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Porcelain shards from Portuguese wrecks: Raman spectroscopic analysis of marine archaeological ceramics

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Abstract

Raman spectroscopic analysis of shards recovered from two Portuguese shipwrecks, the *Santo Espirito* (1608) and the *Santa Maria Madre de Deus* (1643), believed to be carrying porcelains of the Ming period have revealed some interesting and novel results that inform historical ideas of porcelain production. The porcelain body of two of the four shards from the *Santa Maria Madre de Deus* were found to contain anatase, a low temperature polymorph of titanium dioxide, and β -wollastonite a mineral characteristic of soft-paste porcelains that are made at medium-temperature firing conditions. Previously, β -wollastonite has been found in a range of sixteenth to nineteenth century European porcelains but this is the first report of its detection in porcelain believed to be from the Ming period. These same shards exhibited unusual spectral features that were attributed to the resonance enhancement of rare earth elements that resulted from excitation using a near-infrared source.

Keywords: Raman spectroscopy, β -wollastonite, Anatase, Porcelain, Ming period

Background

The application of Raman spectroscopy as a non-destructive technique for the analysis and characterisation of ancient ceramics from museums and archaeological excavations [1, 2] has produced extensive literature which extends over several thousand years of civilisation from Egyptian faience of the eighteenth dynasty (ca. 1400 BC) through to the fine European and Chinese porcelains of the fifteenth to nineteenth centuries. The range of materials investigated includes tin-glazed earthenwares, mediaeval terracotta roof tiles, majolica and bone Chinas from which it has been possible to deduce the salient features of the ceramic bodies, glazes and the applied pigments where appropriate [3–7]. The non-destructive analysis of ceramics poses several challenges for spectroscopists because of their composite nature, where the sintered grain and domain sizes range from a few microns to about 500 μ , the presence of crystalline and glassy phases

along with unreacted starting components, and the inhomogeneity of the ceramic matrices arising from diverse processing technologies, firing sequences and kiln temperatures. Where ancient records exist from porcelain factories, the scale of the problem can be assessed; for example, at the Meissen factory in the eighteenth century there were more than five recorded porcelain bodies which were recommended for use at different levels in the firing kilns to account for temperature inhomogeneities [8]. Another problem of particular significance for Raman spectroscopic analysis arises from the recovery of broken ceramics from archaeological excavations, where the assimilation of fluorescent materials from the burial environment has occurred which often has resulted in high levels of background fluorescent emission and resultant poor quality Raman spectral response.

Nevertheless, the opportunity for the application of non-destructive analytical techniques to the characterisation of ceramics from archaeological excavations is an important one when it is appreciated that much of the earlier chemical characterisation reported often involved the complete destruction of the specimen, as in the classic studies of Eccles and Rackham [9], who required the

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sacrifice of a whole cup, saucer or a plate from early porcelain services in the derivation of the chemical composition of early English porcelains.

In the sixteenth and seventeenth centuries, the native European glazed terracotta, tin-glazed earthenware and majolica had to compete unsuccessfully with imports of hard paste (*pate dure*) porcelains from China; the latter had a beautiful translucency, were thinly potted and possessed a white, smooth surface which readily exhibited applied decoration to the maximum effect. The secret was the addition of kaolin to the china paste before firing. It took until the mid-eighteenth century before European china factories such as Sevres, Meissen, Worcester and Chelsea could compete with their soft paste (*pate tendre*, containing calcined bone ash and glass frit) and hard paste (*pate dure*) versions and meet the increasing demand in society for the new ceramics. From 1498, when Vasco de Gama sailed around the Cape of Good Hope, the emergence of Portuguese and Dutch marine exploration gave rise to a vast trade in spices, ceramics and other goods with Asia, and Chinese porcelains of the Ming period (1368–1644) were much desired in Europe. Portuguese carracks and navetas returning home from China were often overloaded and in poor condition after a long and arduous outward voyage and a significant number perished in the stormy and treacherous seas off Southern Africa. It is known that at least 15 large Portuguese ships sank in this area before 1650, from the records of survivors [10]; nine of these have been identified by field archaeologists and two of these form the subject of the current investigation, namely, the *Santo Espirito*, which sank in 1608 in Morgan's Bay, Eastern Cape, and the *Santa Maria Madre de Deus*, which sank in 1643 in Bonza Bay, East London. Both ships were carrying cargoes of Ming porcelain and five shards recovered by marine archaeologists from the wrecks have been made available for Raman spectroscopic analysis.

Experimental

Five Chinese porcelain shards (Fig. 1) from the two Portuguese wrecks, dating from 1608 and 1643, which places the ceramics firmly in the later Ming period (1368–1644) described as Wanli or immediately post-Wanli, were subjected to Raman spectroscopic analysis. The shards form part of the J.A. van Tilburg Collection at the University of Pretoria. Shards #1 to #4, were from the *Santa Maria Madre de Deus* and, shard #5, was from the *Santo Espirito*; the shards presented several differences in appearance and are described below:

1. Greyish white porcelain body with pale blue decoration, 30 mm × 16 mm; unglazed.

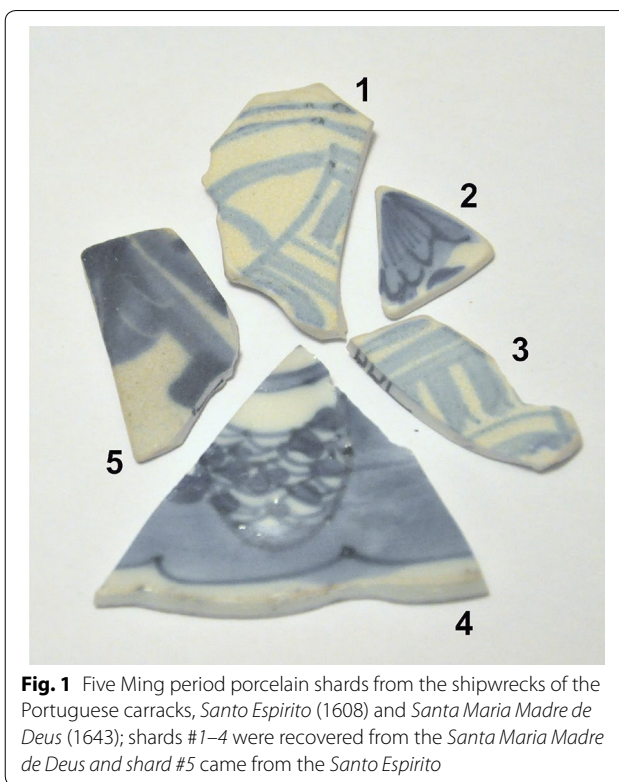


Fig. 1 Five Ming period porcelain shards from the shipwrecks of the Portuguese carracks, *Santo Espirito* (1608) and *Santa Maria Madre de Deus* (1643); shards #1–4 were recovered from the *Santa Maria Madre de Deus* and shard #5 came from the *Santo Espirito*

2. Creamy white porcelain body with pale blue decoration, 15 mm × 13 mm × 15 mm; glazed.
3. Greyish white porcelain body with pale blue decoration, 25 mm × 9 mm; unglazed.
4. White porcelain body with dark blue decoration, 33 mm × 40 mm × 35 mm; glazed.
5. White porcelain body with dark blue decoration, 26 mm × 15 mm; glazed.

Several opportunities for spectral sampling were presented, offering illumination of the blue pigment(s), the glaze and the porcelain body both on the upper and lower surfaces and also on the broken edges of the shards.

Raman spectra were collected using a Renishaw Raman inVia Reflex Microscope (Renishaw plc, Wotton-under-Edge, UK), equipped with an air-cooled charge-coupled device camera. The spectrometer was fitted with holographic notch filters and two gratings (1200 mm per line (visible), 2400 mm per line (near infrared)). The attached microscope was a Leica DM LM and was equipped with three objectives (×50/0.75 NA, ×20/0.40 NA, ×5/0.12 NA) and a trinocular viewer that accommodated a video camera, allowing direct viewing of the sample.

Sample excitation was achieved using a NIR laser (TOPTICA Photonics AG, Graefelfing, Germany) emitting at 785 nm. The spectrometer was controlled using a computer with instrument control software (Renishaw

WiRE Versions 3.0 and 4.2). Spectra were recorded using the 50× objective over the spectral range of 3200–100 cm^{-1} or 1800–100 cm^{-1} with the accumulation of scans, exposure and a laser power modified to suit each sample. Spectra were not corrected for instrument response.

Porcelain manufacture in China

The analysis of archaeological ceramics provides some special challenges because of their composite nature and size range of the microstructural material; sintered grains and domains range from several microns up to about 500 μ . Crystalline and glassy phases can occur together, along with unreacted starting materials and the molecular composition of the porcelain body and of the applied glaze is critically dependent upon the processing technology, firing sequence and kiln temperature. With regard to the latter parameter, inhomogeneity in the temperature of ancient kilns could give rise to variations in molecular composition of the resultant porcelain at the microscopic level.

Porcelain was first made in China during the Song Dynasty (960–1279 AD) and this gave rise to the very desirable, classic blue and white porcelains of the Ming Dynasty (1368–1644 AD); the major production was at Jingdezhen, which was fitted with large wood-burning dragon kilns that could take tens of thousands of items in a single firing. Towards the end of the Ming Dynasty, when the porcelain shards studied here were made, the kilns were modified into ovoid shapes which facilitated the attainment of a higher firing temperature of 1350 °C with the choice of a reducing or oxidising atmosphere. This produced a dramatic effect on both the pigment colours and body of the porcelains; white wares were made from clays that were low in iron, but in the presence of iron, ceramics fired in an oxidising atmosphere were red whilst those fired in a reducing atmosphere were grey.

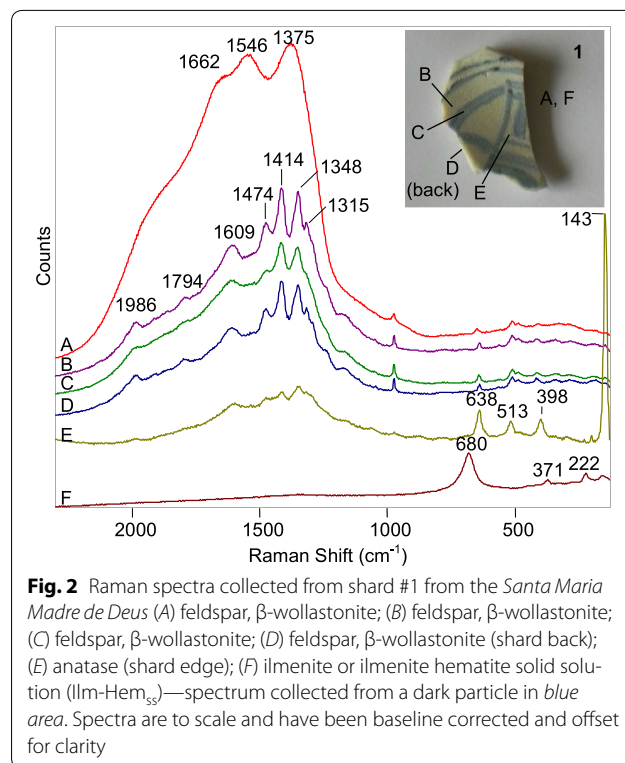
The kaolinite clay used to make porcelain is composed of alumina and silica with added water to confer malleability; on heating to ~500–600 °C water is expelled from the lattice leaving a meta-kaolin phase comprising $2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$. At 925 °C an exothermic reaction results in the formation of a spinel, $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$, where one in four of the silica units are removed from the lattice. Above 1050 °C this structure transforms into mullite, with conversion of the expelled silica into cristobalite; if feldspar is present in the ingredients then this now melts at 1010–1100 °C and dissolves the cristobalite to produce a viscous liquid which cements the quartz crystals together. A decrease in viscosity appears at 1200–1250 °C which results in the filling of the particle interstices. Then finally at 1280 °C, large crystal formation of mullite results in the production of a less viscous state in which the quartz is dissolved—giving a true porcelain. In China,

the availability of a porcelain stone called *petuntse*, which contained a primary clay mineral, sericite, and the aluminosilicate feldspar and quartz, when mixed with an aluminosilicate kaolin clay gave the required ingredients and sustainability of high temperature firing that could produce the beautiful porcelain product that was so much in demand in Europe [11, 12]. A typical composition of hard paste porcelain was kaolin 75%, feldspar (anorthite) 10% and quartz sand 15%.

Results and discussion

The spectroscopic analysis of porcelains can not only determine the molecular composition of the body and glaze but also reveal some information about the production process and kiln firing temperature range in which they were made. Raman spectra of the shards from the early seventeenth century Portuguese shipwrecks, see Figs. 2, 3, 4, 5, 6 and 7, were indicative of several important features of porcelain manufacture as highlighted in the above account; generally, glassy ceramic materials can be classified [13] according to the Q-components of SiO_4 tetrahedra in the material composition:

- Q⁰: monomeric SiO_4 groups, wavenumber range 800–850 cm^{-1} ;
- Q¹: Si_2O_7 groups, wavenumber ~950 cm^{-1} ;
- Q²: silicate chain, Si_3O_9 groups, wavenumber range 1050–1100 cm^{-1} ;



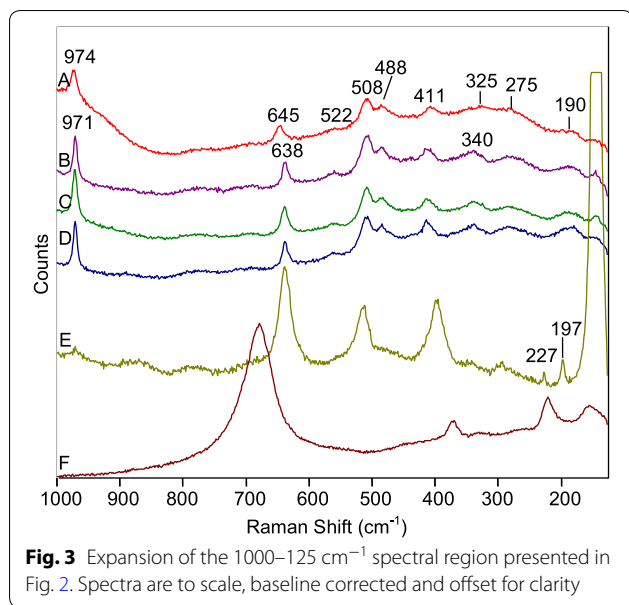


Fig. 3 Expansion of the 1000–125 cm⁻¹ spectral region presented in Fig. 2. Spectra are to scale, baseline corrected and offset for clarity

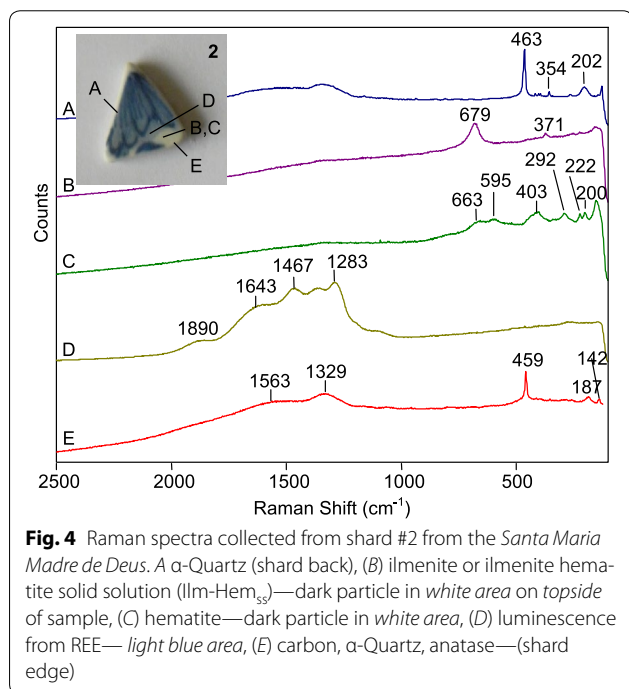


Fig. 4 Raman spectra collected from shard #2 from the *Santa Maria Madre de Deus*. A α -Quartz (shard back), (B) ilmenite or ilmenite hematite solid solution (Ilm-Hem_{ss})—dark particle in white area on topside of sample, (C) hematite—dark particle in white area, (D) luminescence from REE—light blue area, (E) carbon, α -Quartz, anatase—(shard edge)

- Q³: silicate sheets, Si₄O₁₁ groups, wavenumber ~ 1100 cm⁻¹;
- Q⁴: SiO₂ and tectosilicates, wavenumber range 1150–1250 cm⁻¹.

In α -quartz a well-defined structure results in a strong, sharp Raman band, the SiO₂ bending mode of A_{1g} symmetry at 464 cm⁻¹. This broadens in fused silica and

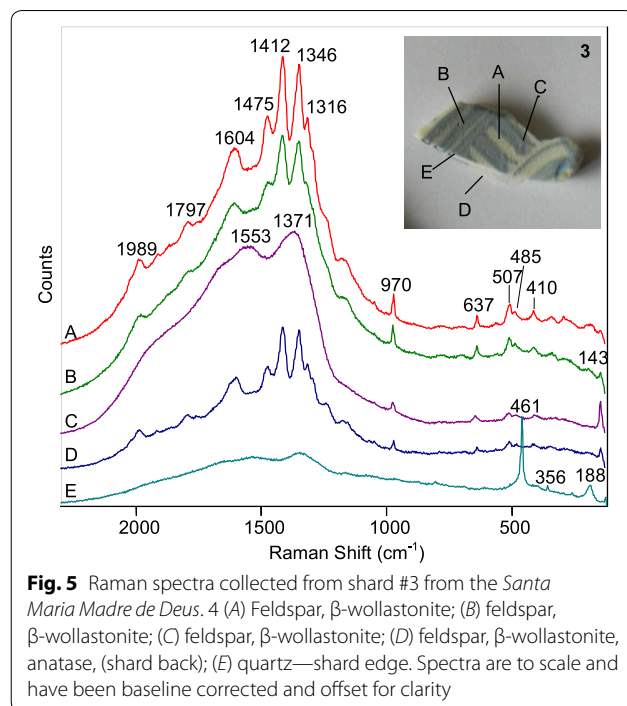
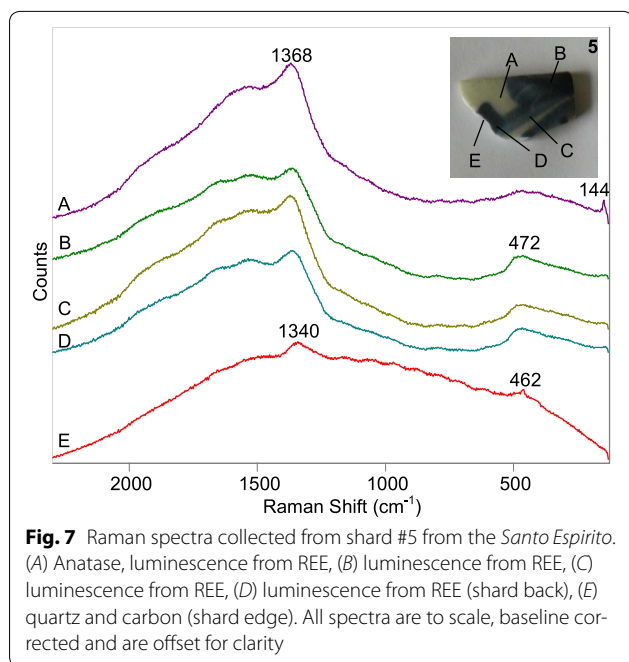
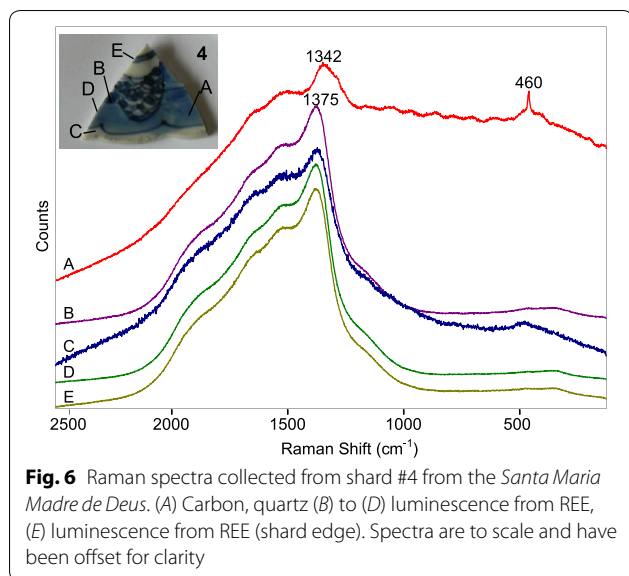


Fig. 5 Raman spectra collected from shard #3 from the *Santa Maria Madre de Deus*. 4 (A) Feldspar, β -wollastonite; (B) feldspar, β -wollastonite; (C) feldspar, β -wollastonite; (D) feldspar, β -wollastonite, anatase, (shard back); (E) quartz—shard edge. Spectra are to scale and have been baseline corrected and offset for clarity

shifts to higher wavenumber when submitted to mechanical stress. A useful parameter for glazed porcelains is the degree of polymerisation (DP) which can be obtained from the relative band intensities of the broad envelopes at 500 and 1000 cm⁻¹; this has been elegantly summarised by Colomban and co-workers [7, 8, 13]. In general, the A₅₀₀:A₁₀₀₀ band intensity ratio is in the range of 0.8–1.1 for soft-paste porcelains which have been fired between 800–900 °C and 1.5–7.0 for hard paste porcelains reflecting their higher firing temperature of between 1100 and 1400 °C.

Shards #1 and #3 from the Santa Maria Madre de Deus

The blue pigment on Ming porcelain has previously been identified [14, 15] as cobalt blue (cobalt aluminate), CoAl₂O₄, which had been known in China from the Tang dynasty but discovered in Europe only in the eighteenth century, when it was known as Thenard’s blue [16]. Here, the Raman spectra of the blue pigment found on the unglazed porcelain shards #1 and #3, shown in Figs. 2, 3 and 5, would suggest the presence of cobalt blue with the characteristic doublet of cobalt aluminate observed at ~488 and 508 cm⁻¹; the spectrum is similar to that of a shard recovered from the wreck of the *São Gonçalo*, which sank in 1630 in Plettenberg Bay, Western Cape [10]. However, it is worthwhile noting that these same features are also observed in the Raman spectra of feldspar minerals and the 488/508 cm⁻¹ doublet is observed in the



spectra collected from both the blue and white areas of the shards (Figs. 2b, 3b, 5). It is therefore more likely that the bands are due to the presence of feldspar in the porcelain body. Any additional experimentation in the future would benefit from this use of x-ray diffraction, if available, to confirm this assignment. A list of characteristic Raman bands for typical components of Chinese and other porcelains is given in Table 1 and Table 2 presents a summary of materials found within the investigated shards.

Darker and paler blue colours were achieved using carbon and a white pigment, respectively; the presence of rutile as a white pigment was previously detected in the pale blue colour in a shard from the *São Bento*, which was wrecked off Msikaba, East Cape, in 1554, and gave rise to the conclusion that this stable, high temperature polymorph of titanium (IV) oxide was produced from the less stable anatase by high firing temperatures in the kiln [10]. No evidence of rutile with the characteristic strong doublet at ~ 610 and 445 cm^{-1} were observed in these spectra. Although amorphous carbon has been observed in the spectra collect from other Ming porcelain samples [10, 14, 17] it was not observed in the data collected from these samples.

In Figs. 2, 3 and 5 the presence of anatase is clearly observed with characteristic bands at 638 , 398 and 143 cm^{-1} [18]. Anatase is a component of the kaolin china clay and is a strong Raman scatterer; it is converted to rutile at temperatures ranging from 400 to $1200\text{ }^{\circ}\text{C}$ and therefore its presence provides a good estimate of kiln temperatures [19–22]. Although it is recorded in the literature of artists' pigments that anatase is a twentieth century pigment, its presence in ancient Chinese porcelains as a component of kaolin is well-founded from Raman spectroscopic data [23, 24]. Further evidence to support that shards #1 and #3 were subjected to lower kiln firing temperatures is the presence of β -wollastonite in the porcelain body [3, 25] with bands observed at ~ 971 , 638 and 340 cm^{-1} . β -Wollastonite is a characteristic marker used to discrimination between soft- and hard-paste porcelains. To date there is no literature which cites the presence of β -wollastonite in Ming Dynasty (1368–1644 AD) period porcelain; although it has been found in a range of other samples including sixteenth century Medici [8] as well as a number of eighteenth and nineteenth century French porcelains [3, 25].

Other interesting spectral features of shards #1 and 3 are observed with the 2000 – 1300 cm^{-1} region in Figs. 2, 3 and 5. It has been recognised that when using an NIR excitation source for analysis of glasses, glazes and ceramics that a broad somewhat featureless luminescence is often observed. This has been attributed to the excitation of electronic transitions of rare earth elements [8, 26]. However, the spectra shown in Figs. 2, 3 and 5 have significantly more structure and bare a great similarity to recent data published by Widjaja et al. [17] who investigated a range of glazed and unglazed Yuan, Ming and Qing shards using a combination of Raman microspectroscopy and band-target entropy minimization (BTEM) which is a self-modeling curve resolution technique. The analysis of over 3700 spectra collected using an excitation wavelength of 785 nm resulted in the reconstruction of six pure component spectra. One of these components

Table 1 Characteristic Raman bands of components in Chinese porcelains and related materials [14, 30, 31]

Component	Characteristic Raman bands (cm ⁻¹)
α-Wollastonite	370 w, 578 s, 985 s, 932 w, 1073 w
β-Wollastonite	410 ms, 635 ms, 980 s
Calcium phosphate	415 m, 970 s
Mullite	302 w, 480 m, 600 dr ms, 960 m, 1130 mw
α-Quartz	194 w, 464 s
Rutile	144 w, 240 mw, 441 mw, 606 mw
Anatase	143 s, 197 w, 398 m, 517 m, 641 m
Brookite	153 w, 245 mw, 320 mw, 364 mw, 449 w
Calcite	151 m, 283 ms, 712 mw, 1086 s
Aragonite	140 mw, 203 m, 705 m, 1086 s
Cristobalite	230 mw, 420 m
Cobalt blue	190 w, 280 w, 404 mw, 485 m, 506 ms, 560 w
Carbon	1320 br ms, 1585 br ms
Feldspar	510 m, 960 s
Hematite	229 m, 299 m, 409 ms, 640 m br

W weak, m medium, s strong, br broad, ms medium to strong, mw medium to weak

Table 2 Summary of materials found in porcelain shards from two Portuguese shipwrecks

Portuguese carrack	Sample	Components
<i>Santa Maria Madre de Deus</i> (1643)	Shard #1	Feldspar, anatase, β-wollastonite, ilmenite or Ilm-Hem _{ss} , calcite (data not shown), luminescence due to REE
	Shard #2	α-Quartz, ilmenite or Ilm-Hem _{ss} , amorphous carbon, anatase, hematite
	Shard #3	Feldspar, anatase, β-wollastonite, luminescence due to REE
	Shard #4	Amorphous quartz, luminescent profile of glaze, α-quartz
<i>Santo Espirito</i> (1608)	Shard #5	Anatase, amorphous quartz, luminescent profile of glaze, α-quartz

Ilm-Hem_{ss}, ilmenite hematite solid solution

was attributed to lanthanide complexes which undergo resonance enhancement when using a NIR source.

The spectrum presented in Fig. 2f, with an expanded spectral region shown in Fig. 3f, is dominated by a broad intense peak at 680 cm⁻¹ with a range of weaker features observed at 371, 332 and 222 cm⁻¹. This spectral pattern is characteristic of a range of Fe–Ti–Cr oxides with the exception of hematite which is dominated by strong features within the 300–200 cm⁻¹ spectral region. The spectrum presented in Fig. 2f is most similar to that of

ilmenite although the peak positions noted earlier are not an exact match with literature [27–29]. At temperatures above 960 °C it is known that ilmenite and hematite can form a solid solution (Ilm-Hem_{ss}), with the critical temperature at which the components are miscible in all proportions being ~650 °C [29]. Hematite was found in shard #1 (data not shown) and the spectrum in Fig. 4c collected from shard #2 has been tentatively assigned to hematite, therefore it is a possibility that the collected spectra are from an ilmenite-hematite solid solution. The identification of this mineral could be confirmed with X-ray diffraction if any future studies are undertaken. Although multiple areas of the shards were interrogated ilmenite, or Ilm-Hem_{ss}, was found only in shards #1 and #2. Interestingly, both spectra were collected from darkly coloured particles, one within one of the blue strips of shard #1 and the other within the white area of shard #2. This raises the question of whether ilmenite was a minor component of the porcelain body or was it added to the blue pigment to produce a darker shade of blue?

Shards #2, #4 from the Santa Maria Madre de Deus and #5 from the Santo Espirito

Figure 4 presents a range of spectra collected from various regions of shard #2 which was glazed. Not surprisingly similar components found in shards #1 and #3 were found in this sample including α-quartz (Fig. 4a, e), ilmenite/Ilm-Hem_{ss} (Fig. 4b), and anatase (Fig. 4e). The Raman spectra also exhibited broad features at ~1563 and 1329 cm⁻¹ which could be attributed to carbon found on the shard edge (Fig. 4b). The spectrum shown in Fig. 4c is tentatively attributed to hematite (595, 403, 292, 222 cm⁻¹) [14] but the bands observed at 663, 200 and 151 cm⁻¹ remain unassigned. Raman spectra collected from the glazed shards numbered #4 (Fig. 6) and #5 (Fig. 7) are dominated by the luminescent profile of the glaze with weak bands of α-quartz and anatase also observed. A band of medium intensity centred at ~472 cm⁻¹ is assigned to the Si–O bending modes of the glaze [13].

Conclusions

Raman spectroscopic analysis of several shards recovered from two Portuguese shipwrecks, 1608–1643, believed to be carrying porcelains of the Ming period have revealed some interesting and novel results that inform historical ideas of porcelain production. Although the spectra generally reinforce earlier studies from similar material recovered from other shipwrecks off the Cape of Good Hope, South Africa, in the period 1554–1650, some noteworthy differences are observed here. The detection of anatase almost exclusively in the porcelain bodies rather than rutile, the higher temperature stable form

of titanium (II) oxide, indicates lower kiln temperatures. The discovery of β -wollastonite characteristic of soft-paste porcelains further suggests two of the shards (#1 and #3) being subjected to lower kiln temperatures. To date there are no studies which have found β -wollastonite in Ming period samples. Are these samples “interlopers” or are they are reflection of changes in the body composition of Ming factory porcelain production in its final years. It was quite common practice for other porcelain manufactories to experiment with their body composition and kiln conditions in an effort to minimise kiln wastage and in the search for higher quality; examples of this practice are the addition of glass frit to porcelains before firing to increase translucency—this was achieved but in practice such glassy porcelains were always rather unstable and kiln losses were significantly higher before bone ash made an entrance as a component.

Abbreviations

BC: Before Christ; BTEM: band-target entropy minimization; DP: degree of polymerisation; NIR: near infrared; REE: rare earth elements.

Authors' contributions

HGME and DDW were involved in the initial concept of the experiments. EAC and MW collected the data used in this paper. EAC and HGME equally contributed to data analysis, interpretation and manuscript writing. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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