Tracing the origin of blue and white Chinese Porcelain ordered for the Portuguese market during the Ming dynasty using INAA

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ABSTRACT

The existing documentary history of Chinese porcelain ordered for the Portuguese market (mainly Ming dynasty.) is reasonably advanced; nevertheless detailed laboratory analyses able to reveal new aspects like the number and/or diversity of producing centers involved in the trade with Portugal are lacking.

In this work, the chemical characterization of porcelain fragments collected during recent archaeological excavations from Portugal (Lisbon and Coimbra) was done for provenance issues: identification/ differentiation of Chinese porcelain kilns used. Chemical analysis was performed by instrumental neutron activation analysis (INAA) using the Portuguese Research Reactor. Core samples were taken from the ceramic body avoiding contamination form the surface layers constituents. The results obtained so far point to: (1) the existence of three main chemical-based clusters; and (2) a general attribution of the porcelains studied to southern China kilns; (3) a few samples are specifically attributed to Jingdezhen and Zhangzhou kiln sites. In a chronological point of view, for the studied samples we assist to an increasing improvement of the production procedure from late 15th till the 17th centuries of the Chinese porcelains sent to Portugal, especially enhanced by the association of late porcelains with refining processes of the original raw material, consistent with removal of more heavy minerals. In the case of some samples a kiln attribution was possible, but for the majority of the samples we haven't found yet the specific kilns.

1. Introduction

Chinese porcelains and Portuguese faience wares were the main subject of a FCT research project (Dias, 2006, in press), which had as major achievement the increase of the knowledge of the Portuguese movable assets from the 16th–18th centuries. In this project public research laboratories and museums worked together in an interdisciplinary approach. In the present work results obtained for Chinese porcelains ordered for the Portuguese market (15th–17th cent.) are presented. The first stage of the work comprised a detailed typological/decorative classification of porcelain shards which was used for a first chronological and provenance approach.

Nevertheless we are aware that this customary method for dating ancient Chinese porcelain based on shapes and decorations by its changes in the different dynasties, it is sometimes problematic, as visual features may vary only a little. Also they may be imitated in later dynasties. Therefore, chemical analyses have

played an important role in the study of these ancient ceramics. As enhanced by Li et al. (2003) most ancient Chinese kilns used clays mined from local areas and some geochemical and mineralogical differences may be expected. On the other hand, also other variables may influence composition, like production techniques, including processing, washing and mixing diverse raw materials.

Regarding the Chinese porcelain ordered for the Portuguese market, the existing documentary history is reasonably advanced; nevertheless it is necessary to proceed with detailed laboratory analyses so that new relevant aspects can be unraveled like the number and/or diversity of producing centers involved in the trade with Portugal. The spreading of Chinese porcelain in Europe is a consequence of the Portuguese naval expansion to the Orient. Returning from the first great trip, Vasco da Gama will have brought exemplars to offer to king D. Manuel who will have become interested in fine porcelains; thereafter, in 1507 the Portuguese Monarch ordered several objects. In this way, the armillary sphere, the royal weapons and religious symbols like the monogram IHS (Iesus Hominum Salvator) encircled by a crown of thorns, were immortalized on the first porcelains manufactured specifically for the Portuguese market and dated about 1520. Between 1540 and

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1552 objects with registrations in Portuguese were ordered, and the difficulties felt by Chinese craftsmen in copying alphabetic inscriptions, strange for them, are perceptible in those pieces. They certify that a clandestine trade proceeded between Portugal and China despite the cut of official relations. To these decorative patterns others were joined like the armory of noble families and emblems of religious Orders dedicated to consolidate the missions of the Portuguese empire in the Orient. This particular anthology of objects, expressing that the Portuguese were pioneers in the commerce of porcelain, is spread all over the world and treasured in national and foreign museums, and private collections (Harrison-Hall, 2001; Pinto de Matos, 2002/03, 2003; Pinto de Matos and Salgado, 2002).

Using instrumental neutron activation analysis (INAA) major (a few), minor and trace elements contents of around 30 porcelains wares excavated from different sites in central Lisbon and Coimbra were determined. By virtue of various statistical methods we attempt to find out the provenance characteristics/kilns attribution of the Porcelain wares ordered for the Portuguese market, found in different Portuguese archaeological excavations, in terms of trace elements composition.

Blue and white porcelains are undoubtedly considered the most important of the Chinese porcelains produced along the various dynasties, from the Yuan, Ming to the Qing. One of our purposes is to locate the origin(s), at a regional scale, of the porcelains found in Lisbon and Coimbra archaeological excavations. To do so, it is assumed that there is already a chemical fingerprint of Chinese kilns. On the other hand, if not possible to attain such an ambitious goal, at least contribute to figure out the diversity of productions centers involved in the commercial trade to Portugal.

In ancient times (usually before 1900 AD), it was very difficult to transport raw materials from one place to another in China, so potters usually employed local materials to manufacture pottery and porcelain and also employed specific raw materials and/or batch composition in certain time periods, which provides a very good scientific basis for employing element characterization in provenance and dating studies (Leung and Luo, 2000). Another important feature is that chemical composition difference between samples from different kiln sites is usually much greater than that between samples from the same kiln but different time periods, because a change of emperor did not influence the raw materials and/or batch composition significantly. So, in this work, considering that same materials might have been used in a certain kiln along dynasties, we will also compare chemical composition of our samples with others from Yan to Qing dynasties, in certain kilns. So, we can better ascertain kiln(s) identification of porcelains ordered for the Portuguese market.

We are aware that, as previously noted by Leung and Luo (2000), in provenance studies, comparing data from different researchers/ and institutions/and methods is always a challenge, with risks, because the differences in equipment, measuring conditions, standard samples, etc., strongly influence the measurement results. So, in order to reduce and eliminate the influence of these difficulties and to better establish a comparison between chemical results obtained from diverse methods, and in different laboratories, the use of element ratios is recommended, as well as normalized values for example relatively to the mean composition of the continental crust. It is the recommended way, complementing typological classification studies, to attribute provenance.

Thus, the main goals of this work are: (i) the chemical characterization by INAA of the ceramic body of Chinese porcelains found in Lisbon and Coimbra (Portugal) archaeological excavations (15th–17th centuries, Ming–early Qing dynasties); (ii) establishment of correlation between chemical composition and typological/

decorative features; and (iii) identification of the Chinese kilns/region of production.

2. Materials selection and methods

The sample selection methodology for the present work was as following:

Fifty excavation reports were consulted and around 100 boxes of ceramic material found in various parts of Lisbon were selected for detailed macroscopic study. After the inventory of this huge amount of material, about 50 shards of different objects were selected for compositional analysis. Thus the selection took into account the representativeness of major historic-stylistic-chronological-decorative features macroscopically identified, and also the potential production centers attribution and historic problematic.

The materials studied comprise samples of Chinese porcelain (15th–17th cent.) selected from archaeological findings from Central Lisbon excavations (yielded by the company Era Arqueologia SA) and Coimbra excavations (at the Museum of Santa Clara a Velha). Samples from the National Museum of Ancient Art collection, as well as from excavations taken in this Museum were also studied.

In Table 1 together with photograph, sample reference and archaeological site, the typological/stylistic/visual data are presented, as well as geographical and chronological frameworks.

For the study of compositional ceramic body of porcelain, sampling was conducted with a diamond drill with a small diameter (2 mm $< \emptyset <$ 5 mm), which obtained cores depends on the thickness of the fragments. This was done to avoid any contamination resulting from the composition of the glaze and decoration, as well as from the extraction tool itself (Fig. 1). It is important to enhance that only for a few shards it was possible to obtain appropriate cores to further analyses. So, only 24 shards were sampled for analysis, because of the thinness and hardness of most of them.

Chemical analyses were done by instrumental neutron activation analyses (INAA), determining major and trace elements contents with very good accuracy and precision (in general <5%). Core samples were ground into a fine powder in an agate mortar and then dried in an oven at 100 °C for 24 h and stored in desiccators until the samples can be weighed. Irradiations were done in the core grid of the Portuguese Research Reactor (Sacavém), as neutron source. GSD-9 (sediment) and GSS-1 (soil) of the "Institute of Geophysical and Geochemical Prospecting" (IGGE) were used as reference materials. The reference values were taken from data tabulated by Govindaraju (1994). The following elements were determined: Na, K, Mn, Fe, Sc, Cr, Co, Zn, As, Ga, Br, Sb, Rb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Ta, Th, U. Samples and standards were irradiated together in the core grid of the Portuguese Research Reactor (ITN, Sacavém) for 2 min (short irradiation) and 7 h (longer irradiation). The irradiations are carried out in two positions: A short, pneumatic-tube irradiation is 2 min long, at a thermal neutron flux of 2.6E12 n/cm^2/s; the long irradiation is 7 h long, at a thermal neutron flux of 4.0E12 n/cm^2/s, epithermal 3.7E10 n/cm^2/s and fast flux of 1.6E10 n/cm^2/s. The gamma-ray analysis is performed using a Ge γ spectrometer consisting of a 150 cm^3 coaxial detector and a low energy photon detector (LEPD), connected through Canberra 2020 amplifiers to Accuspec B (Canberra) multi-channel analyser. This system has a FWHM of 1.9 keV at 1.33 MeV (coaxial Ge detector), of 300 eV at 5.9 keV and of 550 eV at 122 keV (LEPD) (more details can be found in Dias and Prudêncio, 2007).

A multivariate statistical analysis of chemical data was done by using the Statistica data analysis software system (StatSoft, Inc., 2011).

Table 1
Photographs and description of studied Chinese blue-and-white porcelain samples.
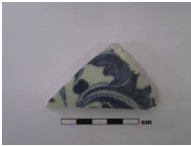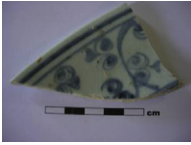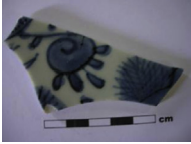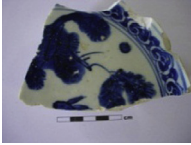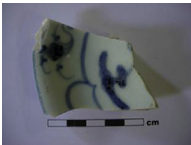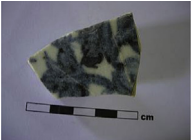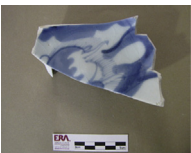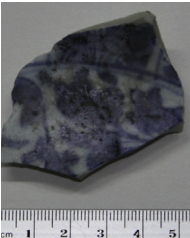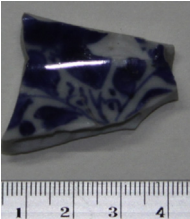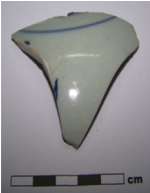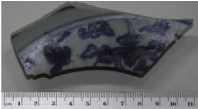
Photo	Sample ref.	Archaeological site	Decoration/chronology
	A8/016	*National Museum of Ancient Art* Lisbon, Portugal	Chinese; late 15th cent–early 16th cent.
	A8/021	*National Museum of Ancient Art* Lisbon, Portugal	Chinese; 2nd half 16th cent.
	A8/022	*National Museum of Ancient Art* Lisbon, Portugal	Chinese; 16th cent. (beginning)
	A8/458	*R. Madalena* Lisbon, Portugal	Chinese; 16th century (1st quarter) Zhengde? (1506–1521) or Wanli? (1573–1619)
	A8/459	*R. Madalena* Lisbon, Portugal	Chinese "Wanli" piece; 1573–1619?
	A8/461	*Rua de O Século,* Lisbon, Portugal	Chinese; 16th century (half). Imported from Persia? Zhengde? Jiajing?
	A8/465	*Rua da Saudade/Beco da Achada* Lisbon, Portugal	Chinese; 16th–17th cent. (not very common)
	A8/466	*Rua da Saudade* Lisbon, Portugal	Chinese; 1st half 16th cent. (1540?) Very refine piece Beaded leaf plum/winding/continuous
	A8/467	*Rua da Saudade/Calçada do Conde de Penafiel,* Lisbon, Portugal	Chinese "Wanli" piece; 1573–1619?

Table 1 (*continued*)

Photo	Sample ref.	Archaeological site	Decoration/chronology
	A8/469	*R. do Caldal de S. José* Lisbon, Portugal	Chinese; 16th century (3rd quarter?) Jiajing? (1522–1566) or later Decoration with horse
	A8/470	*R. do Caldal de S. José* Lisbon, Portugal	Chinese; 1st half 16th cent. Different blue tone
	A8/478	*R. Entremuros do Mirante* Lisbon, Portugal	Chinese; 16th cent. With Chang Ming Fu Gui brand (wishes for longevity, wealth and honor)
	A8/479	*Rua do Instituto Bacteriológico* Lisbon, Portugal	Chinese; 16th century; middle/3rd quarter (with peaches)
	A8/480	*Rua do Instituto Bacteriológico* Lisbon, Portugal	Chinese; 16th century; 3rd quarter
	A8/481	*Rua do Instituto Bacteriológico* Lisbon, Portugal	Chinese; 16th century; 3rd quarter (with brand and lotus flowers)
	A8/482	*Rua do Instituto Bacteriológico* Lisbon, Portugal	Chinese; Late 15th cent–early 16th cent.
	A10/079	*Largo de santos*, n° 11 Lisbon, Portugal	Chinese; Ming dynasty. With peaches
	A10/080	*Largo de santos*, n° 11 Lisbon, Portugal	Japonese? ("da" inscription)

Table 1 (*continued*)

Photo	Sample ref.	Archaeological site	Decoration/chronology
	A10/081	*Rua Augusta* (*edifício Benetton*) Lisbon, Portugal	Chinese; 15th cent. Kraak imitation?
	A10/082	*Rua Augusta* (*edifício Benetton*) Lisbon, Portugal	Chinese; 16th cent.? Kraak imitation ?
	A08/085	*Sta. Clara a Velha Monastery* Coimbra, Portugal	Chinese; middle–2nd half 16th cent.
	A08/096	*Sta. Clara a Velha Monastery* Coimbra, Portugal	Chinese; middle–2nd half 16th cent.
	A08/102	*Sta. Clara a Velha Monastery* Coimbra, Portugal	
	A08/103	*Sta. Clara a Velha Monastery* Coimbra, Portugal	1st half 16th cent.

3. Chinese kiln sites

3.1. State of the art overview and scoping study

In the underlying state of the art a description of the compositional features of Chinese kilns for porcelain production, their location and related raw materials is presented, followed by an overview of the main results obtained so far and used methods, tracing a broad picture of the compositional data available. The objective of this is building on the existing data, bringing more insights into the kilns identification of Chinese Porcelain production ordered for the Portuguese market during the Ming dynasty—
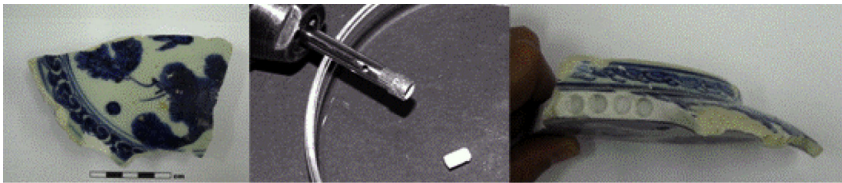

Fig. 1. Photos of sherds analyzed where drilled cores extracted can be seen.

early Qing dynasty (only in a few cases). In this way, the main purposes of this state of the art study are to get compositional background for the current provenance study, giving clues to attain our main goals. Anyway it is important to emphasize that our methodological approach to achieve chemical composition of porcelains ordered for the Portuguese market (INAA), enables to obtain with precision and accuracy almost 30 trace elements, but most of the available data in the literature comprises major and minor elements. So, even it was of great importance to make the state of the art in this chapter, in a compositional comparison point of view it will be limited, but even so, very useful. Especially because major elements have been found not especially useful for accurate provenance in porcelain's production (involving roughly the same raw materials), and more research focuses on the use of trace elements analysis for provenance porcelain wares (Xie et al., 2009; Ma et al., 2012).

3.2. The raw materials

Regarding raw materials for porcelain production in China, two main types were employed in the various regions of China, mostly related to the North and South parts, considering a separation "line" that follows the Nanshan and Qinling hill systems, crossing China from West to East, and then from North of the Huai river and West toward Tibet, that is an imaginary line that occurs across the Nanshan-Jinling divide, reflecting on the basis of a plate tectonic theory, that North and South China were separate land masses that came together on the Triassic (Wood, 1999, 2000; Yin et al., 2011). Undoubtedly the available raw materials on both parts for porcelain production are responsible for the existing variation in appearance of the main ware types and location of the kilns (Tite et al., 2012).

Northern China clays are different from those in the south, being clay rich minerals, mostly deriving from sedimentary secondary clay, especially in Henan, Hebei, Shaanxi and Shandong provinces, and they are often associated with coal deposits. Considering the nature of the clays, this raw material is more heterogenous in a mineralogical, thus chemical, point of view. The nature of the clays (feldspar, quartz, calcite and dolomite), together with other feldspar rich materials, in Hebei, Henan and Shaanxi, brings that northern porcelain bodies are rich in alumina and are called "clay" or "feldspar-clay" porcelains. Some are richer in carbonates (calcite and/or dolomite), and others in feldspars, that are used as flux. Sometimes several types of clay may be used together, some kind of refractory clay is the main constituent of all northern porcelain bodies. In this way, the quality and inherent characteristics of each kiln products depend on the nature and mixture of local raw materials, producing buff-firing opaque stoneware to white translucent porcelains.

On the other hand, South China clays are originated from deeply weathered and/or hydrothermally altered acidic volcanic and intrusive igneous rocks (Tite et al., 2012). So, these southern raw materials mainly formed from igneous rocks are not as rich in true clays as northern ones, containing larger amounts of fine quartz and secondary potassium mica (Wood, 1999), being referred as "porcelain stone". The use of porcelain stone as raw material was indeed a decisive issue in the development of Chinese porcelain, as it is very suitable for making porcelain, and abundant in all southern provinces of China. It is a rock composed mainly of quartz and sericite (fine-particled hydromuscovite) and is plastic like kaolin and fusible like feldspar, and it can be transformed, after being shaped and fired, into porcelain. The mineral composition varies according to the degree of weathering, and will contain a small amount of either feldspar or kaolin. In general highly weathered materials are usually used for making the porcelain body, and poorly weathered for making the porcelain glaze. The presence of sericite makes the difference as it acts as a flux but it also disperses more easily than feldspar, reacts very easily at a high temperature with feldspar and kaolinite, forming a uniformly dispersed vitreous material, increasing density of vitrification and translucency of the porcelain, characteristic of Jingdezhen porcelain (Yanyi, 1987). The porcelain stone used at the major production center of Jingdezhen consisted of a mixture of quartz, secondary mica and sodium feldspar (albite) (Tite et al., 1984). Indeed this kind of raw material is spread all over the southern China provinces of Zhejiang, Jiangxi, Fujian, Jiangsu and southern Anhui, and is formed from pegmatite or other quartz-feldspar rocks through the action of weathering and sericitization by hydrothermal fluids during late stages of volcanic processes. At the different kilns of those provinces and along dynasties, differences occurred mainly due to the diversification of the resource of porcelain stones used, as well as differences in management and working practices specially from Yuan to Ming and Qing dynasties, with different ware quality.

At Yuan dynasty a large scale production arisen and porcelain stone alone was no longer able to achieve the technical requirements, and so kaolin was added to the body, marking an important progress in porcelain manufacturing technology, with changes in firing temperature, kiln construction, kiln furniture and kiln loading. As a consequence the alumina content increases at the Jingdezhen porcelain from Yuan dynasty ($\sim$22%). In the Ming dynasty the situation was similar ($\sim$26%), and in the Qing dynasty Al_2O_3 content rising to 30% (Yanyi, 1987). Considering the known kilns producing for the diverse dynasties, variations in the porcelain stone used have certainly occurred, as well as, in the working practices, resulting in different qualities of wares.

Undoubtedly available raw material played an important role in the development of traditional porcelain in the South of China. Other authors (Yap and Hua, 1992) have also analyzed the available raw materials for making Jingdezhen porcelain bodies during the Five dynasties (907–960), Song dynasty (960–1280), Yuan dynasty (1280–1368), Ming dynasty (1368–1644), and Qing dynasty (1644–1911) and their comparison with related porcelain body. In a chemical point of view good differentiation between the various dynasties was achieved, pointing to the use of different raw materials in different periods, as expected, as well as the use of mixtures of kaolin and porcelain stone (Yuan dynasty). Another important result was the establishment that the percentage of silica in the porcelain body decreases and that alumina increases as a function of time, with the exception of the porcelain of the Yuan and Ming dynasties, when this trend was reversed. For the Ming dynasty the mean concentration of each chemical element analyzed for Jingdezhen porcelains was of SiO_2 − 74.04%; Al_2O_3 − 19.58%; Fe_2O_3 − 0.96%; K_2O − 3.44%; Na_2O − 1.29%; Cao − 0.61%; MgO − 0.21% (Yap and Hua, 1992). Indeed, a development occurred in the production procedure in southern potter's, particularly of Jingdezhen kilns by varying the clay to rock ratios in the original body recipes. At these kilns the use of kaolin in late 15th and 16th centuries reaches useful amounts of the material, and from 17th onwards kaolin became increasingly important in porcelain recipes. At other southern porcelain kilns kaolin was used in lower amounts or even non-used, consisting the bodies mainly of porcelain stone (Wood, 1999).

As mentioned above, raw materials of southern wares were much closer to "rocks" than to "clays", especially to weathered igneous rocks (Wood, 1999). So, regarding the raw materials available and suitable for porcelain production in China, it is important to emphasize that kaolin deposits in North and South differ, and so generally speaking two main types of porcelain body was produced, on one hand the northern china kaolinitic clays are sedimentary deposits, richer in alumina ($\sim$40%) being much plastic materials and very refractory in firing (Yanyi, 1987). On the other

hand, kaolinitic rocks from southern China are felsic, or porcelain stones rich in residual quartz, poor in alumina (~20%), being less plastic and refractory (Tite, 2008; Yanyi, 1987; Yin et al., 2011). Concerning the iron content, Tite et al., 2012, enhances that sometimes stoneware clays with relatively high iron contents, which in an oxidizing atmosphere would result in red-firing pots, sometimes they were used alone, or mixed with porcelain stone; in South China kilns iron contents may vary from 0.6 to rich 5.2%, but the lower amounts occur in Jiangxi province (where Jingdezhen kilns are located) in contrast with higher iron contents in Zhejiang province kilns (Tite et al., 2012).

The observed contrast between northern and southern raw materials is mainly due to geological differences than to preferences of the Chinese potters.

3.3. The most well-known kilns (north and south)

Although the most famous ancient Chinese white porcelain was produced at Xing kiln, Ding kiln and Jingxing kiln in northern China, particularly in the Song dynasty (AD 960–1279), the more widespread ancient Chinese white porcelains were produced in southern China, particularly at Jingdezhen from the Yuan (AD 1271–1368) to the Ming dynasties (AD 1368–1644). Considering that the Ming dynasty lasted 276 years and had 17 emperors, necessarily technological and recipes changes occurred along those different periods, as well as a wider range in the raw materials resources exploitation.

Here it will be especially emphasized the compositional characterization of southern kilns, the most important porcelains producers for the overseas market during Ming dynasty.

3.3.1. Southern China kilns

Jingdezhen has been one of the most important porcelain production center in China from 13th to 19th century, so several authors have devoted to their study.

Elemental characterization of ancient Chinese porcelain from Jingdezhen was performed by INAA (Xie et al., 2009). These authors considered, on one hand the Yuang dynasty, and on the other hand the Ming dynasty, and within this latter, the Hongwu era (AD 1368–1398), Yongle-Xuande era (AD 1403–1435), Zhengtong-Tianshun era (AD 1436–1464), and Chenghua-Zhengde era (AD 1465–1521). They found that the average value of Fe_2O_3 in porcelain bodies of the Yuan dynasty is $1.39 \pm 0.33\%$, while that of the Ming dynasty is $0.86 \pm 0.19\%$ (less Fe in porcelain body implies purer white body). According with Xie et al., 2009, the concentrations of Fe and Na are the best fingerprints to classify, in a chronological point of view, ancient Chinese white porcelains into the Yuan and Ming dynasties, pointing to a change in the raw materials resource between those two dynasties, presenting Yuan shards higher amounts of Na, Fe, U, Yb, Ta, Rb and Cs and lower of Ba, then Ming ones.

Yu and Miao (1997) also studied ancient (Yuan, Ming and Qing dynasties) blue and white porcelains from the Jingdezhen of Jiangxi Province, Yuxi and Jianshui kilns of Yunnan Province and Pinghe kilns of Fujian Province. Regarding results obtained by these authors for Ming porcelains, it was possible to observe a chemical similarity between Yuxi and Jianshui kilns, and a differentiation from late Ming Pinghe kilns (Yu and Miao, 1997). In later studies the same authors (Yu and Miao, 1998) reinforce the idea of kilns similarity in Ming period, and also they enhance that the used raw materials did not change along Qing dynasties, in the three studied periods (Kangxi, Yongzheng and Qialong). Cheng et al., 2002 also studied Jingdezhen material, particularly from the Kuan along the Yuan, Ming and Qing dynasties. Special attention was made to Ming dynasty (Xuande, Chenghua and Jiajing), as in the diverse emperor

periods differences may occur, as a result of the different mineral resources used and of the preparation procedure of body. It was noticed that Al_2O_3 increase largely in the Qing dynasty, due to the increase of kaolin used in the body (to enhance mechanical strength and widen the firing temperature range). Also some differences were observed within the Ming dynasty, according with the different emperor, such as the lower content of CaO in the body of Chenghua period. Another important observation is related with the inhomogeneity of raw material used at Jingdezhen, as there are discrepancies of 5–10% for the contents of Al_2O_3, K_2O, CaO and Fe_2O_3 among the different samples made in the same emperor period. It was also found that contents measured may vary between 2% and 5% within the same shard resulting, according with authors, of the non-uniformity of material (Cheng et al., 2002). Other samples from the Imperial Factory at Zhushan, Jingdezhen, were studied by Wu et al. (2000). Chemical composition allowed a reasonable separation between the groups of imperial production of Yuan dynasty (JYI), Ming dynasty (JMI), Yuan common ware (JYC) and imperial Qing dynasty (JQI). Qing dynasty porcelains have higher contents of Al, Mn, Cu and lower of Si, Pb, Ba and Cr, relatively to all the others. A change of recipes occurred along dynasties. Owing to improvements in firing conditions, the firing temperature of Blue and White porcelain during the Qing dynasty (~1300 °C) would be higher than that in the Yuan and Ming periods (~1250 °C), and as a consequence also a change in the raw materials might have occurred. Yuan and Ming have more similarity, assisting in Qing materials to an increase of kaolin in ceramic bodies. Higher proportions of kaolin, with high Al concentration, were added to the sample bodies, thus explaining the variations in trace elements, like Mn, Pb, Ba and Cr concentration, between the groups. Although major element composition from Yuan to Ming dynasty remains unchanged, and considering that JYI has higher Ti content, this may be related with diverse raw materials. Also the lower Fe content in Ming and Qing dynasties porcelains compared with those from Yuan, may be related with the production process, of remove of iron as it is a coloring agent in clay from southern China. So, this study demonstrates the evolution of raw materials processing techniques and the origin of raw materials in Jingdezhen.

Chemical ratios for discriminating the Jingdezhen blue and white porcelains along dynasties, from Yuan, Ming and Qing were established (Leung and Luo, 2000). In this way, samples from the Yuan were divided according production, one comprising wares not produced for the emperor (Min Yao) and the other producing for the emperor (Guan Yao), with respectively Cr/Rb > 0.3 and Zr/Rb > 0.72; and Cr/Rb > 0.3 and Zr/Rb < 0.58. Samples from the Qing dynasty have Cr/Rb < 0.3. Ming samples are more spread, having the majority (~90%) 0.58 < Zr/Rb < 0.72. In this work it was also presented the ratios obtained for the same dynasties in Dehua kilns: Ming are located in an area where Rb/Y − 1.81Zr/Y < 0.82; and the samples from Song to Yuan dynasties in the area where Rb/Y − 1.81Zr/Y > 0.82 (Leung and Luo, 2000). Also SiO_2/Al_2O_3 wt% ratios were calculated for Song-Yuan Qingbai bodies and Yuan underglaze blue porcelain from Jingdezhen by Tite et al. (2012), and they were >5:1.

Other samples of bodies and glazes of Chinese porcelain of the Yuan dynasty from Jingdezhen, as well as samples of porcelain-stone and glaze-stone from the same region were studied by electron microprobe analysis and X-ray diffraction (Tite et al., 1984). The results indicate that the porcelain bodies were made using a kaolinized porcelain-stone whereas the underglaze blue porcelain bodies were prepared by the addition of kaolin to a kaolinite-free porcelain-stone. In both cases, the glazes were made by mixing 'glaze-ash' with the porcelain stone used to make the bodies (Tite et al., 1984). An important aspect of those results, is that, again, is

emphasized the possible change from the use of kaolinized porcelain-stone to that of mixture of kaolin and porcelain-stone from the Yuan dynasty.

Another important production center comprises the Dehua county located in central Fujian Province on the southeast coast of China. Dehua white porcelain production was largely exported to Europe in the Ming dynasty (1368−1644 A.D.) (Li et al., 2011). Again in Dehua ware the high whiteness is due to the low content of the coloring element (Fe_2O_3), that together with higher K_2O content in body (more amount of glass phase) increases the translucency of body, forming the special features of "ivory-white"/"blanc-de-Chine". The unusual low proportions of iron allowed to fire porcelains in oxidation to about 1280 °C, producing a superb ivory-white material (Wood, 1999). The success of Dehua porcelain is mainly due to the availability of raw material, an unusual purity of the local porcelain stone, in different stages of weathering, useful for both body (heavily weathered) and glaze (lightly weathered and feldspar richer) preparation. Here it was only used the local porcelain stone without adding other materials, the called "Unitary formula" (Li et al., 2011).

In a more recent work (Ma et al., 2012) the chemical composition of Chinese late Ming export blue-and-white porcelains from Zhangzhou and Jingdezhen kilns, as well as of possible clay sources, is used to establish provenance of Chinese porcelain, especially by using rare earth elements distribution curves. Undeniably in the late Ming dynasty, two major production areas in China were identified, Jingdezhen and the southeast coast, particularly the Zhangzhou kilns, around Pinghe in the Fujian province. According with some authors (Harisson, 1979; Rinaldi, 1989) two main differences occur with these two productions: (i) the high and middle quality export blue-and-white porcelains, the typical "kraak ware" were produced for the European market in Jingdezhen; (ii) the middle and low quality export blue-and-white porcelains − "swatow", were manufactured for the Japanese and southeast Asian markets. Moreover other authors (Pei, 2002; Cao, 2002) suggest that in Jingdezhen also low quality porcelains were produced, and on the contrary, also at Zhangzhou kilns "kraak ware" was produced. A contribution to overcoming such a discrepancy of opinions was made by Ma et al. (2012) work, with a chemical distinction between late Ming dynasty Chinese export blue-and-white porcelains of both Zhangzhou and Jingdezhen kilns, and identification of clay raw materials, enhancing the role of trace elements, especially of rare earth elements (REE). REE are in higher amounts in Zhangzhou kilns, as well as a higher REE fractionating was found, together with negative Ce anomalies; on the other hand Jingdezhen kiln samples have lower concentrations of REE, positive Ce anomaly and higher negative Eu anomaly. In the Ming dynasty the export porcelain from the Jingdezhen kilns belongs to the "folk kiln" category (families run), rather than an official one, diversifying the productions. An important achievement of this work is related with the use of rare earth elements as important fingerprints in provenance of porcelain wares, as they are very stable and not easily changed during production and burial.

3.3.2. Northern China kilns

Considering the reputation of the Ding kiln (Hebei province), several imitations were done, namely from Guantai and Jiexiu kilns during the Song dynasty (960−1279 AD). Nevertheless chemical analysis was able to differentiate those three kilns: Guantai porcelain kilns higher contents of Ti, Sc, V, Cr, Zr, Cs, Y, REE, and higher negative Eu anomaly; Jiexiu kilns have lower contents of these elements; and Ding kiln present an intermediate composition. Trace element ratios, particularly Nb/Ta, Y/Ho and Zr/Hf also helped in that differentiation (Li et al., 2005).

3.3.3. North versus South China kilns

Indeed, due to diverse geological contexts, as mentioned above, important geochemical and mineralogical differences occur between northern and southern kilns, and also within them. Several studies enhances this fact, like the compositional characterization performed by Li et al. (2003) on ancient porcelains from the Song-Yuan period, which enables to distinguish productions from Cizhou (Hebei province) and Longquanwu (Hebei Province) from the North and Jizhou (Jiangxi Province) from the South; and also within periods in Cizhou kiln (Guantai production center). In that study a clear differentiation of the southern Jizhou kiln was obtained, as they have higher contents of Rb and Ba, and lower of Sr, pointing to the use of porcelain stone, rich in sericite; on the other hand northern Lonquanwu kiln has higher Sr, Ba, Na contents, sometimes Eu/Eu* > 1 and low Rb/Sr ratio, suggesting the adding of feldspar in mixing the paste; Cizhou kiln has in general lower levels of Sr, Ba and Rb, pointing to the use of local kaolinite, and subtle differences were found along periods, with ceramics from Yuan dynasty having lower contents of Ti, Cr, Zr, Hf, Th, Nb and Ta, and higher of Rb, Ba and total REE (Li et al., 2003). Also Leung and Luo (2000) research contributes to northern−southern differentiation, by studying porcelains from southern kilns Jingdezhen (Jiangxi Province) and Dehua (Fujian Province), and from northern kilns Xing, Ding and Cizhou (Hebei Province), which were chemically distinguished by considering element ratios, namely Zr/Rb = 1.29 and/or 0.79 (Rb/Y + Zr/Y) = 6.00. Considering this, Jingdezhen porcelains have Zr/Rb < 1.29 and 0.79 (Rb/Y + Zr/Y) > 6.00; Dehua porcelains have 0.79 (Rb/Y + Zr/Y) < 6.00; and Hebei porcelains have Zr/Rb > 1.29.

4. Results and discussion

The chemical results obtained by INAA for the studied porcelain samples from Lisbon and Coimbra in this work, are given in Table 2. Significant chemical variations were found. Before any interpretation leading to the establishment of provenance, careful attention was paid to eventual discrepancies due to the different number of samples analyzed from each site (higher number of samples from Lisbon), and also to the different thickness of the ceramic bodies (0.2 cm < Lisbon Ø < 2.2 cm; 0.2 cm < Coimbra Ø < 0.9 cm).

Among the elements obtained by INAA some can be used as indicators of the origin (provenance) of the raw material. These elements are the so called immobile and/or incompatible elements and are also resistant to the effects of manufacturing of the pottery and/or post-depositional processes. Considering the elements we have determined, we may use Zr, Hf, Ta, Th, U and REE (and also some of the first row transition elements Sc, Cr, Co and Zn). These chemical components stay stable after the formation of the raw materials (clay, silt, sand and rock) and refer to the origin of the applied natural materials. Another important group of chemical components is less resistant to the post-manufacturing effects (e.g. washing of the raw clay, drying, firing, application for cooking or liquid's storage, burial in soil forming conditions) because they are mobile/compatible elements. From the obtained ones by INAA, these are the K and Na from the major elements and Cs, Rb and Ba from trace elements.

Considering all porcelains studied in this work (Table 1) and analyzed chemical elements (Table 2), five samples (all from Lisbon sites, three of them from the same site) are detachable from all the others in several chemical elements (Fig. 2): (1) sample A8/465 has much lower contents of Na, Rb, Cs, and much higher of Zr and REE and Hf, and more pronounced negative Ce anomaly (this porcelain may have been produced with raw materials enriched in heavy minerals, as they tend to accommodate more REE, Zr and Hf; and with lower feldspar contents due to lower Na, Rb and Cs). This chemical differentiations are rather interesting, as in a typological/

Table 2
Concentration of elements obtained by INAA for Lisbon and Coimbra samples of Chinese Porcelain ordered for the Portuguese market during the 16th–17th cent. Major elements (Na$_2$O, K$_2$O, Fe$_2$O$_3$T) in % and trace elements in µg/g (ppm).

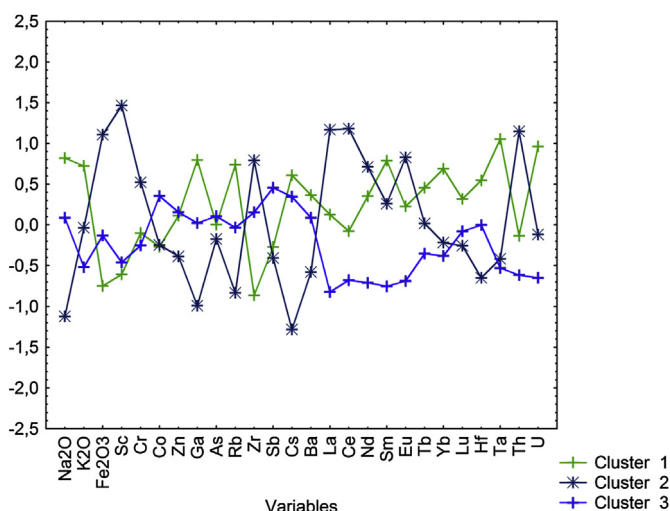| ITN reference (location)	Na$_2$O	K$_2$O	Fe$_2$O$_3$T	Sc	Cr	Co	Zn	Ga	As	Rb	Zr	Sb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Hf	Ta	Th	U
A8/016 (Lisbon)	0.746	3.5	1.4	4.35	7.39	6.1	53	22.3	0.695	256	61.19	0.638	24.6	107.3	22.4	32.0	15.9	3.97	0.668	0.629	1.75	0.204	2.42	3.77	14.8	6.12
A8/021 (Lisbon)	0.984	3.58	1	3.46	11.9	7.06	72.6	32.1	0.923	269	88.62	6.25	34.9	173.2	18.7	17.7	4.15	0.731	0.804	2.15	0.218	3.54	5.51	8.15	5.54
A8/022 (Lisbon)	0.746	3.5	1.5	4.66	12.1	7.22	73.2	24.8	1.14	255	67.29	1.51	25.9	116.7	21.6	36.1	16.0	3.8	0.661	0.721	2.08	0.245	2.52	3.96	16	5.75
A8/458 (Lisbon)	0.59	3.75	1.31	4.57	12.9	18.3	161	31.4	2.91	327	77.74	1.57	31.6	95.38	22.5	37.7	21.3	5.33	0.899	1.05	2.46	0.222	3.53	6.91	19.1	6.07
A8/459 (Lisbon)	1.43	3.03	1.35	2.62	9.27	38.4	106	28.3	1.03	257	67.92	2.46	39	194.4	18.1	35.7	17.2	4.07	0.691	0.637	1.61	0.198	2.79	3.17	9.79	4.7
A8/461 (Lisbon)	1.78	3.5	0.819	2.3	5.00	26.2	63	30.3	2	357	20.90	1.47	49.6	123.0	14.1	22.6	16.0	4.43	0.586	0.811	2.39	0.233	3.33	8.36	10.4	7.95
A8/465 (Lisbon)	0.125	3.74	1.38	4.58	12.4	11.3	97.8	19.1	0.01	210	118.7	0.306	6.84	153.7	76.4	46.4	64.6	12.1	1.74	1.81	6.4	0.892	4.74	2.26	19.3	2.55
A8/466 (Lisbon)	1.47	3.61	0.844	2.52	9.24	6.61	151	27.1	0.01	337	77.16	0.82	48	110.7	12.8	18.0	10.9	3.53	0.514	0.816	2.13	0.214	3.12	4.43	11.2	5.22
A8/467 (Lisbon)	1.8	3.05	1.14	2.93	13.3	9.47	98	38.9	0.01	362	22.09	2.5	49.6	85.67	11.3	18.2	9.9	3.44	0.439	0.667	2.01	0.213	2.56	4.46	9.66	5.75
A8/469 (Lisbon)	1.54	4.21	1.14	3.38	12.7	11.3	102	35.7	1.64	368	59.54	1.11	44.8	200.7	22.1	32.1	18.6	5.1	0.786	1.04	2.85	0.264	3.73	7.44	13.1	6.63
A8/470 (Lisbon)	0.514	3.32	1.44	4.69	23.7	23.1	84.2	23.1	1.7	300	75.63	1.11	32.8	139.7	25.7	37.0	20.9	4.22	0.906	0.791	2.23	0.234	2.65	5.97	15.4	5.9
A8/478 (Lisbon)	1.04	3.31	1.02	3.33	13.9	13.3	89.6	29.1	3.93	344	57.80	2.4	51.5	140.1	12.8	19.1	11.9	3.34	0.651	0.962	2.31	0.234	3.82	4.97	12.2	4.26
A8/479 (Lisbon)	2.04	3.50	1.11	3.04	16.8	22	132	33.5	1.28	365	39.66	2.01	49.8	160.9	18.1	32.9	19.5	4.84	0.82	0.829	2.76	0.247	3.36	7.96	11.4	6.8
A8/480 (Lisbon)	1.17	3.29	1.6	3.01	12.7	26.2	99.4	23.7	1.47	302	55.06	1.23	44.4	140.2	15.9	24.7	14.3	3.87	0.608	0.729	2.09	0.233	2.95	4.65	11.4	5.33
A8/481 (Lisbon)	1.45	3.32	1.07	2.88	13.3	46.9	70.2	29.6	6.03	271	55.06	1.86	31.8	147.3	19.2	26.7	19.4	4.75	0.715	0.806	2.06	0.184	3.23	4.06	10.5	5.59
A8/482 (Lisbon)	0.991	3.63	2.01	5.33	11.0	15.6	99.5	37.6	1.2	591	55.45	1.03	114	129.8	20.8	36.0	20.3	4.64	0.767	1.13	2.69	0.202	3.14	8.98	16.3	7.18
A10/079 (Lisbon)	1.19	3.27	1.66	5.39	37.9	28.1	64.2	21.9	0.887	215	72.50	2.28	24.2	151.6	24.8	43.8	24.8	5.28	0.932	0.751	1.97	0.235	3.36	2.58	11.7	5.46
A10/080 (Lisbon)	1.68	3.1	1.71	3.81	29.7	51.3	133	40.1	1.25	378	44.39	5.45	41.1	87.50	10.4	23.8	13.2	3.95	0.383	0.835	2.29	0.235	2.7	4.4	11.7	8.99
A10/081 (Lisbon)	1.61	1.96	0.998	2.4	26.2	17.7	52.2	25.7	0.01	252	36.79	2.62	33.6	49.52	5.14	13.3	6.09	2.12	0.24	0.447	1.4	0.151	1.73	3.25	6.62	4.73
A10/082 (Lisbon)	1.58	1.95	0.933	2.51	23.5	13.5	50.3	26.2	0.647	243	25.80	2.01	29.5	38.86	5.73	13.3	5.3	2.24	0.251	0.502	1.46	0.155	1.73	3.08	6.5	5.65
A08/085 (Coimbra)	1.48	3.44	0.912	2.25	20.7	10.5	81.7	37.9	1.9	346	22.83	1.68	42.7	113.9	20.3	22.8	20.6	5.23	0.707	0.779	1.8	0.199	3.32	10.7	8.3	6.92
A08/096 (Coimbra)	1.1	3.52	1.18	3.27	21.8	48.8	461	29.9	1.47	316	45.07	2.02	41.4	191.4	11.9	20.6	12.1	3.09	0.546	0.484	2	0.402	3.28	4.03	5.19	5.86
A08/102 (Coimbra)	1.98	3.59	0.948	2.83	13.9	19.2	350	34.4	2.48	279	28.16	1.76	36.4	125.5	18.2	24.2	19.7	5.38	0.766	0.784	2	0.329	3.18	6.46	10.5	8.83
A08/103 (Coimbra)	1.0	3.79	1.04	3.42	16.6	8.52	105	30.8	0.98	341	48.94	1.46	46.5	227.8	20	30.1	15.7	4.45	0.735	0.846	2.55	0.27	3.39	4.96	14.1	5.06
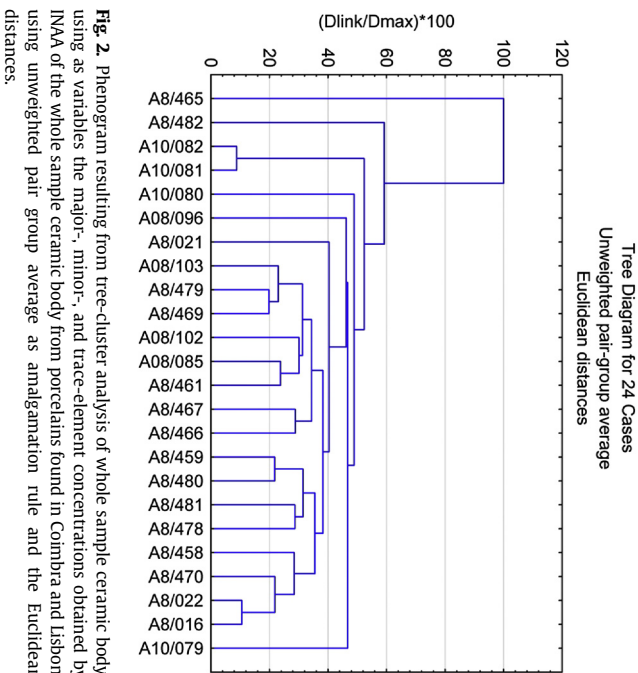
decoration classification point of view, this ceramic it was considered not very usual in the Portuguese market; (2) sample A8/482 has higher contents of Rb, Cs and Ba (pointing to sericite rich materials); (3) samples A10/081 and A10/082 are very similar in a chemical point of view, and are the ones with lower K, Ba, REE (specially light rare earth elements – LREE and middle rare earth elements – MREE), Hf and Th contents, and higher Cr content, more pronounced negative Eu anomalies, and positive Ce anomalies (reflecting Fe-oxid-rich oxic conditions). Again these two samples were differentially classified, as the "kraak" ones; (4) a fifth sample with diverse chemical features is the A10/80 samples, with high Cr, Co and U contents (and also Fe, Sb and Ga), and also positive Ce anomaly and pronounced negative Eu anomaly. This ceramic was also stylistic classified in a different way and has an unusual inscription ("da") maybe pointing to a Japanese origin.

Disregarding the above mentioned samples, chemical compositions suggest the use of different clays, and by using statistic approach (tree diagrams using the unweighted pair-group average as amalgamation rule and the Euclidean distances and the Pearson coefficient as correlation factor; k-means clustering method; principal component analysis; biplots of elements) three main chemical groups were defined (Fig. 3): cluster 1 – comprising three samples from diverse Lisbon sites (A8/461; A8/469; A8/479); cluster 2 includes two of the three samples from MNAA collection (A8/016; A8/22), and three samples from different Lisbon sites (A8/458; A8/470; A10/079); cluster 3 contains all the other eight samples (A8/021; A8/459; A8/466; A8/467; A8/478; A8/480; A8/481; A08/096), all from Lisbon downtown sites (only one from Coimbra).

Several elements differentiates these clusters, specially REE, as cluster 1 has higher REE, especially the heavy ones (HREE), cluster 2 has the higher degree of REE fractionation, clearly enriched in LREE, and relatively higher MREE; and cluster 3 lower REE (REE patterns were obtained after normalization of values to chondrites according with values from Anders and Grevesse, 1989, multiplied by a factor of 1.36, according with Korotev, 1996). In addition to REE differences, other elements differ: (i) cluster 1 has lower amounts of Fe, Sc and Zr (and slightly lower of Co), and higher of Na, K, Ga, Rb, Cs, Ba, Hf, Ta and U; (ii) cluster 2 has lower amounts of Co, Rb, Cs, Ba and Hf (and relatively lower of K, Co and U), and higher of Fe, Sc, Cr, Zr and Th; (iii) cluster 3 has lower amounts of K, Ta, Th and

Fig. 2. Phenogram resulting from tree-cluster analysis of whole sample ceramic body, using as variables the major-, minor-, and trace-element concentrations obtained by INAA of the whole sample ceramic body from porcelains found in Coimbra and Lisbon, using unweighted pair group average as amalgamation rule and the Euclidean distances.

Fig. 3. Plot of means for each cluster obtained by the k-mean clustering method, using as variables the major-, minor-, and trace-element concentrations obtained by INAA of the whole sample ceramic body from porcelains found in Coimbra and Lisbon.

U (and relatively lower of Fe, Sc and Cr), and higher of Co and Sb (and relatively higher of Na, Rb, Cs, Ba, Zr and Hf). These differences surely reflect the distinctive mineralogy and geochemistry of used raw materials, as well as may also be indicative of the use of purification processes made by the potters. In this kind of porcelains usually higher Na and Ba contents, and positive Eu anomalies, point to the feldspar add to the clay during production, as already mentioned by Li et al., 2003. Indeed, cluster 1 has higher Na, K, Rb, Cs, Ba, but no positive Eu anomaly was observed, so it may reflects the resource to sericite like materials (like those from the Jizhou kilns, South China; Li et al., 2003, 2005), also typically enriched in Rb and Ba, and iron depleted; on the other hand the high contents of REE (mainly HREE and MREE) may reflect the presence of heavy minerals, specially garnet, what may indicate that no purification process was done, like levigation (a technique in which the clays are thrown into large tanks for gravitational separations, thus heavy minerals are settled out and finer particles are separated by remaining in the suspension). So, this reinforces the southern provenance for porcelains from cluster 1. In contrast cluster 3, which chemistry may point to a refining process of the original raw material, as lower contents of REE, Ta, Th, U and also Fe, Sc, and Cr were found; the markedly lower concentrations of these elements in porcelains is thus qualitatively consistent with removal of more heavy minerals (Fe and Ti oxides, like magnetite, ilmenite, rutile can have very high concentrations of Ti, Ta, Sc, Cr; apatite, monazite and allanite can have very high concentrations of REE, U and Th; zircons have very high concentrations of Zr, Hf, HREE) by careful levigation of their raw materials, as previously mentioned by some authors (Li et al., 2005), also set by the relatively high content of elements like Cs, clearly related with its concentration in clay minerals and unaffected by removal of heavy minerals. Samples from cluster 2 have higher amounts of Fe, Sc, Cr, Zr, LREE and Th, together with more pronounced Eu anomalies, thus pointing to raw materials enriched in monazite, sphene, zircon and plagioclase.

It is interesting to note, that in a chronological point of view, the above mentioned geochemical and mineralogical features may be related with different production technology procedures. Samples included in cluster 2 correspond to the earlier productions (late 15th–early 16th) which chemistry points to an enrichment in heavy minerals, samples from cluster 1 are from the middle 16th and are very rich in feldspars (that plays an important role in porcelain body as flux), and samples from cluster 3 are late
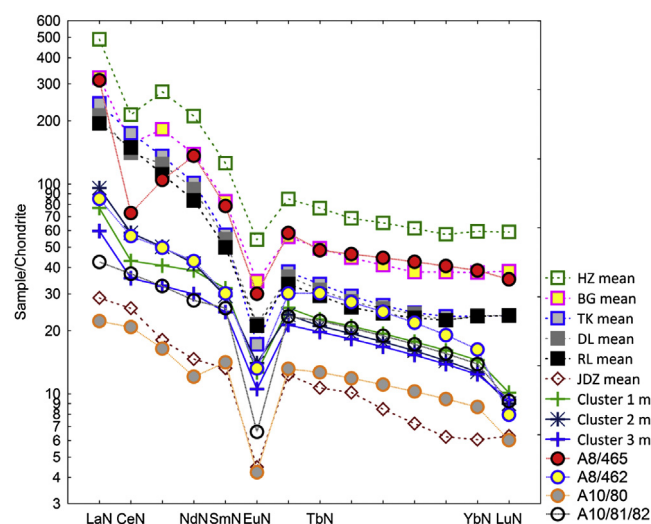
productions (2nd half–early 17th), that, seems to point to porcelains production with refining process of the original raw material, consistent with removal of more heavy minerals. So, we may consider that an increasing improvement of the production procedure occurred from late 15th till 17th cent. Chinese studied porcelains.

In an attempt to better achieve a chemical differentiation between samples, the trace elements were also normalized to the mean composition of the upper continental crust (UCC), as well as to Sc, a lithogenic, immobile and conservative element (Dias and Prudêncio, 2008), so anomalies may be easily recognized and geochemical inferences may be done. It is seen that the trace element compositions of different porcelains are readily distinguished from one another, nevertheless a general tendency was observed in the majority of element concentrations behavior when comparing the chemical composition of the studied porcelains with the estimated composition for the upper continental crust (Rudnick and Gao, 2003), exhibiting variations that generally don't go beyond two times, above and below, the estimated levels for the UCC. The main exception to this general tendency is the accentuated enrichment in Rb, Cs, Ta and U (from 3 times up to 10 times enriched). Enrichments in Zn, Ga, Sb, Tb, Yb and Th relatively to the UCC were also observed. A Rb level about six times enriched and a Cs level of ten times enriched was still observed in one sample (outlier A8/482); an Sb level of about five times enriched in one sample (outlier A10/80). A general depletion of all REE occur in almost all samples (exception outlier A8/465), especially pronounced in the LREE, as well as of Na, Fe, Sc, Cr, As, Zr, Ba and Hf, being more accentuated in Cr and Ba (up to five times). An As level about five times depleted was still observed in one sample (A8/465). The incompatible/compatible element ratios, such as Th/Sc, La/Sc and Th/Co, are especially sensitive to source composition and thus are useful in distinguishing between felsic and mafic sources, respectively associated with micaceous/basic minerals and heavy minerals/intrusive felsic rocks. When plotted against each other Th/Sc vs. La/Sc most of the samples have higher ratios much above those estimated for UCC, probably due to the presence of clay materials with higher incompatible element abundances, clearly suggesting contribution of felsic source (granites) in the genesis of raw materials. The linear tendency that is observed reflects the increase in the contribution of a granite source, particularly for samples of cluster 1.
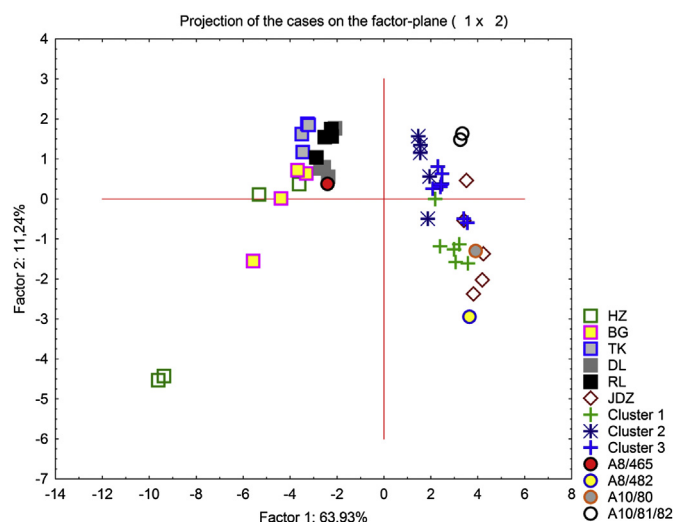
This geochemical approach and comparison with available data for Chinese porcelains and related raw materials enable the establishment of a certain differentiation between samples, to group them and to enhance outliers, and also to reinforce the southern China origin for the samples. Nevertheless, a kiln attribution was difficult, even after comparing with available data (already pointed out in Chapter 3 of this work). Ratios of elements including Zr, Rb, Y, Cu and Cr obtained from XRF analysis have been used by Leung and Luo (2000) to separate the Jingdezhen Blue and white porcelains made during Yuan, Ming and Qing periods and between white porcelain of Jingdezhen, Dehua and Hebei. Indeed our samples obey some of these authors statement, however not completely. So, our samples have a Zr/Rb ratio lower then 1.29, accordingly with Jingdezhen kilns attribution, however, Cr/Rb ratios don't fit with the ones established by these authors for the Ming dynasty, indeed they will match with Qing dynasty (Cr/Rb < 0.3). Another pair of elements used, was the Ta vs W ratio mentioned by Li et al. (2003, 2005), as a good fingerprint of North China kilns (Song dynasty), but we cannot use it as most probably our sample is contaminated with W by the sampler extractor. These authors also enhance other trace elements like Hf vs Zr/Hf to differentiate kilns, but again in our case Zr/Hf ratio is lower (17.86 ± 6.58), than the ratios found for the three studied North

China kilns by Li et al., 2005 for earlier porcelains, even lower then Jiexiu kiln; also K and Na contents are lower in North China. So with this data we again reinforce the southern China origin for our samples. Also the Na and Fe were considered (Xie et al., 2009) the characteristic elements to be used for identifying the date of porcelains, particularly separating the Yuan from the Ming dynasty from the same region (Jingdezhen, South China), however, when plotting our samples, these same chemical features didn't happen, and we didn't find the same Fe_2O_3 mean that was found for Ming dynasty of southern China by Xie et al. (2009) (0.86 ± 0.19%), but a higher one (1.23 ± 0.31% one standard deviation), yet in Na vs Fe_2O_3 graph half of the samples are plotted in the "Ming dynasty area" form Jingdezhen kilns. Considering Yap and Hua (1992) studies of raw materials for making Jingdezhen porcelains from Five to the Qing dynasty, a mean of Na, K and Fe_2O_3 respectively of 1.29, 3.44 and 0.96 is proposed for chemical composition of Ming dynasty porcelains, and our samples are within this range, with 1.25 (±0.49% one standard deviation) for Na, 3.35 (±0.50% one standard deviation) for K and 1.23 (±0.31% one standard deviation) for Fe_2O_3. But iron in our samples has higher contents, as it should be less than 1% and all cases have higher amounts.

An important improvement to our research was the comparisons with trace element composition of shards of Chinese Late Ming export blue-and-white porcelain from Zhangzhou and Jingdezhen kilns, especially the REE behavior (Ma et al., 2012). We have compared our trace elements results, particularly REE, with the available results for six Jingdezhen kilns typically producing Kraak style shards of late Ming, and for five Zhangzhou kiln sites (three kilns from Wuzhai town in Pinghe county: Bei-Gou, Er-Long, Da-Long; and two from Nansheng town in Pinghe county: Hua-Zai-Lou, Tian-Keng) with the finest product quality, representing the kilns specializing in producing export porcelain of late Ming and early Qing dynasty (precisely our chronological range). REE distribution curves easily separate Zhangzhou from Jingdezhen kiln samples, as the first have several times higher concentrations and higher fractionating, and the later has a higher negative Eu anomaly. Also some differences were found within REE behavior of Zhangzhou kiln sites (Ma et al., 2012). The comparison with our samples became interesting, as our two "outlier" samples A10/081

Fig. 5. Component score plot. Projection of the cases on the first and second factor-plane for Zhangzhou kilns' samples, Jingdezhen's samples, each cluster obtained by the k-mean clustering method for studied samples and the identified outliers. (Er-Long kiln-RL; Tian-Keng kiln − TK; Hua-Zai-Lou kiln − HZ; Da-Long kiln − DL; Bei-Gou kiln − BG; Jingdezhen − JDZ).

and A10/082, classified as the "kraak" ones, are also the only ones clearly related with Jingdezhen kilns that typically produced kraak style pottery, with lower amounts of REE, pronounced negative Eu anomaly and positive Ce anomaly. Another "outlier" sample A8/465 is the only one with similar geochemical behavior as the Zhangzhou samples, more likely with Bei-Gou kilns, with higher amounts of REE and higher negative Ce anomaly (Fig. 4). Regarding the other analyzed samples, again it is difficult to ascribe them to specific kilns, even we can state that none of them have became from Zhangzhou kiln sites, what is accordance with a traditional attribution of productions from these later kilns for the Japanese and Southeast Asian market. And on the other hand, it seems that REE and other analyzed trace elements points in some cases to a slightly relationship with Jingdezhen kilns (Fig. 5), even, it seems that we haven't found yet the specific kilns producing for the generality of our analyzed Chinese porcelains.

Combining available data of kiln sites and Chinese porcelains samples ordered for the Portuguese market, especially trace elements, for our attempt to trace their provenance, revealed to be a useful tool, and important geochemical features and relations were found.

5. Conclusions

INAA has been used to determine the elemental composition of the ancient Chinese blue and white porcelain body from Lisbon and Coimbra excavations, thus providing a large amount of valuable information concerning the chemical composition of Chinese porcelain ordered for the Portuguese market. According to the experimental data, the elemental composition of porcelain bodies is possible to be differentiated in three main clusters and five outliers were identified. A general attribution of samples to southern China kilns was achieved, as expected In a chronological point of view, we assist to an increasing improvement of the production procedure from late 15th till the 17th Chinese studied porcelains, as we have cluster 2 comprising earlier productions (late 15th−early 16th) which chemistry points to an enrichment in heavy minerals, cluster 1 including samples from middle 16th very rich in feldspars, both clusters not indicating purification processes, and cluster 3 embracing late productions (2nd half 16th−17th), that, as

Fig. 4. REE distribution curves of Zhangzhou kilns' samples and Jingdezhen's samples, together with means for each cluster obtained by the k-mean clustering method for studied samples and the identified outliers. Elements' means of each group are used for the plot (Er-Long kiln-RL; Tian-Keng kiln − TK; Hua-Zai-Lou kiln − HZ; Da-Long kiln − DL; Bei-Gou kiln − BG; Jingdezhen − JDZ). In this graph the average of C1 chondrites of Evensen et al. (1978) has been used.

previously mentioned points to porcelains production with refining process of the original raw material, consistent with removal of more heavy minerals.

Important achievements were obtained when comparing our chemical data with available data for Jingdezhen and Zhangzhou kiln sites, enhancing the importance in using trace elements, particularly REE, in provenance studies, as they are very stable and not easily changed during production, especially with firing (Trindade et al., 2011) or burial. In the case of some samples a kiln attribution was possible, in a few samples to Zhangzhou kilns and to Jingdezhen kilns. But for the majority of the samples we haven't found yet the specific kilns.

The geochemical behavior overview presented in this work for porcelain samples found in Lisbon and Coimbra intends to be the first phase for further works concerning provenance and kilns attribution of Chinese porcelain ordered for the Portuguese market. The Ming dynasty was a period of great prosperity of white porcelain production representing one of the most important and highest technological level of this kind of production, but widespread China, especially South, in a long lasted period, what makes a real challenge to assign our porcelains to a specific kiln. Most surely ancient Chinese potters had produced many kinds of porcelains in different kiln sites along dynasties, and within Ming dynasty as well. Those kilns surely used clays mined from the local areas and geochemical differences are expected, that together with production techniques (washing, mixing) may provide a chemical signature, allowing their provenance determination. It is our intention in a near future to be able to establish such a comparison enlarging the number of samples from Portuguese excavations and museum collections, as well as, including porcelains with known Chinese kilns assignment. We hope that this work will create the synergies to walk in such direction.

Acknowledgments

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