

Chemical composition and provenance of Chinese porcelain shards recovered from Old Goa, West Coast of India

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Abstract

During recent archaeological explorations at old Goa, west coast of India, twenty three Chinese porcelain shards of the Ming (Middle to late 16th century), Qing (17th century) and late Qing period (late 17th century) have been recovered. In order to understand the nature and source of raw material and kilns, these shards were analysed for major elements with X-ray fluorescence (XRF), trace and rare earth elements by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). The analysis suggests that porcelain shards are siliceous in nature ($\text{SiO}_2 \sim 70\%$) and contain high Al_2O_3 (21.6%), Rb (388 ppm) and Ba (160 ppm) but have low Sr (48 ppm). This composition suggests that the raw materials used for producing porcelain were silica, kaolinite and sericite which are characteristics of porcelains manufactured in Southern China. Comparatively, high Al_2O_3 (kaolinite) content in porcelains of the Qing Dynasty suggest improvement of quality, particularly mechanical strength, of Jingdezhen porcelain. In general, major element composition, trace metals, total rare earth elements ($\sum\text{REE-67}$ ppm) and their chondrite - normalised pattern of the Ming, Qing and late Qing period are nearly similar and appears to be made of identical raw materials.

Keywords: Chinese porcelain, Jingdezhen kiln, Maritime trade, Ming and Qing period, Old Goa, South China, ICP-MS and XRF analysis

Introduction

In archaeology, pottery plays an important role in reconstructing the history of human civilisation. The nature and type of pottery is determined by the chemical composition of the clay and the way it was prepared; the temperature at which it was fired; and the type of glazes used. Comparatively, ceramics are more durable than earthen pottery and never disintegrate either buried in subsoil or underwater, unless low fired, therefore ceramics are considered the best indicators of contacts both within and outside the country. Similar to ceramics, lithics are more durable and provide evidence for interchange. Other materials such as shell have also been identified as indicators of long distance interchange between Europe, West Asia and Africa.

The history of pottery making in China goes back to the Neolithic period. In the second half of 2nd century AD, porcelain was initially produced in the Yue kilns and its export started from the 7th century AD onwards to many parts of the world which gradually helped to establish trade and cultural contacts with China (Li 1998; Lin 1999; and Hongjiao et al., 2012). Moreover, travellers have left accounts of Chinese ceramics after visiting China. Suleiman (851 AD), the Arab merchant, visited China and observed manufacturing of porcelain made of fine clay at Guangzhou (Shen, 1996). Al-Biruni (973-1048 AD), detailed how the Chinese potters took care in the preparation and maturing of clay (Lane, 1950). Al-Biruni has further delineated the trade contacts between Africa and some part of India and China (Sastri, 1939). Marco Polo (1254-1324 AD) visited a porcelain factory in China in 1280 AD and commented that Chinese porcelain was exported all over the world and Indian traders were active in Quanzhou between 1280 and early 1290 (Christie, 1998).

The blue and white porcelain was first produced during the Yuan period (1279-1368 AD) and new decorative motifs and shapes were adopted. The Yuan ceramics provided a thread of tradition and innovation in the entire ceramic history of China (Valenstein 1989). The blue and white porcelain reached its zenith during the Ming (1368-1644 AD) and Qing dynasties (1644-1911 AD). During the Ming Dynasty perfection in the blue and white wares was attained and changes were made in style of decorative motifs. Jingdezhen kiln was the main centre of production of porcelain. Ming porcelain was an indelible high water mark in the history of world art (Savage, 1961). The Majority of decorative elements and symbols used in decorating Ming porcelain have originated from Chinese folklore, tradition, mythology, religious significance and history. Patterns of general decorations are hardly ever used. The qualities of the Ming blue and white porcelains were indisputably superior to those of all the other periods (Lion-Goldschmidt, 1978). In the maritime trade, Chinese porcelain was exported to many countries on overseas trade networks from the 7th-8th centuries and this trade increased substantially from the 13th century onwards to the Middle East, East Asia and Europe

along the Indo-Chinese coast with ships sailing through the Malacca Straits and into the Indian Ocean. From there, traders delivered ceramics to markets in Sri Lanka and India, throughout the Persian Gulf region and along the East African coast. Besides other cargo, Chinese porcelain was the main consignment on ships and this has been confirmed from the exploration of shipwrecks in the seas around Southeast Asia. For instance, the Belitung shipwreck of 826 AD is the earliest known wreck on the Maritime Silk Route off Sumatra, Indonesia, carrying Tang Dynasty ceramics (618-907 AD) (Flecker, 2001, 2008 and Guy, 2010). Thousands of Chinese ceramics have been recovered from the *Intan*, a 10th century shipwreck off the Java Sea (Flecker, 2002). Moreover, Chinese porcelain has been recovered from several shipwrecks of later periods, where the ceramics were carried either as a part of cargo or used daily onboard. In the Indian context, Chinese ceramics has been recovered from land and shipwreck sites datable to the post 10th century AD onwards. From the medieval period onwards Chinese porcelain became more common in almost every site in India and there are hardly any sites without it (Muhammed, 1994).

The process of development of porcelain in north and south China is closely bound with the use of different raw materials. Rich deposits of porcelain stones (porcelain stone is a natural stone/rock and its chemical composition is nearly similar to porcelain) in south China were used for manufacturing of the characteristic siliceous southern Chinese porcelain wares. In the case of northern Chinese porcelain, different types of clay were found which are characterised by high Al content (Guo, 1987). It has been observed that the composition of ceramics is based on the nature, quality and quantity of raw materials available in the region. The nature, types and provenance of raw material, the production processes such as washing and mixing of raw material, and period all influence the chemical composition of Chinese porcelain (Yin et al., 2000; Wu et al., 2000; Li et al., 2003). The elemental concentration in porcelains can be achieved by the most common analytical techniques: namely X-ray fluorescence (XRF), energy dispersive X-ray Fluorescence (EDXRF), neutron activation analysis (NAA), electron probe micro analysis (EPMA) and proton-induced X-ray emission (PIXE) (Li et al., 2000; Cheng et al., 2002; Li et al., 2003; 2005; Leung et al., 2000). The major element composition of the raw material used in porcelain may not vary much, whereas trace element concentration vary considerably and those can be analysed on Inductively Coupled Plasma - Mass Spectrometer (ICP-MS) because of the excellent accuracy, precision and detection limits of this technique (Li et al., 2003; Li et al., 2005). The ICP-MS has capability to analyse over 40 elements with very small sample weight (10-50 mg) within 3 to 4 minutes. In the Indian sub-continent, large quantities of Chinese porcelain, both shards and complete specimens, have been recovered during archaeological studies; however no attempt has been made in the past to understand

their chemical composition, nature of raw materials and provenance based on chemical composition. Therefore, for the first time an attempt has been made to analyse major elements with XRF, and trace and rare earth elements on ICP-MS of twenty three Chinese porcelain shards collected from Old Goa during recent exploration, mainly to understand the raw materials used in manufacturing and their provenance.

Previous work

Chinese ceramics of different periods have been reported from different parts of the world as well as in India. With the development of tools and techniques, diverse methods have been adopted by the researchers to understand the composition of clay, clay sources and manufacturing methods of the Chinese ceramics more precisely. Similarly, historians and archaeologists of China, India and other countries have studied the Chinese ceramics from their perspectives. In order to understand major element oxides and trace element concentration of blue and white Chinese Jingdezhen porcelains of the Yuan, Qing and Ming dynasties, energy-dispersive x-ray fluorescence (EDXRF) analysis was carried out and the data were subjected to multivariate statistical analysis and different compositional patterns of different period have been observed (Wu et al., 2000). Proton induced X-ray emission (PIXE) method was followed to understand the chemical composition of porcelain fragments from Jingdezhen in Jiangxi, Dehua in Fujian and Xing, Ding and Cizou in Hebei (Leung and Luo, 2000; Cheng et al., 2002). The Song period ceramics and Egyptian pottery were examined for trace and rare earth elements with ICP-MS to understand the raw material used for manufacturing the ceramics (Mallory-Greenough et al., 1998; Gu et al., 2000; Li et al., 2003; 2005; Ma et al., 2012). Instrumental Neutron activation analysis (INAA) was carried out to study the trace element concentration of blue and white Chinese Porcelain of the Ming Dynasty (Li et al., 2000; Dias et al., 2013).

In India, Chinese ceramics have been reported from 13th and 14th centuries AD onwards and their period was determined based on the typology and designs of the shards and on the history of the site. Thus, in the Indian subcontinent, this is the first attempt to undertake chemical analysis of Chinese ceramics. Under this effort chemical analysis of ceramics were carried out by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and X-ray Florescence (XRF) analysis to understand the source of raw material and kiln. Prior to this study, data on chemical analysis of Chinese ceramics was not available in the Indian Subcontinent (Muhammed, 1994; Pande, 2014; Sila Tripathi et al., 2014; Sila Tripathi et al., 2011).

Chinese ceramic Trade in India

Chinese porcelains of different periods have been found in explorations and excavations in coastal and hinterland sites of India. As regard to the earliest date of the Chinese ceramics in India, strangely nothing is known before the tenth century AD. The evidence shows that Chinese porcelain which was shipped to Sri Lanka, the Persian Gulf, Egypt and the African Coast bypassed the south Indian coast. The recent excavations at Mantai and other sites of Sri Lanka have yielded Chinese ceramic of the Tang Dynasty (618-906 AD), and later periods (Jayasingha, 2006; Prematilleke, 1990). Further, Carswell (1976, 1978) has suggested that the Chinese and Islamic pottery collected from Mantai in Sri Lanka would be datable to between ninth and eleventh centuries. The Chinese ceramics of Mantai have a close affinity with the findings at Siraf on the Persian Gulf and Sohan on the Oman coast (Karashima, 2004). The excavations at Siraf have brought to light plentiful Chinese ceramics (Hourani, 1995; Rougeulle, 1996). As mentioned above, the Chinese ceramics started coming to India from the 10th century onwards, but tangible evidence indicates that maritime trade contact between India and China continued from the Ming Dynasty (1368-1644 AD) onwards (Bushell, 1904.) The first blue and white porcelain was imported into India by the rulers of Bijapur, then the Nawab of Arcot (Sila Tripathi et al., 2011). Karashima (2004) and his colleagues had undertaken exploration along south India and unearthed Chinese porcelain of the 11th and 12th centuries at Gangaikondacholapuram in Tamil Nadu. Chinese celadon and porcelain of the 13th and 14th centuries have been recorded at Periyapattinam in Tamil Nadu and Ibn Battuta (1304-1368-9 AD), the traveller has referred to Periyapattinam port as Fattan (Karashima, and Kanazawa, 2002). Chinese celadon and blue and white porcelain of the Ming period (1368-1644 AD) has been collected from Devipattinam, the medieval Pandyan port of Tamil Nadu coast (Subbarayalu, 1996). Recently Chinese coins, Chinese porcelain, and Chinese celadon ware datable to the 12th to 14th centuries, including antiquities of different periods were found during dredging off Tangasseri coast in Kollam district of Kerala indicating the maritime contacts of China with the West coast of India (Rajendran, 2014). Ibn Battuta (Gibb, 1971; Smart, 1975) has mentioned about the incoming of Chinese porcelain to Delhi during the reign of Muhammad Bin Tughlaq (1324-1351 AD). In the 16th and 17th centuries, large quantity of Chinese porcelain was being imported to India as evidenced from the Mughal paintings; even some Chinese porcelain shards have Mughal inscriptions (Smart, 1975; Gray, 1964). This has been further corroborated by the exploration and excavation findings of Chinese porcelain at old Delhi region datable to the 14th century onwards (IAR 1961-62). Vasco-da-Gama, during his return trip to Lisboa, carried pieces of Chinese porcelain from India to present to King Manuel of Portugal (Gerritsen, 2009), then Chinese porcelain reached Europe (Calvao, 1999).

The import of Chinese porcelain increased three to four fold during the European rule in India and the places associated with the European regime have yielded more Chinese porcelain along with other pottery. The porcelain found from different parts of India has been identified on the basis of designs, stamp marks and associated findings and most of them have been published in various monographs, reports and volumes (Ghosh, 1989; Karashima, 2004, Sharma, 2015; Rajendran, 2014; Ray, 2013).

Old Goa was the capital of Goa during the Portuguese reign and an important port on the west coast of India in the 16th and 18th centuries. During this period the King of Portugal reserved the right on the monopoly of trade on all goods and articles such as ivory, Chinese porcelains, gold, slaves, including tobacco were imported (Fonseca, 1986; Mathew, 1990; Sila Tripathi et al, 2014). In order to locate maritime structures and other remains if any, a thorough inshore survey between the bank of the River Mandovi and the Church complex was conducted on foot because the area is full of shrubs and coconut groves (Fig. 1). During explorations a number of blue on white Chinese porcelain shards were collected from the area and they belong to bowls, cups, and dishes with varied designs and decorations on them which serve as denotation of Chinese culture, history or folklore. None of the pieces found in Old Goa is complete. However, porcelain fragments were found all over Old Goa region. After exploration, these shards were classified based on the available literature and experts, namely Noboru Karashima and Hanae Sasaki, who have extensively worked on the Chinese ceramics of the east coast of India, were consulted on the history of the shards including their probable dynasties, period and kiln. The collected shards are described in Table 1 and shown in Fig. 2 a-c. The shards were from the Jingdezhen kiln and datable to the 16th and 17th centuries belonging to the Ming and Qing Dynasties. Among them, one shard is of Kraak ware (Sila Tripathi et al., 2011). The high and middle quality Chinese blue and white ceramics typical of Kraak ware were manufactured at the Jingdezhen kiln as well as the Southeast coast of China during the late Ming Dynasty and exported to the European market (Harrison, 1979).

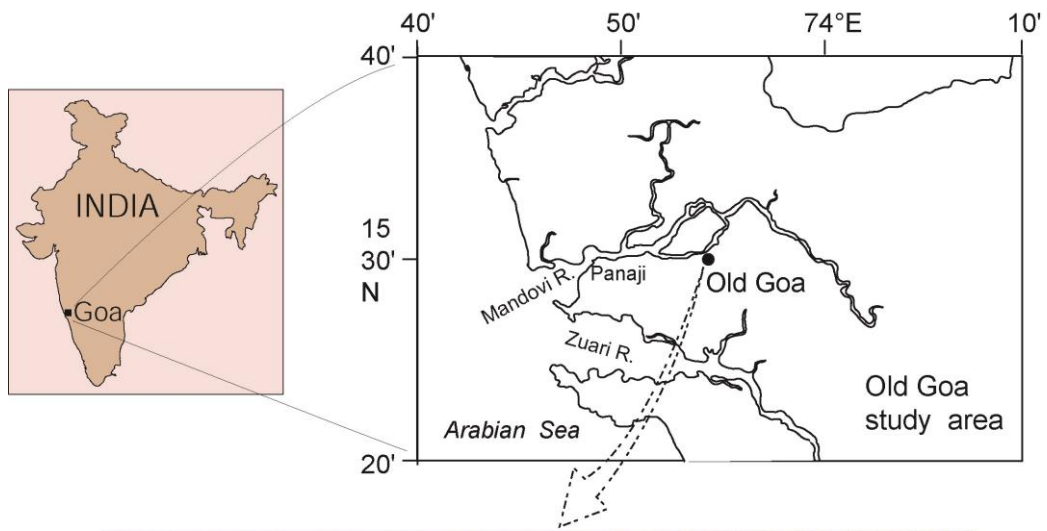


Fig. 1. Figure showing exploration area of Old Goa, Goa.

Table 1. Showing name of the Dynasty, Period and Kiln of Chinese ceramic shards.

Shard No	Dynasty	Period	Name of the Kiln	Description of Chinese ceramic shards
1	Ming	Middle to Late 16th century	Jingdezhen	Shard of a bowl, medium fabric and straight rim. A flower with leaves is decorated at intervals between two bands on the rim. A circular medallion design is depicted with spreading wings, probably an insect, with rays coming out from the body.
2	Ming (Jiajing Period)	Middle to Late 16th century (1522-1566 AD)	Jingdezhen	Base of a dish, thin fabric and fine glaze. Two deer (male and female) are looking at each other with playful passion and bordered by a bamboo fence. The base has two concentric lines with eight Chinese characters. Six characters denote the reign mark of emperor Chia Ching (Jiajing?) (1522-1566 CE) of the Ming Dynasty and two characters bear the mark of emperor Cheng Hua (1465 - 1487 CE)
3	Ming	Middle to Late 16th century	Jingdezhen	Base of a small cup with a ringed base. An under glaze lotus flower (a peony perhaps?) with leaves shown and bordered by a single concentric line. This type of 'Lotus Blossom' is known as Lien Hua.
4	Late Qing	17th century	Jingdezhen	Shard of a plate with foot ring and medium fabric. The coarse outline and wash design features the tip of a long leaf and flower stem along with three small leaves.
5	Ming	Middle to Late 16th century	Jingdezhen	Base of a dish with foot ring, thick fabric with a fine glaze. Varieties of plants and trees are decorated behind the hills, with three flags fastened on a bamboo. A band of creepers with leaves are decorated on the foot ring encircled by a band.
6	Qing (Kangxi Period)	Late 17th century	Jingdezhen	Base of a polychrome bowl with foot ring. A square mark at the base which is further subdivided into four smaller squares. Two concentric circles surround the mark.
7	Ming	Middle to Late 16th century	Jingdezhen	Base of a fine fabric bowl with foot ring. The mythical animal dominates the central decoration. Its flying wings and tail is also represented.
8	Ming	Middle to Late 16th century	Jingdezhen	Shard of a dish with thin fabric. Flower stems, leaves and grass roots decorates the outer cavetto while the central decoration is a flower/plant design surrounded by two blue concentric lines.

9	Late Qing	17th century	Jingdezhen	Thin fabric rim shard. On one side are freely-drawn rectangular lines surrounding a possible potter's mark, possibly one of the eight precious things mentioned by Fang-Sheng, a lozenge, a symbol of victory, which is encircled by two uneven concentric lines. It is Kraak ware
10	Late Qing	17th century	Jingdezhen	Shard of a dish. The outer cavetto is decorated with possibly floral scrolls in an unending style with wavy pattern.
11	Ming	Middle to Late 16th century	Jingdezhen	Base of a fine fabric bowl with foot ring. Floral design with leaves, buds and stem are at the center, surrounded by two concentric lines. An unidentified Chinese stamp mark is in the base.
12	Ming	Middle to Late 16th century	Jingdezhen	Rim shard of a bowl. The rim is foliated and has two small perforations which were used for rebating the broken shards with copper wire. 'Classic scroll design' is running on the inner side, while floral design on the outer rim. On the outer cavetto is a flying horse poised in a leap bordered by a circle.
13	Late Qing	17th century	Jingdezhen	Base of a bowl with footring. A running horse is depicted in a landscape with rocks and bushes. On the outer cavetto decorated with hills, flowers, bushes and straight horizontal lines. Four Chinese characters arranged in two columns, some characters are missing which could probably dated to the Chinese emperor Hsuan Te' reign (1426- 1435 CE) of the Ming Dynasty.
14	Late Qing	17th century	Jingdezhen	Base of a bowl with footring. The base has four Chinese characters, among them two letters resembling Chinese emperor Cheng Hua's mark (1465 - 1487 CE).
15	Qing	Late 17th century	Jingdezhen	Rim shard of a thin fabric dish. A landscape consisting of trees and bushes represent the central decoration. Full-grown flowers and stems are shown at intervals on the rim. Two leaves with stem are visible on the outer rim surface.
16	Ming	Middle to Late 16th century	Jingdezhen	Shard of a plate with footring. The central decoration consists of lotus flowers, stems and petals. The 'SHU' mark (a pair of books) is on the outer cavetto. This mark is one among the eight treasures of Buddhism.
17	Ming	Middle to Late 16th century	Jingdezhen	Base of a plate with footring. The central decoration consists of a flower in full blossom with petals and filled lines of hatching design. The 'Hua' mark on base denotes one of the eight treasures of Buddhism.
18	Ming	Middle to Late 16th century	Jingdezhen	Base of a bowl of medium fabric. Flowers and grasses are depicted in the center and encircled with two bands and dotted designs.

19	Ming	Middle to Late 16th century	Jingdezhen	Shard of a shallow bowl with a foliated rim and a grooved cavetto. Traces of leaves are the central decoration and encircled with two concentric lines. A thick band of wavy lines and thin lines are shown along with dots on the rim.
20	Ming	Middle to Late 16th century	Jingdezhen	Shard of a bowl. The central decoration consists of a flower with two shoots. On the outer cavetto flowers and leaves are spread all over the body. Two concentric lines are present on the upper side and at the ring base.
21	Late Qing	17th century	Jingdezhen	Shard of a bowl base. Four Chinese characters bordered by a concentric line at the base.
22	Ming	Middle to Late 16th century	Jingdezhen	Thin fabric fine glazed shard. Lotus flower with stems and leaves on inner surface denote 'Hua' means happy augury and one of the eight Buddhist emblems. The outer side symbol could be 'SHU,' meaning a pair of books and is also one of the eight precious things of Buddhism.
23	Ming	Middle to Late 16th century	Jingdezhen	Thin fabric fine glaze base of a bowl. A three-legged decorated basket is depicted at the center of the shard which is filled with fruits and leaves.

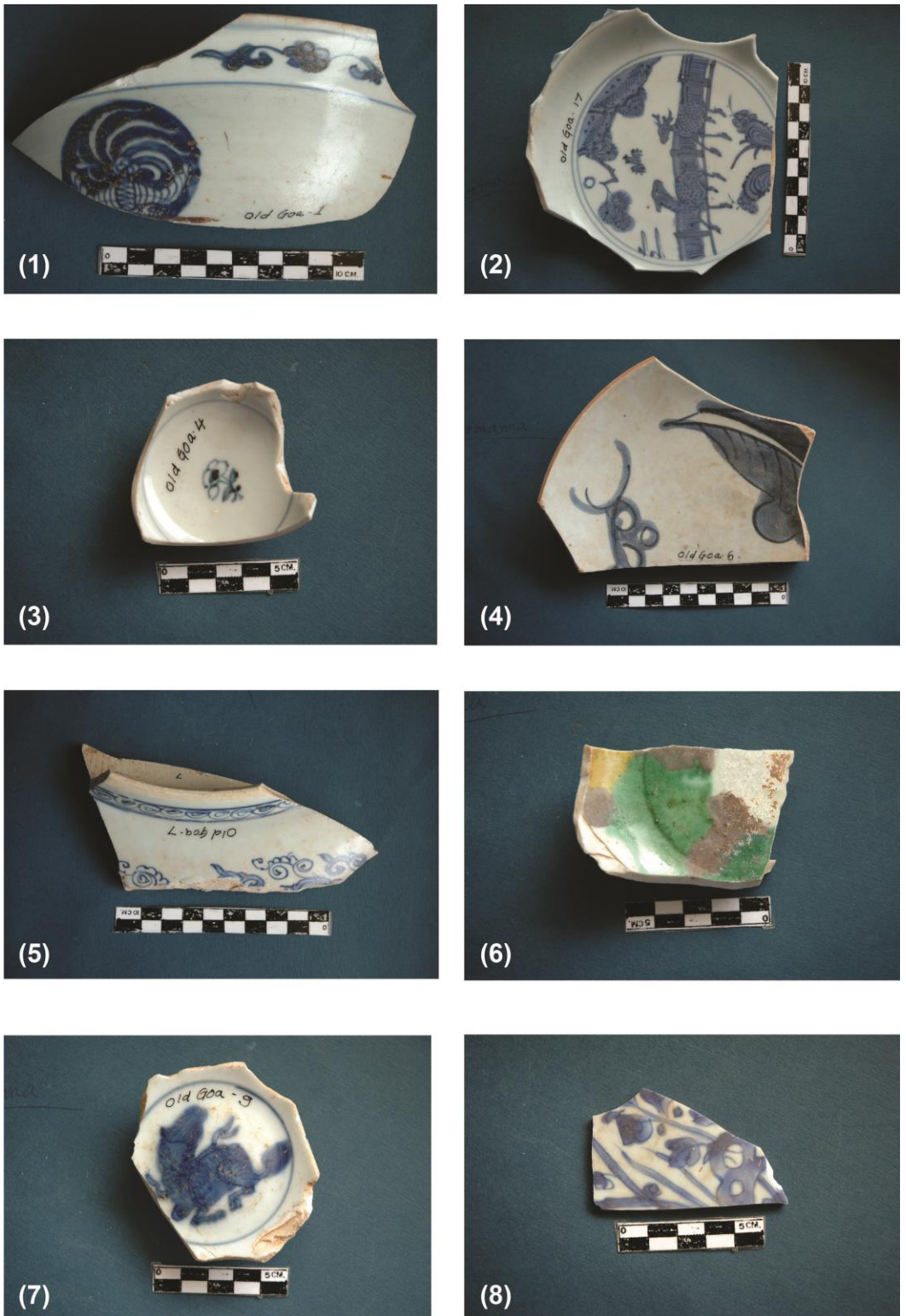


Fig. 2 (a). Chinese porcelain shards of the Ming, Qing and late Qing Dynasties collected from Old Goa, west coast of India.



Fig. 2 (b). Chinese porcelain shards of the Ming, Qing and late Qing Dynasties collected from Old Goa, west coast of India.



Fig. 2 (c). Chinese porcelain shards of the Ming, Qing and late Qing Dynasties collected from Old Goa, west coast of India.

Materials and methods

A small chip of porcelain sample was cut from individual shards. In order to remove the glaze and paint coating from the surface, the shards were ground on a grinding machine and then rubbed with fine sand paper to remove the glaze and paint stains. Afterwards, those chips were cleaned with 0.1 N HCl and ultrasonically cleaned in an ultrasonic bath and washed with Milli-Q water, then dried at 60° in an oven and finely powdered in an agate mortar. About 0.5 gm of dried and powdered porcelain was mixed with Merck's Spectromelt A12 Flux and borate beads were prepared in a Minifuse-2 induction furnace at ~ 1000° C. These beads were used for major elements by X-ray fluorescence (PAN analytical Axios) analysis at CSIR-National Institute of Oceanography, Goa. Accuracy and precision of the data was checked with international standard reference materials (MAG-1 and JMS) and it was better than $\pm 5\%$. For the trace element analysis, about 50 mg of finely powdered porcelain sample was weighed in a PTFE beaker and 10 ml of an acid mixture of HF+HClO₄+HNO₃ (7:1:1) were added and heated on a hot plate until it became a paste. Once again the same quantity of acid mixture was added and heated till it became a paste. Subsequently 4 ml of HNO₃ and 1 ml of Rh (internal standard) were added and heated for 5 minutes, then filtered and made to the final volume of 100 ml by adding Milli-Q water. Similarly International Standard, reference materials (MAG-1, JR-1, BR-1 and SGR), duplicate samples and blanks were prepared. Trace elements were analysed on Inductively Coupled Plasma-Mass Spectrometer (Thermo X Series 2) at CSIR-National Institute of Oceanography, Goa. The accuracy and precision of the data is better than $\pm 7\%$.

Results

The chemical composition obtained from X-ray fluorescence of porcelains from the Ming, Qing and late Qing Dynasties have high SiO₂ content ranging from 66 to 74 % with an average of 70 %, Al₂O₃ varies from 17 to 26 % with an average of 21.8 %-and K₂O varies from 3 to 4 % with an average of 3.27 % (Table 2). Trace elements such as Rb and Ba also have high concentration of 388 ppm (average) and 160 ppm (average) respectively whereas Sr content is low (48 ppm) in all the porcelains. These porcelain shards have very high content of Cu ranging from 4435 ppm to 8952 ppm with an

average of 5346 ppm whereas Zn concentration is also high and varies from 1627 ppm to 3487 ppm with an average of 2105 ppm (Table 2). Total rare earth elements (Σ REE) content of these porcelain is low and ranges from 50 to 128 ppm with a strong negative Eu/Eu* anomaly.

Discussion

The concentration of major element oxides, trace and rare earth elements (REE) data of Chinese porcelains from the Ming, Qing and late Qing Dynasties along with their mean values are presented in Tables 2 and 3. All the porcelain bodies from the Ming, Qing and late Qing Dynasties have very high contents of SiO₂, Al₂O₃ and K₂O (Table 2). This suggests the presence of silica and kaolinite which were used as a raw material. These results are in a similar range to porcelains as reported by Wu et al., (2000). The presence of high Al₂O₃ contents in the Qing porcelain probably suggests improvement of quality, particularly mechanical strength, of Jingdezhen porcelain (Cheng et al., 2002; Table 2). In the Ming porcelain Al₂O₃ is as high as 26 % and 25 %

Table 2. Major element oxide (wt%) data (recalculated on water free basis) analysed with XRF of porcelains from Old Goa, west coast of India.

Sample	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
	(------ % -----)									
MING-1	74.07	18.55	0.15	1.27	0.05	0.28	0.79	1.27	3.51	0.06
MING-2	74.33	18.19	0.14	1.32	0.04	0.31	0.77	1.47	3.37	0.06
MING-4	69.02	21.87	0.18	1.80	0.08	0.35	1.24	1.24	4.16	0.07
MING-7	72.72	19.79	0.12	1.25	0.05	0.27	0.68	1.69	3.37	0.05
MING-9	68.80	23.19	0.14	1.49	0.08	0.28	0.90	1.50	3.53	0.07
MING-10	71.68	20.20	0.18	1.74	0.06	0.36	0.92	1.47	3.32	0.07
MING-11	72.68	19.83	0.12	1.27	0.06	0.27	0.69	1.48	3.55	0.05
MING-14	70.71	21.41	0.12	1.22	0.07	0.26	1.19	1.68	3.27	0.07
MING-15	67.70	23.27	0.13	1.62	0.10	0.28	1.72	2.34	2.75	0.09
MING-19	74.59	17.73	0.13	1.23	0.05	0.31	1.14	1.41	3.36	0.06
MING-20	70.13	21.17	0.14	1.49	0.09	0.26	1.36	1.82	3.44	0.09
MING-21	64.98	26.09	0.20	1.87	0.12	0.33	1.43	1.77	3.12	0.08
MING-22	67.92	24.93	0.12	1.35	0.08	0.22	0.85	1.20	3.24	0.08
MING-23	69.24	21.69	0.19	1.85	0.07	0.36	1.31	1.20	4.01	0.07
Mean (14)	70.60	21.28	0.15	1.48	0.07	0.29	1.07	1.54	3.43	0.07
QING-3	67.72	23.92	0.10	1.46	0.10	0.21	1.34	2.33	2.73	0.09
QING-8	66.09	25.47	0.14	1.53	0.10	0.28	1.42	1.70	3.18	0.08
QING-18	71.68	20.07	0.14	1.55	0.07	0.29	1.00	1.66	3.47	0.06
Mean (3)	68.50	23.16	0.13	1.51	0.09	0.26	1.25	1.90	3.13	0.08
Late QING-5	71.71	20.29	0.14	1.39	0.07	0.28	0.94	1.44	3.68	0.06
Late QING-6	68.67	23.95	0.11	1.32	0.09	0.21	0.76	1.84	2.97	0.08
Late QING-12	74.40	18.20	0.14	1.22	0.04	0.28	0.81	1.54	3.33	0.05
Late QING-13	70.51	21.37	0.19	1.67	0.07	0.30	0.95	1.69	3.19	0.06
Late QING-16	69.39	21.42	0.20	1.78	0.09	0.31	1.47	1.74	3.52	0.09
Late QING-17	67.20	24.19	0.17	1.71	0.10	0.30	1.11	2.20	2.94	0.08
Mean (6)	70.32	21.56	0.16	1.51	0.08	0.28	1.01	1.74	3.27	0.07

in the Qing porcelain The provinces of Zhejiang, Jiangxi, Fujian, Jiangsu and southern Anhui in South China have vast deposits of porcelain stone which is rich in silica and used as the main raw material for making porcelain. The scatter plot of SiO₂ against Al₂O₃ shows a strong inverse correlation (Fig. 3). This is similar to the observation made by Wu et al., (2000) earlier. Low TiO₂ content in these porcelains may be due to its removal by the gravity process or source rocks might be containing low Ti content. The low Na₂O content (< 2 %) in these porcelains could be due to the presence of small amount of feldspars (Guo, 1987).

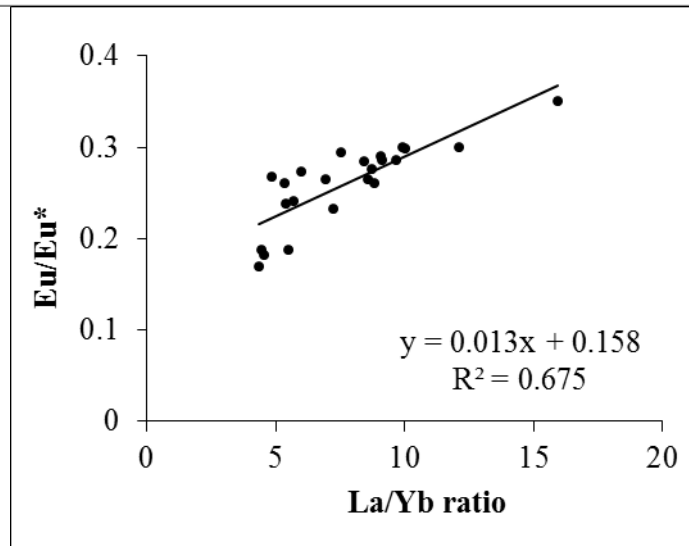
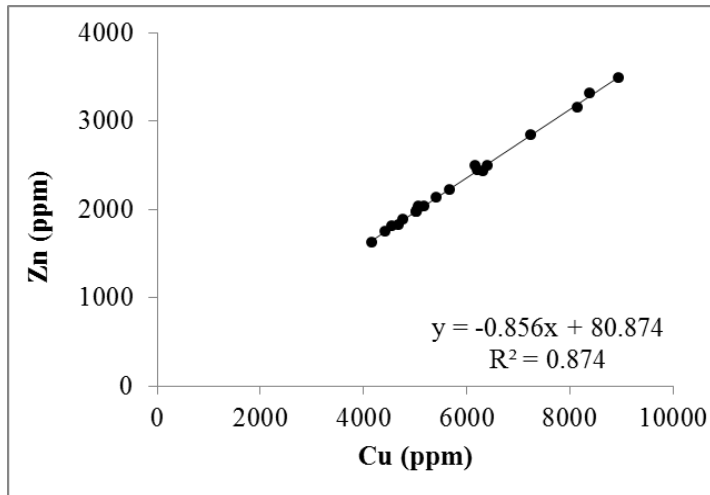
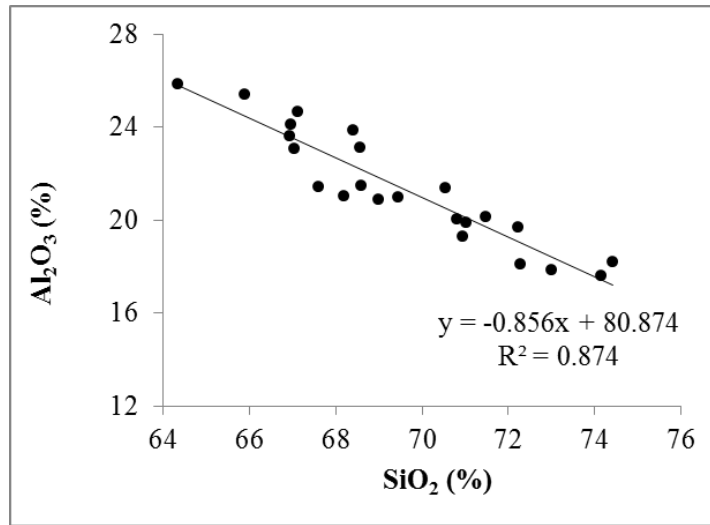


Fig. 3. Scatter plots of $\text{SiO}_2 - \text{Al}_2\text{O}_3$ (top), $\text{Cu} - \text{Zn}$ (middle) and $\text{Eu/Eu}^* - \text{La/Yb}$ (bottom) ratio for all the ceramics recovered from Old Goa, west coast of India.

All the porcelain shards have a high concentration of Rb and Ba, but Sr content is low (Table 3). These concentrations are the characteristics of Sericite is a fine grained micaceous mineral often formed by the degradation of orthoclase or plagioclase and enriched in Rb and Ba and depleted in Sr. Sericite in the porcelain stone mainly acts as a flux, reacting very easily at a high temperature without feldspar and kaolinite. This forms a uniformly vitreous material which increases the density of verification and translucency of the porcelain. As a result, Jingdezhen porcelains have a high degree of translucency. This suggests that raw materials used in these porcelains are silica; kaolinite and sericite and were typically used as the raw materials in South China (Guo, 1987). Clay is the main raw material used for north China ceramics which come from mostly coal mining areas and they contain Al_2O_3 up to 40% i.e. as good as pure kaolinite and other impurities are feldspar, mica, dolomite /carbonate, titanium and iron (Guo, 1987). On the contrary, mean Al_2O_3 content in all Old Goa shards is ~ 21.6 and they are rich in Silica, which clearly indicates porcelain shards collected from Old Goa were manufactured in South China. Moreover, shards from old Goa have very high content of Cu (5346 ppm-mean) and Zn (2105 ppm. mean) and both of them show very strong positive correlation ($r=0.99$) suggesting their single source most probably as a paint (Fig. 3). The nearly similar composition of major, trace elements analysed and some of the elemental ratios such as Rb/Sr, Nb/Ta and Yb/La are nearly in the same range for all the shards. This indicates that Old Goa porcelain is the product of one kiln and further signifies the use of the same type of raw materials.

Table 3. Trace and REE data of porcelains from Ming, Qing and Late Qing Dynasty

Element	Ming													Qing				Late Qing					
	1	2	7	9	10	11	15	19	20	21	22	23	Mean	3	8	18	Mean	5	12	13	16	17	Mean
Be	6.65	6.89	12.43	10.69	9.89	12.08	10.16	7.35	11.08	12.11	13.16	11.54	10.34	12.28	12.92	9.69	11.63	10.89	7.06	10.43	12.98	12.84	10.84
Sc	3.77	3.73	3.26	5.13	3.70	3.67	3.80	3.68	5.06	4.32	3.65	6.41	4.18	3.23	3.66	3.83	3.57	4.13	3.90	5.50	4.35	4.17	4.41
Ti	0.09	0.08	0.06	0.09	0.07	0.07	0.07	0.07	0.09	0.09	0.07	0.11	0.08	0.06	0.07	0.08	0.07	0.08	0.07	0.11	0.08	0.07	0.08
V	18.34	15.47	10.32	19.58	11.76	13.56	13.28	13.22	16.11	16.01	10.05	21.74	14.95	8.44	12.30	14.91	11.88	14.34	11.43	24.62	13.82	12.08	15.26
Cr	4.84	5.20	2.60	6.69	3.73	5.52	7.43	5.98	9.84	5.64	4.08	7.52	5.76	3.65	6.92		5.28	6.63	2.59	8.43		3.64	5.32
Mn	372	298	409	508	625	433	636	421	671	935	703	639	554.06	716	679	565	653.27	495	335	628	825	766	609.44
Co	5.40	4.99	6.06	7.79	11.92	8.31	10.62	8.66	9.64	11.48	7.83	5.71	8.20	8.37	13.08	7.52	9.66	8.09	8.43	15.21	9.61	7.38	9.74
Ni	43.95	65.49	48.57	35.63	66.83	33.58	45.00	36.30	45.59	44.42	35.09	45.54	45.50	58.85	35.29	39.13	44.42	55.89	37.12	39.27	36.52	35.86	40.93
Cu	5186	8392	6318	4780	8952	4170	6212	5031	5682	6412	5031	6179	6028.75	8146	4684	5083	5971.00	7254	5423	4435	4559	5060	5346.20
Zn	2032	3314	2437	1883	3487	1627	2441	1979	2219	2499	1972	2500	2365.83	3149	1825	2037	2337.00	2837	2137	1751	1809	1994	2105.60
Ga	26.33	18.89	20.71	22.03	24.01	20.87	22.59	18.80	20.79	26.31	25.38	22.34	22.42	24.57	23.79	22.29	23.55	21.96	20.93	22.06	24.26	24.78	22.80
As	2.47	2.66	2.11	3.76	2.76	2.16	2.31	2.50	3.12	2.81	2.59	3.90	2.76	2.60	2.62	2.93	2.71	2.70	3.65	3.27	3.54	3.01	3.24
Se	4.78	4.66	4.51	5.10	4.94	4.69	5.65	5.17	4.97	5.09	5.66	5.23	5.04	4.62	4.70	4.99	4.77	5.21	5.15	5.74	5.26	5.04	5.28
Rb	315	312	341	392	429	353	407	337	468	515	491	456	401.25	430	433	437	433.40	380	316	367	421	460	388.78
Sr	39.26	37.48	37.06	48.00	49.86	36.52	51.76	51.54	54.86	59.10	46.58	48.10	46.68	56.68	49.25	49.83	51.92	40.99	39.42	47.99	59.92	52.45	48.15
Y	18.64	11.16	15.70	17.62	17.58	15.30	13.40	12.54	17.84	15.60	16.60	21.01	16.08	17.10	16.91	19.21	17.74	19.56	11.29	14.90	15.73	18.38	15.97
Zr	45.53	41.50	43.80	47.25	39.83	39.91	42.44	40.84	48.16	49.99	40.86	55.02	44.59	44.65	42.29	40.67	42.54	43.32	40.82	47.68	54.03	48.22	46.81
Nb	10.40	10.18	13.76	12.53	12.41	12.27	12.43	12.94	19.86	14.57	11.51	16.82	13.31	13.65	14.77	16.10	14.84	13.97	15.44	12.21	15.75	12.95	14.06
Ag	3.34	4.77	3.46	2.71	4.74	2.42	3.31	2.93	3.42	3.62	2.90	3.61	3.44	4.62	2.68	3.13	3.48	3.94	4.59	2.42	4.02	2.97	3.59
Sn	62.36	101.20	69.83	54.67	99.84	46.59	63.01	52.08	71.46	79.75	58.72	74.67	69.52	104.90	56.02	56.09	72.34	79.90	50.87	48.85	53.43	61.14	58.84
Sb	5.57	11.44	6.40	7.83	9.54	5.38	7.00	6.98	9.40	7.16	9.37	10.95	8.08	9.69	5.97	6.89	7.51	8.68	6.59	6.08	7.32	7.60	7.25
Cs	38.12	44.45	39.37	53.14	50.29	43.83	48.64	46.38	65.21	59.84	49.79	63.19	50.19	47.79	48.78	58.14	51.57	47.76	40.66	47.46	44.89	47.51	45.66
Ba		188.70	152.90	218.40	172.50	174.40	157.40	196.10	177.50	136.00	100.90	208.00	171.16	92.40	147.70	191.60	143.90	223.70	201.10	180.80	94.58	95.27	159.09
La	29.42	12.83	14.58	12.39	10.75	16.46	11.94	11.61	11.83	9.48	8.23	12.61	13.51	7.78	12.79	18.44	13.00	18.01	8.46	16.18	8.67	9.11	12.09
Ce	48.94	25.11	19.50	23.97	20.18	27.58	21.34	19.18	23.55	19.92	16.90	25.72	24.32	17.15	22.85	22.94	20.98	27.41	17.02	29.38	17.67	19.16	22.13
Pr	5.79	2.87	3.44	2.94	2.57	3.83	2.74	2.69	2.86	2.38	2.08	3.07	3.10	1.93	3.01	4.37	3.10	4.08	2.10	3.72	2.11	2.27	2.86
Nd	22.03	11.77	11.79	11.75	10.01	14.28	10.58	10.04	11.43	9.51	8.20	12.54	11.99	7.80	11.44	14.67	11.30	14.91	8.51	14.37	8.31	8.97	11.02
Sm	5.37	3.51	4.18	3.72	3.58	4.50	3.27	3.25	3.76	3.31	3.21	4.13	3.82	2.91	3.76	5.03	3.90	4.71	3.12	4.12	3.05	3.35	3.67
Eu	1.05	0.62	0.63	0.69	0.53	0.73	0.56	0.61	0.67	0.54	0.38	0.78	0.65	0.33	0.55	0.84	0.57	0.80	0.52	0.76	0.39	0.43	0.58
Gd	4.50	2.93	3.56	3.41	3.18	3.78	2.79	2.91	3.49	3.11	2.99	3.88	3.38	2.78	3.43	4.38	3.53	4.12	2.65	3.35	2.82	3.21	3.23
Tb	0.85	0.58	0.77	0.74	0.75	0.77	0.60	0.62	0.81	0.72	0.71	0.85	0.73	0.68	0.76	0.91	0.78	0.88	0.54	0.67	0.67	0.76	0.71
Dy	4.65	3.19	4.33	4.42	4.49	4.28	3.30	3.63	4.80	4.19	4.20	5.33	4.23	4.08	4.34	5.17	4.53	5.12	2.96	3.78	3.83	4.67	4.07
Ho	0.86	0.58	0.79	0.86	0.81	0.78	0.60	0.67	0.90	0.75	0.76	1.05	0.78	0.76	0.79	0.97	0.84	0.97	0.54	0.69	0.67	0.85	0.74
Er	2.27	1.57	2.12	2.36	2.24	2.11	1.64	1.82	2.50	1.98	2.08	2.96	2.14	2.03	2.12	2.57	2.24	2.66	1.46	1.95	1.80	2.25	2.02
Tm	0.32	0.23	0.30	0.35	0.33	0.29	0.23	0.25	0.37	0.29	0.31	0.44	0.31	0.30	0.31	0.36	0.32	0.37	0.21	0.28	0.26	0.34	0.29
Yb	1.85	1.28	1.69	2.06	1.89	1.70	1.36	1.54	2.20	1.74	1.81	2.60	1.81	1.78	1.76	2.02	1.85	2.13	1.22	1.63	1.57	2.03	1.72
Lu	0.25	0.18	0.23	0.28	0.26	0.23	0.18	0.20	0.30	0.24	0.25	0.36	0.25	0.24	0.24	0.27	0.25	0.29	0.17	0.23	0.21	0.26	0.23
Hf	2.77	2.78	3.54	2.88	2.74	3.12	2.52	3.09	3.07	2.98	2.63	3.12	2.94	2.98	2.99	3.03	3.00	3.20	2.71	2.41	3.00	2.98	2.86
Ta	0.99	0.95	1.97	1.42	1.52	1.32	1.26	1.41	4.77	2.73	1.84	2.31	1.88	2.32	1.86	2.63	2.27	2.06	2.33	1.64	2.98	2.57	2.31
Tl	1.45	1.13	1.41	1.59	2.12	1.56	1.44	1.02	1.83	2.88	2.46	1.56	1.70	2.16	1.95	1.65	1.92	1.52	1.43	1.36	1.78	2.45	1.71
Pb	204	309	266	228	367	203	217	223	253	308	234	258	255.74	313	189	221	240.73	300	223	173	160	235	217.98
Th	11.84	12.50	11.80	10.71	10.84	12.04	7.48	9.98	10.95	8.86	10.27	12.12	10.78	10.79	9.42	10.50	10.24	11.74	9.96	9.12	7.52	10.98	9.87
U	5.56	5.19	6.96	7.38	9.01	6.56	4.90	5.21	8.64	8.89	9.96	8.92	7.26	12.65	7.53	7.44	9.21	7.67	6.08	5.57	7.59	10.56	7.49

Rare earth elements (REE) provide important information on provenance, bottom redox conditions and source of elements (Pattan et al., 2005; Ma et al., 2012; Dias et al., 2013). Total REE content in the porcelain varies from 50 to 86 ppm except for one sample (Ming-1) which has little highs of 128 ppm with an average of 67 ppm. This concentration is similar to the Jiexiu Ding style porcelain (62 ppm) of China (Li et al., 2005). However, the total REE content in the present porcelains are higher than the porcelain products of Jingdezhen (43 ppm) but quite lower than that of Bei-Gou Kiln (258 ppm), Da-Long Kiln (234 ppm), Hua-Zai Kiln (440 ppm) and Tian-leng Kiln (295 ppm) as reported by Ma et al., (2012). This variation could be due to the type of source rock, weathering intensity and type of clay minerals used in these ceramics. The bulk REE concentrations of these porcelains are generally normalized to eliminate the effect of comosynthesis on natural abundances (Ma et al., 2012). Normalisation is done by dividing the concentration of each REE found in porcelains with respective REE in the CI-chondrite. The CI-chondrite normalized REE pattern of all three dynasties show very similar patterns where light REE are highly enriched with negative Eu-anomaly and heavy REE are flat in nature (Fig. 4). Eu/Eu* anomaly value of these porcelains ranges from 0.18 to 0.36 with an average of 0.26 suggesting a strong negative Eu anomaly. The negative Eu/Eu* anomaly is the characteristic of many ancient porcelain materials of China (Li et al., 2005). However, earlier, Li et al, (2003) have reported Eu/Eu* >1 (positive anomaly) for some ancient porcelain material of China and suggested that sodium feldspar might have been added as a raw material. The absence of positive Eu/Eu* anomaly in the shards of Old Goa, clearly indicates no feldspars have been added as the raw material.

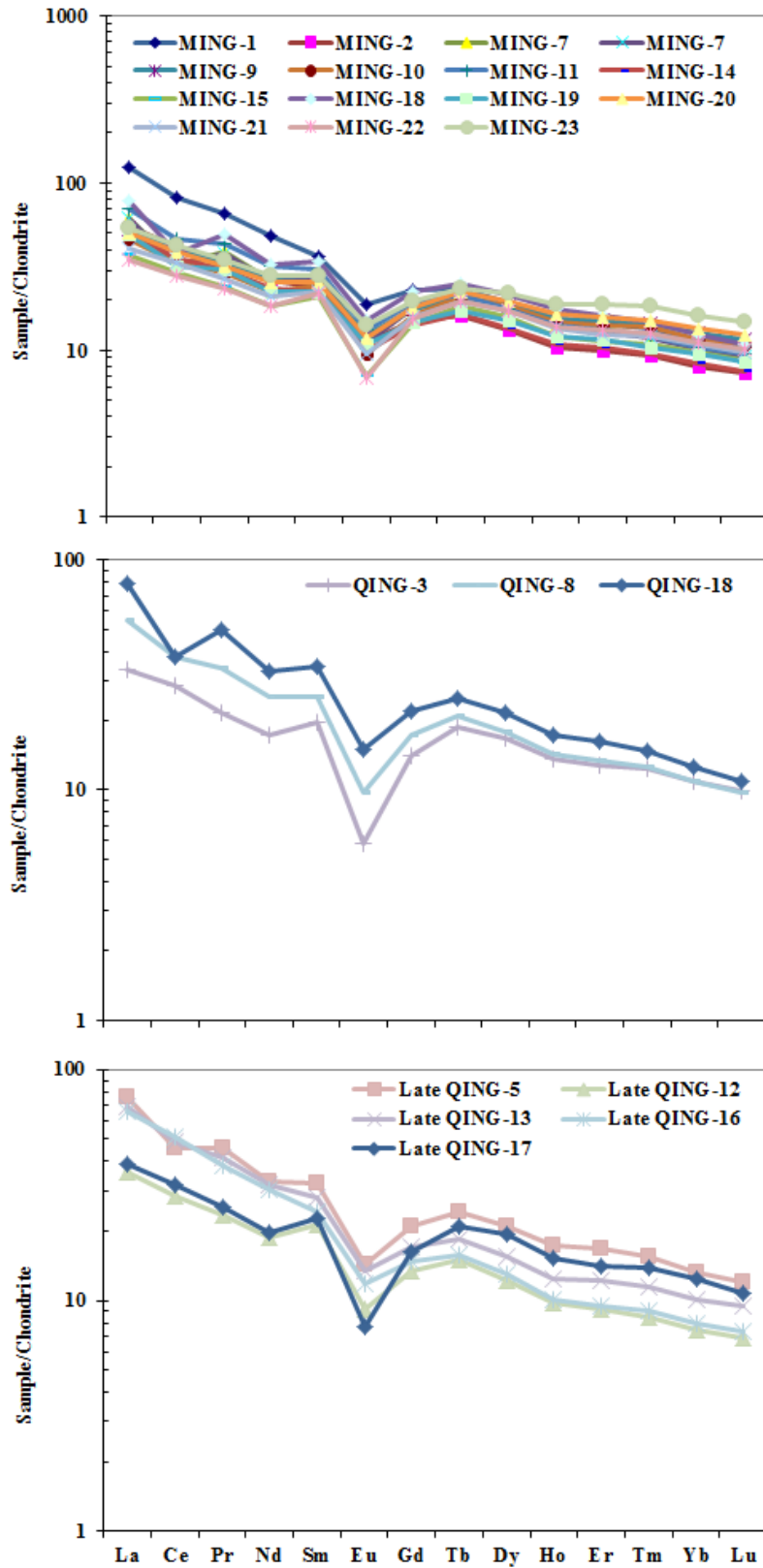


Fig. 4. Chondrite - normalised REE patterns of porcelain shards from late Qing (top), Qing (middle) and Ming Dynasties (bottom).

Principal component analysis shows mainly four components and accounts for 81.4 % of the total variance (Table 4). The highlighted variables have their absolute values of loadings greater than 0.5 indicating the participation of the variables in each principal component (PC). PC-1 has accounts for 35.8% of the total variance and is characterized by very strong positive loadings of SiO₂ (0.89) Th and light REE (La to Eu). This phase can be designated as silica which is the major raw material used in the ceramic industry. PC-2 contributes 24.3 % of the total variance and has positive loadings of Ti, Na, Cu and Zn and appears to be associated with paint in the ceramics. PC-3 and 4 represents 13.5% and 7.7% of total variance and no element has positive loadings of > 0.5 (Table 4). The bi-variable plot of PC-1 against PC-2 is helpful in providing clear information about the relationship between elements. The location of element away from the origin will tend to have high values for those and indicates its magnitude (Ma et al., 2012). The scatter plot of PC-1 against PC-2 for all the elements analysed in all the ceramics suggests mainly four groups based on their similar behaviour (Fig. 5). Group I has only one element oxide (SiO₂) which has a concentration of ~ 70% and is the major raw material used in the ceramics. Group II consists of a majority of elements (26) occupying between -0.65 to +0.7. Interestingly in this group light REE (La, Ce, Nd, Pr, Sm, Eu) are concentrated in one area whereas heavy REE (Tb, Dy, Ho, Tm, Yb and Lu) form another end. This suggests REE fractionation between light and heavy REEs. Group III comprises of 18 elements is the second highest and have values ranging from -0.3 to +0.4 which are not significant. Group IV has six elements and mostly have values of ~ +0.4.

Table 4. Factor loading of all the ceramics recovered from Old Goa, west coast of India

Element	PC1	PC2	PC3	PC4
SiO ₂	0.89	-0.18	-0.14	0.02
Al ₂ O ₃	-0.88	0.21	0.20	-0.03
TiO ₂	-0.17	-0.39	-0.56	-0.30
Fe ₂ O ₃	-0.80	-0.11	-0.35	-0.19
MnO	-0.91	0.20	0.20	-0.08
MgO	0.12	-0.31	-0.56	-0.41
CaO	-0.81	0.18	0.07	-0.31
Na ₂ O	-0.50	0.51	0.16	0.05
K ₂ O	0.27	-0.83	-0.23	-0.10
P ₂ O ₅	-0.84	0.31	-0.01	-0.14
Be	-0.80	0.10	0.26	0.27
Sc	-0.37	-0.65	-0.39	-0.44
Ti	-0.12	-0.74	-0.40	-0.41
V	0.20	-0.73	-0.31	-0.49
Cr	-0.52	-0.39	0.13	-0.53
Mn	-0.96	0.15	0.04	0.02
Co	-0.67	0.33	0.22	-0.13
Ni	0.33	0.35	-0.80	0.24
Cu	0.14	0.51	-0.82	0.21
Zn	0.14	0.51	-0.84	0.19
Ga	-0.52	0.00	0.10	0.30
As	-0.53	-0.53	-0.42	-0.28
Se	-0.39	0.06	0.12	-0.60
Rb	-0.97	0.02	0.01	0.02
Sr	-0.89	0.18	-0.02	-0.13
Y	-0.64	-0.61	-0.03	0.36
Zr	-0.43	-0.49	-0.39	-0.18
Nb	-0.81	-0.30	0.02	0.05
Ag	0.15	0.38	-0.84	0.26
Sn	-0.01	0.42	-0.83	0.30
Sb	-0.24	0.15	-0.80	-0.05
Cs	-0.87	-0.26	-0.18	-0.21
Ba	0.43	-0.53	-0.26	-0.49
La	0.69	-0.54	0.18	0.13
Ce	0.66	-0.50	0.01	0.01
Pr	0.62	-0.61	0.22	0.16
Nd	0.65	-0.61	0.12	0.08
Sm	0.43	-0.76	0.20	0.27
Eu	0.58	-0.75	0.03	-0.08
Gd	0.14	-0.87	0.19	0.30
Tb	-0.39	-0.77	0.13	0.43
Dy	-0.57	-0.72	0.00	0.36
Ho	-0.56	-0.76	-0.04	0.29
Er	-0.56	-0.76	-0.10	0.24
Tm	-0.62	-0.70	-0.18	0.22
Yb	-0.65	-0.69	-0.18	0.16
Lu	-0.64	-0.68	-0.23	0.16
Hf	-0.06	-0.31	0.09	0.40
Ta	-0.78	-0.17	-0.02	0.14
Tl	-0.81	0.19	0.01	0.25
Pb	0.01	0.38	-0.84	0.24
Th	0.61	-0.40	-0.38	0.38
U	-0.84	0.11	-0.13	0.45
Eigen	19.00	12.90	7.14	4.11
Varia (%)	35.84	24.34	13.46	7.76
Cum var	35.84	60.18	73.65	81.40

Conclusions

The analysis confirmed the porcelain shards collected from Old Goa are made of silica, kaolinite and sericite and manufactured in southern China. Further, it establishes that Chinese kilns used local clays for manufacturing porcelains according to the geochemistry and mineralogy of soil. It has also been understood that the clay of southern China is different from that of northern China: for instance southern China clay contained silica, kaolinite and sericite and northern China ceramics comprised of various kinds of clay minerals, feldspar, quartz, dolomite/carbonate; and each kiln had their technology which subsequently developed. The chemical composition of Old Goa shards correspond to the porcelain shards reported from Portugal (Dias et al., 2013) and the shards of Old Goa and Portugal belong to the same period. During the 16th and 17th centuries Portuguese had strong hold of maritime trade with Goa and Chinese porcelain along with other cargo were sent to Lisboa from Old Goa. Old Goa was a port before the arrival of Portuguese, but some of the shards could be of the pre-Portuguese period, which cannot be ignored, but most of the shards belong to the Portuguese period. With the availability of new tools and technology such as XRF, ICP-MS, INAA it became possible to understand the precise details of Chinese porcelain and this can be correlated and compared with the traditional methods adopted by scholars to identify the period and provenance of the porcelain. The provenance and kilns of Chinese porcelain which has been found from different parts of the Indian subcontinent can be deciphered by this kind of analysis to understand the unknown maritime contacts between India and China over the centuries. The study infers that the Chinese ceramics of old Goa were produced at Jingdezhen kiln and the source of raw material was from South China. The results of this study are novel and would be useful for future research from the perspective of Chinese ceramics in an Indian context and might also add to the existing information.

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References

- Bushell, S.W., 1904. *Chinese Art*, Vol. 1. His Majesty's Stationery Office, London.
- Calvao, J. R., (Ed.) 1999. *The Porcelain Route Ming and Qing Dynasties*. Fundacao Oriente, Lisboa.
- Carswell, J., 1976. China and Maldives Islands. *Transactions of the Oriental Ceramic Society* 41, 121-198.
- Carswell, J., 1978. China and Islam: A survey of the coast of India and Ceylon. *Transactions of the Oriental Ceramic Society* 42, 25-68.
- Cheng, H.S., Zhang, Z.Q., Xia, H.N., Jiang, J.C., Yang, F.J. 2002. Non-destructive analysis and appraisal of ancient Chinese porcelain by PIXE, *Nuclear Instruments & Methods in Physics Research Section B- Beam Interactions with Materials and Atoms. Nuclear Instruments and Methods in Physics Research B* 190, 488-491.
- Christie, J. W., 1998. The Medieval Tamil-Language Inscriptions in Southeast Asia and China. *Journal of Southeast Asian Studies* 29 (2), 239-268.
- Dias, M. I., Prudêncio, M. I., Pinto de Matos, M.A., Rodrigues, A. L., 2013. Tracing the origin of blue and white Chinese Porcelain ordered for the Portuguese market during the Ming dynasty using INAA. *Journal of Archaeological Science* 40 (7), 3046-3057.
- Flecker, M., 2001. A ninth Century AD Arab or Indian shipwreck in Indonesia: First evidence for direct trade with China. *World Archaeology* 32 (3), 335-354.
- Flecker, M., 2002. *The Archaeological Excavation of the 10th Century Intan Wreck*, Ph.D. thesis, National University of Singapore, 2001: BAR International Series 1047, Oxford.
- Flecker, M., 2008. A 9th-Century Arab or Indian shipwreck in Indonesian Waters: Addendum. *International Journal of Nautical Archaeology* 37 (2), 384-386.
- Fonseca, J. N., 1986. *A Historical and Archaeological Sketch of the City of Goa*. Asian Educational Services, New Delhi.
- Gerritsen, A., 2009. Fragments of a Global Past: Ceramics Manufacture in Song-Yuan-Ming Jingdezhen. *Journal of the Economic and Social History of the Orient* 52, 117-152.
- Ghosh, A., (ed.) 1989 *An Encyclopaedia of Indian Archaeology*, Vol. II, Munshiram Manoharlal Publishers, New Delhi.
- Gibb, H. A. R., (Trans. & Ed.) 1971. *The Travels of Ibn Battuta 1325-1354 AD*, Vol. 3. Cambridge University Press, Cambridge.
- Gray, B., 1964. The export of Chinese porcelain to India. *Transactions of the Oriental Ceramic Society* 36, 21-37.
- Gu, L. B., Shao, H. X., Chen, T. M., Determination of rare earth elements in Shang proto-porcelain by ICP-MS, *Rock and Mineral Analysis (in Chinese)*. 19 (1), 70-73.

- Guo, Yanvi., 1987. Raw materials for making porcelain and the characteristics of porcelain wares in north and south China in ancient times. *Archaeometry* 29 (1), 3-19.
- Guy, J., 2010. Rare and strange goods: International trade in Ninth century Asia. In: Krahl, R., Guy, J., Wilson, J. K., and Raby, J. (Eds.), *Shipwrecked Tang Treasures and Monsoon winds*, Arthur M. Sackler Gallery, Smithsonian Institution, Washington, pp. 19-27.
- Harrison, B., 1979. Swatow in "Het Princessehof": the analysis of a museum collection of Chinese trade wares from Indonesia. *Gemeentelijk Museum Princessehof Leeuwarden*, p. 131.
- Hirst, K. K., <http://archaeology.about.com/od/medieval/qt/Exporting-Chinese-Porcelains-A-History.htm>
- Hourani, G. F., 1995. *Arab Seafaring in the Indian Ocean in ancient and early medieval times*. Princeton University Press, New Jersey.
- Indian Archaeology-A Review 1961-62. 1964. Archaeological Survey of India, New Delhi, p. 97.
- Jayasingha, P., 2006. Tang Dynasty pottery in Sri Lanka. *Antiquity* 80 (309) (Antiquity Project Gallery).
- Karashima, N., (Ed.), 2004. *In search of Chinese Ceramic sherds in South India and Sri Lanka*. Taisho University Press, Tokyo.
- Karashima, N., and Kanazawa, Y., 2002. Testimony of Chinese Ceramic Sherds. *Ancient and Medieval Commercial activities in the Indian Ocean: Testimony of Inscriptions and Ceramic sherds*. Taisho University Press, Tokyo, pp. 109-118.
- Lane, A. 1950. *Early Islamic Pottery*. Faber and Faber, London.
- Leung, P.L., and Luo, H., 2000. A study of provenance and dating of ancient Chinese porcelain by X-ray fluorescence spectrometry. *X-ray Spectroscopy* 29 (1), 34-38.
- Leung, P.L., Stokes, M. J., Chen, T., Dashu, Q., 2000. A study of ancient Chinese porcelain wares of the Song-Yuan dynasties from Cizhou and Ding kilns with energy dispersive X-ray fluorescence. *Archaeometry* 42 (1), 129-140.
- Li, Bao-ping., Greig, A., Zhao, Jian-xin, Collerson, K.D., Quan, Kui-shan, Meng, Yao-hu, Ma, Zhong-li, 2005. ICP-MS trace element analysis of Song dynasty porcelains from Ding, Jiexiu and Guantai kilns, North China. *Journal of Archaeological Science* 32 (2), 251-259.
- Li, Bao-ping., Zhao, J., Collerson, K. D., Greig, A., 2003. Application of ICP-MS trace element analysis in study of ancient Chinese ceramics. *Chinese Science Bulletin* 48 (12), 1219-1224.
- Li, G.X., Zhao, W.J., Gao, Z.Y., et al., 2000. Application of neutron activation analysis in study of ancient ceramics. *Nuclear Physics Review (Chinese)*, 17 (4), 248-250.
- Li, J., 1998. *History of Science and Technology of China: Ceramics Volume*. Science Press, Beijing.
- Lin, S., 1999. *Celadon and Yue Kiln*. Shanghai Guji Press, Shanghai.

- Lion-Goldschmidt, Daisy., 1978. *Ming Porcelain*. Translated by Katherine Watson. Rizzoli, New York.
- Mathew, K. S., 1990. Trade and Commerce in Sixteenth Century Goa. In: De Souza T.R. (Ed.), *Goa through the Ages*, vol. II, Concept Publishing Company, New Delhi, pp. 137-145.
- Ma, Hongjiao, Zhua, Jian., Hendersonb, J., Li, Naisheng., 2012. Provenance of Zhangzhou export blue-and-white and its clay source. *Journal of Archaeological Science* 39 (5), 1218-1226.
- Mallory-Greenough, L.M., Greenough, J. D., and Owen, J.V., 1998. New data for old pots: Trace - element characterization of ancient Egyptian pottery using ICP-MS. *Journal of Archaeological Science* 25 (1), 85-97.
- Muhammed, K.K., 1994. *Chinese Pottery: A Study on Decorative Motifs and Inscriptions*. In: Rao, S.R. (Ed.), *Role of Universities and Research Institutions in Marine Archaeology*, Proceedings of the Third Indian Conference on Marine Archaeology of Indian Ocean Countries, Dharwad - 1992, NIO, Goa, pp. 181-201.
- Pande, R., 2014. *A study of porcelain from ruins of Augustine Complex, Old Goa*. Unpublished Ph.D. thesis, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur.
- Pattan, J.N., Peacre, N.J.G., and Mislankar, P.G., 2005. Constraints in using Cerium-anomaly of bulk sediments as an indicator of palaeo-bottom water redox environment: A case study from the Central Indian Ocean Basin. *Chemical Geology* 221 (3-4), 260-278.
- Prematilleke, P.L., 1990. Chinese Ceramics discovered in Sri Lanka – An overview. In: Bandaranayake, S., Dewaraja, L., Silva, R., and Wimalaratne, K.D.G. (Eds.), *Sri Lanka and the Silk Road of the sea*, The Sri Lanka National Commission for UNESCO and the Central Cultural Fund, Colombo, pp. 233-244.
- Rajendran, P., 2014. Antiquities from the Sea-Bed at Tangasseri, Kollam District, Keralam, South India. *Puratattva* 44, 58-62.
- Ray, H.P., 2013. Archaeology of Maritime Travel: Chinese ceramics in the Indian Ocean Trade. In Tripathi, A. (Ed.), *Maritime Heritage of Indian Ocean*, Sharada Publishing House, New Delhi, pp. 195-212.
- Rougeulle, A., 1996. Medieval trade networks in the Western Indian Ocean (8th-14th centuries). In: Ray, H.P., and Salles, J.F. (Eds.), *Tradition and Archaeology Early maritime contacts in the Indian Ocean*, Manohar Publishers and Distributors, New Delhi, pp.159-180.
- Sastri, K.A.N., 1939. *Foreign Notices of South India: From Megasthenes to Ma Huan*. University of Madras, Chennai.
- Savage, G., 1961. *Porcelain through ages*. Penguin Books, London.
- Sharma, A., A study of Chinese porcelain found in the Indian Ocean. In Gaur, A.S., Sundaresh. (Ed.), *Recent Researches on Indus Civilization and Maritime Archaeology in India*, Agam Kala Prakashan, New Delhi, pp. 167-179.
- Shen, Fuwei., 1996. *Cultural flow between China and the outside world*. Foreign Languages Press, Beijing.

- Sila Tripathi., Gaur, A.S., and Sundaresh., 2014. Maritime Archaeology and Shipwrecks off Goa. Kaveri Books, New Delhi.
- Sila Tripathi., Pande, R., and Rao, V.G., 2011. Study of Chinese porcelain sherds of Old Goa, India: Indicators of Trade Contacts. *Man and Environment* 36 (2), 107-116.
- Smart, S.E., 1975. Fourteenth century Chinese Porcelain from a Tughlaq palace in Delhi. *Transactions of the Oriental Ceramic Society* 41, 199-230.
- Subbarayalu, Y., 1996. Chinese ceramics of Tamilnadu and Kerala coasts. In: Ray, H.P., and Salles, J.F. (Eds.), *Tradition and Archaeology Early maritime contacts in the Indian Ocean*, Manohar Publishers and Distributors, New Delhi, pp. 109-114.
- Valenstein, S.C., 1989. *A Handbook of Chinese Ceramics*. The Metropolitan Museum of Art, New York.
- Yin, C.S., Qui, P., Wang, C.S et al., 2000. Application of artificial neural network in provenance study of ancient potteries. *Chinese Science Bulletin (Chinese)* 45 (19), 2109-2112.
- Wu, J., Leung, P. L., Li, J.Z., Stokes, M. J. and Mike, T.W. Li. 2000. EDXRF studies on blue and white Chinese Jingdezhen porcelains samples from the Yuan, Ming and Qing dynasties. *X-ray Spectrometry* 29 (3), 239-244.

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