastern India, such as Kopia, eastern Uttar Pradesh. However, The isotopic composition of strontium and neodymium of the raw material available at the site differs from that of the glass, indicating that the raw glass was imported to the site to be transformed into finished products [64]. Fifty-nine glass samples in this study are from Xinjiang and Yunnan, yet, no glass made in northeastern India was found in Yunnan and Xinjiang, despite these two regions being geologically closer to northeastern Indian than Guangxi. There are quite a few sites in Southeast Asia that unearthed potash and m-Na-Al glasses with similar chemical composition as discovered in Khao Sam Kaeo, such as Phu Khao Thong as a secondary glass production centre, Khlong Thorn on the western coast of the Thai/Malay peninsula, Samon Valley, Myanmar, the southern Sa Huynh site of Giong Ca, Vietnam (possible primary and secondary production site), Hitam Cave in Sarawak, and the Tabon Cave complex in Palawan, etc. [45]. As the glass trade between India and Thailand lasted for centuries, it should come as no surprise to find evidence of primary glass production in Southeast Asia (potentially Thailand or Myanmar) that produced m-Na-Al-3 glass or potash glass. Although we cannot rule out the possibility that the m-Na-Al glass and most of the potash glass in Guangxi were from northeastern India, it is more likely their primary glasses were produced in Southeast Asia. This hypothesis is further supported by the lead isotope analysis of the m-Na-Al-3 glass coloured with lead-containing pigments, which indicates two possible provenances for the lead: Thailand and north-western South Asia [64]. As mentioned, *Hepu* was one of the trade ports as the starting point of the Maritime Silk Road. Jiuzhiling Site is located 4 km south of *Hepu* port, it is quite certain that glasses from this site were traded through the Maritime Silk Road.

Conclusion
This paper focuses on the study of glasses in different provinces in China through major and trace element analyses. Kernel Density Estimation and Maximum Mean Discrepancy as two strong tools showed merits in trace element cluster analysis. The combination of tetrahedron plot and KDE is one of the novelties of this research. It not only reveal the interrelationship between four trace elements that cannot be completed by biplots, but also estimates the distribution shape of each assemblage for comparison purpose. According to the major element analysis, glasses in this study can be classified as m-Na-Al glass and potash glass. According to trace elements analysis, two different silica sources were used to produce these glasses. The m-Na-Al glass from Henan and potash glass from southwest, northwest and central plains of China were probably produced in southern India or Sri

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Lanka and traded in China through the North Silk and Southwest Silk Roads during the Han period. The m-Na-Al glass and most of the potash glass from Guangxi show similar silica sources, and they were likely produced in northern India or Southeast Asia and traded here through the Maritime Silk Road. Combining trace element analysis and historical documents, we conclude that North, Southwest and Maritime Roads all play roles in trading potash and m-Na-Al glasses. Future research shoud more rely on the isotopic analysis of glass findings in China. LA-MC-ICP-MS is also a virtually non-destructive technique for isotopic analysis with excellent sensitivity, analytical precision and accuracy. The Nd and Hf isotopic analyses will reveal more information of the silica source [68, 69], specifically, if a single silica source was both used to produce m-Na-Al and potash glasses. The Sr isotopic analysis shows merit to understand the source of lime of the glass [69, 70]. For example, if the lime source for potash glass was contributed by the shell fragments in beach sand, then the $^{87}Sr/^{86}Sr$ ratios should be close to the modern marine level. The research of isotopic analysis and archaeological excavation of the primary glass production will reveal more evidence of glass trade in China, South and Southeast Asia.

Abbreviations
LA-ICP-MS: Laser ablation inductively coupled plasma mass spectrometry; KDE: Kernel Density Estimation; MMD: Maximum mean discrepancy.

Supplementary Information
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Additional file 1. Additional information on samples and methods.

Additional file 2. Data analysed in this study and published data used for comparison.

Availability of data and materials
All data generated or analysed during this study are included in this published article [and its Additional files].

Declarations

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