Identification of microstructure and chemical composition of Celadon wares from the Harireh ancient city of Kish Island, Iran

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ABSTRACT

The Celadon samples of the ancient port of Harireh in Kish Island from 11th-14th centuries were studied. The crystallite and chemical compositions of samples were investigated using quantitative X-ray diffraction (QXRD), X-ray fluorescence (XRF), and simultaneous thermos-analytic (STA). Moreover, thin section petrography and environmental scanning electron microscopy (ESEM-EDX) were applied to explore microstructural characteristics. The bulk chemical analysis of the investigated samples shows not only the high amount of K_2O and CaO as flux but also SiO_2 and Al_2O_3 as the major oxides. According to the STA and XRD results, the firing temperature of the samples is similar to the Chinese ones. The presence of mullite and moganite phases indicates a firing temperature up to 1050 °C for the samples. The formation of mullite derived from kaolinite clay and is more similar to the Chinese productions rather than the Islamic. The colorant element in Celadon samples is mainly Fe^{2+}. Chemical compositions of these Celadons and Chines wares also show strong similarities in raw materials and manufacturing processes.

Keywords: Celadon; Archaeometry; Composition; Microstructure; Kish Island; Harireh-Ancient city.

INTRODUCTION

Stonewares with Celadon glazes are firstly made by Chinese during the early Bronze Age in Shang Dynasty (Feng et al., 2008; Zhu et al., 2011; Tite et al., 2012). Chinese ancient Celadon began to be fired early in the Late Eastern Han Dynasty (AD 25-220) in South China (Li et al., 2012). Firing temperature of Celadon wares has been estimated around 1200 °C (Zhu et al., 2011; Hao et al., 2013; Wood and Li, 2015). The color of Celadon develops through the formation of glassy and crystalline phases, generated by chemical reactions between the glaze and the clay-based body at high temperature under reduction atmosphere (Kim et al., 2011). The similarities and differences between the chemical compositions and microstructures of Celadon wares from China, South Korea, Vietnam, and Japan have been previously analyzed using various analytical methods (Colobman et al., 2003; Kerr et al., 2004; Hidaka et al., 2011; Hao et al., 2013). The investigations on Chinese ceramics (Shanglinhu- in the late Tang Dynasty) have shed light on the provenance and manufacturing techniques of the body as well as the glaze (Wood et al., 2005). However, Vietnamese ceramics show enrichment of Ca (+K), which lead to better understanding the firing conditions. The presence of calc rich inclusions in a ceramic body chiefly provide the estimation about the firing temperature, due to their grain size since calcium carbonate decomposed very rapidly to calcium oxide (ca. 750°-850 °C) to form porous calcined calcium oxide (Tite, 1969). The grain size of carbonate has a high impact on the extent structural
disturbance in the ceramic body, at the temperature in which the carbonate being decomposed during the firing processes (Leicht, 1977).

Mineralogical and chemical investigations on the raw materials from the south and north China clay source have been essentially carried out based on the characterization of Mullite’s habit and SiO$_2$/Al$_2$O$_3$ ratios in the body of the ceramics (Tite et al., 2012). The major chemical compositions of the body of Chines ware are characterized by SiO$_2$ (80.7-65.4 w%), Al$_2$O$_3$ (32.7-16.0 w%), and K$_2$O (6.1-1.1 w%) (Tite et al., 2012). The investigation of Li et al., (2012) indicates the high contents of K$_2$O, CaO, TiO$_2$ and Fe$_2$O$_3$ in Chines Celadon wares. Therefore, many systems are suggested, to provide a valid comparison of the chemical compositions such as SiO$_2$-Al$_2$O$_3$-(CaO+K$_2$O+Na$_2$O) and CaO-K$_2$O-Na$_2$O (Colomban et al., 2003; Colomban et al., 2004).

Chinese Celadons with very smooth green-grey surface reached this coastal line of Iran in around 1100-1500 AD (Pierson, 2012). The production of Celadon reached its peak in the 14th century when they were exported widely from East coast of China to the Middle East through the Indian Ocean (Hobson, 1915; Cho, 2008). These kinds of ceramics had a very large distance of migration between the China Sea to the Persian Gulf through an extensive maritime trade. South Persian coastline has been a very important region for many centuries based on marine export/import of goods (McConkey and McErlean, 2007). Celadon wares have been reported in many provinces in Iran such as Kerman, Shiraz, Port of Siraf, Kish and Gheshm Island in the Persian Gulf (Pierson, 2012). This paper presents the chemical composition and firing temperatures of 7 pieces of Kish Celadon wares which were produced during the 11th-14th centuries to determine the raw materials and manufacturing process. The Celadon wares were sampled from the Port of Harireh in Kish Island, in the Persian Gulf (Figure 1). It also comparatively analyzes the composition and microstructure of the Celadons from China. The identification of the compositions and microstructures would lead the results to get suggestions about the origin of these Celadon wares (Colomban et al., 2003).

ARCHAEOLOGICAL SETTING

Kish is a ca. 95-square-kilometre Island in the Persian Gulf which is a part of the Hormozgān Province in the south of Iran (Figure 2). In the Middle Ages, Kish became an important trading center under its capital; Port of Harireh. The archaeological research of Whitehouse (1976), in Harireh port also provided a great collection of imported ceramics, such as Martaban stoneware, Celadon, porcelain and Ting ware (Whitehouse, 1976).

MATERIAL AND METHODS

Seven Celadon wares were collected from the excavation at the ancient port of Harireh and subjected to mineralogical and chemical analyses. The characteristic shape and surface of these samples show macroscopically a very compact and homogeneous body with greenish-gray glaze on the external and the internal surface (Figure 3). All analytical method carried out at the department of building material chemistry, University Siegen in Germany. XRF analysis has been done with an instrument Bruker® SPECTRAplus 2008, in order to have the bulk chemical composition of Celadons’ body. Rh-anode end-window X-ray tube is used for analytical conditions. Long count times were used at both peak and background positions. It is essential that the whole sample has the same grain size; therefore the sample should be sieved through a 125 µm mesh. Because altered minerals within the ancient ceramic’s matrices, they have a different hardness. In this case, 8g powder samples and 1ml PVP (polyvinyl alcohol) solution mixed together for making the pellet.

Quantitative XRD analysis was used for determining the crystalline phase occurrences in the body of ceramics by a PANalytical instrument (analyses were carried out using an X-ray generator operated with a copper target at 45 kV and 40 mA. The powder patterns of ceramics were measured between 2θ=5° and 2θ=60°, with a scanning rate of 2θ=0.01° per minute. This large scanning area was required in order to gain a complete diffraction pattern
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The measured peaks refined with the Rietveld method for getting the best-preferred orientation of the phases. Clustering of analysis was carried out for distinguishing the ceramics according to the crystalline phase constituents (Emami and Trettin, 2010; Emami, 2012). Microscopic investigations are performed on thin sections. These samples were also examined by a polarizing microscope (an instrument from Olympus, XB 51 with Analysis Software) and high-resolution ESEM (ESEM Quanta FEG 250 FEI with Apollo XL30 EDX) fitted with an energy-dispersive X-ray (EDX) spectrometer. Finally, simultaneous thermal analysis (STA) was carried out with using a NETZSCH STA 449C instrument with a Jupiter & Proteus Analysis Software Version 4.8 in order to determine the firing process and crystalline phase decompositions in Celadons.

RESULTS

Bulk chemical composition of the body and Celadon glaze

Bulk chemical compositions of the body of the samples investigated samples are presented in Table 1. The Celadons are classified as high silica ware after Noll classification in the system SiO₂-Al₂O₃-CaO+MgO (Noll, 1991). SiO₂ and Al₂O₃ are mentioned as the major compositions in the investigated samples and show a negative correlation to each other which is probably associated to the clay source. CaO and K₂O are the major for minerals with low symmetry (Emami et al., 2016).
oxides occurred within the body and discussed with two essentially points; firstly the origin of the clay or burial conditions and secondly the manufacturing process. CaO is a major oxide which varied between 2.41-4.05 w%. K$_2$O varied also from 2.69-5.42 w% which would be described as secondary contamination via alteration of potash bearing minerals. K bearing feldspar is also used as a fluxing material to form the shiny character to the glaze (Kim et al., 2011). However, due to the high fluxing effect of K$_2$O, even though via increasing the K$_2$O, decrease the shiny effect of the glaze and the glaze surface became matt. The variation of MgO usually associated with CaO due to the usage of dolomitic additives in the body (Daghmehchi et al., 2016). The amounts of FeO devise from different raw clayey materials and are furthermore responsible for the color of the glaze via a reduction atmosphere.

According to the chemical analysis, the amount of Iron is mostly constant which would be a reason for constant green-blue color for the glazes (Kim et al., 2011; Jeon et al., 2014). The chemical composition of the glazes is measured in some areas by SEM-EDX illustrated in Figure 4. In this case, the glazes have definite chemistry with a major amount of SiO$_2$ and Al$_2$O$_3$ (zone A and B in both samples) and the most varieties are shown by the amount of K$_2$O and sometimes CaO. The glazes are classified as high Potash glaze. They are mostly homogeneous and the bubbles which are visible within the sample CHK1 proved the high-temperature manufacturing process.

### X-ray Diffraction of the samples for determining the crystalline phases

Figure 5 shows the X-ray diffraction patterns refined via Rietveld methods of the investigated samples from Harireh (Table 2). The diffraction patterns are not largely different and the crystalline phase occurrences have not essentially changed in compared to each other. In the measured diffraction pattern, “Qz” is denoted for the reflection of α-quartz (quartz low) with its best intensity peaks in diffractogram at 2θ=26.32 on (011) plane. The quartz peaks are in similar positions in the diffraction pattern and illustrated similar intensity. The XRD patterns illustrate the best crystallographic preferred orientation of quartz at 2θ=21.12 on (100) and 26.32 on (011) crystallographic plane. The appearance of mullite as mineral composition of SiO$_2$+Al$_2$O$_3$ is also mentioned in this ceramics as it reported within the texture of Izumiyama ceramics (Hidaka et al., 2011). Mullite (in general Al$_6$Si$_2$O$_13$) have been used and reported in a very varied range of applications in high-temperature ceramic-based materials as well as technical ceramics (crucibles).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$%</th>
<th>Al$_2$O$_3$%</th>
<th>Fe$_2$O$_3$%</th>
<th>CaO%</th>
<th>Na$_2$O%</th>
<th>K$_2$O%</th>
<th>MgO%</th>
<th>TiO$_2$%</th>
<th>MnO%</th>
<th>P$_2$O$_5$%</th>
<th>S%</th>
<th>LOI%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHK1</td>
<td>66.96</td>
<td>21.61</td>
<td>1.96</td>
<td>3.89</td>
<td>0.87</td>
<td>4.86</td>
<td>0.19</td>
<td>0.140</td>
<td>0.057</td>
<td>0.014</td>
<td>0.015</td>
<td>1.79</td>
</tr>
<tr>
<td>CHK2</td>
<td>72.53</td>
<td>17.79</td>
<td>2.00</td>
<td>3.24</td>
<td>0.16</td>
<td>5.02</td>
<td>0.45</td>
<td>0.212</td>
<td>0.092</td>
<td>0.045</td>
<td>0.008</td>
<td>0.07</td>
</tr>
<tr>
<td>CHK3</td>
<td>74.26</td>
<td>15.86</td>
<td>1.45</td>
<td>4.05</td>
<td>0.27</td>
<td>4.12</td>
<td>0.20</td>
<td>0.103</td>
<td>0.113</td>
<td>0.025</td>
<td>0.026</td>
<td>2.21</td>
</tr>
<tr>
<td>CHK4</td>
<td>70.63</td>
<td>20.32</td>
<td>2.27</td>
<td>3.39</td>
<td>0.03</td>
<td>2.69</td>
<td>0.17</td>
<td>0.147</td>
<td>0.054</td>
<td>0.011</td>
<td>0.011</td>
<td>1.50</td>
</tr>
<tr>
<td>CHK5</td>
<td>66.35</td>
<td>20.71</td>
<td>2.01</td>
<td>2.41</td>
<td>0.29</td>
<td>3.35</td>
<td>0.24</td>
<td>0.261</td>
<td>0.033</td>
<td>0.002</td>
<td>0.023</td>
<td>6.04</td>
</tr>
<tr>
<td>CHK6</td>
<td>71.45</td>
<td>19.96</td>
<td>1.77</td>
<td>3.51</td>
<td>0.29</td>
<td>5.42</td>
<td>0.17</td>
<td>0.106</td>
<td>0.088</td>
<td>0.002</td>
<td>0.008</td>
<td>0.03</td>
</tr>
<tr>
<td>CHK7</td>
<td>74.21</td>
<td>17.06</td>
<td>1.45</td>
<td>4.40</td>
<td>0.43</td>
<td>2.92</td>
<td>0.39</td>
<td>0.242</td>
<td>0.053</td>
<td>0.043</td>
<td>0.019</td>
<td>1.59</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition of oxides in the investigated Celadon shards.
Figure 5. Diffraction patterns of all measured Celadons and crystalline phase composition due to their best preferred orientation.

Table 2. Quantitative Rietveld refining methods of the investigated Celadons.

<table>
<thead>
<tr>
<th></th>
<th>Quartz low-ICSD 62406 in %</th>
<th>Mullite-ICSD 66263 in %</th>
<th>Moganite-ICSD 67669 in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHK1</td>
<td>47.2</td>
<td>52.9</td>
<td>4.2</td>
</tr>
<tr>
<td>CHK2</td>
<td>91.4</td>
<td>2.8</td>
<td>5.8</td>
</tr>
<tr>
<td>CHK3</td>
<td>96.9</td>
<td>2.4</td>
<td>0.7</td>
</tr>
<tr>
<td>CHK4</td>
<td>90.0</td>
<td>4.9</td>
<td>4.2</td>
</tr>
<tr>
<td>CHK5</td>
<td>44.1</td>
<td>53.1</td>
<td>2.8</td>
</tr>
<tr>
<td>CHK6</td>
<td>51.2</td>
<td>47.2</td>
<td>1.6</td>
</tr>
<tr>
<td>CHK7</td>
<td>87.9</td>
<td>9.4</td>
<td>2.7</td>
</tr>
</tbody>
</table>
Mullite is dominated with its low thermal expansion, high temperatures formation, and its outstanding stability in aggressive chemical environments (Martinon-Torres et al., 2006).

The high intensity of mullite has been detected at 2θ=26.07 on (210) plane and 2θ=25.79 on (120) plane and the quality of mullite is increased by increasing the temperature (1000°-1200 °C) (Ntah et al., 2017). The other phase is Moganite which is appeared on 2θ=26.70 on (-112) crystallographic plane and 2θ=26.27 on (-202) crystallographic plane. This phase is a quartz polymorph structure with optically length-slow character. Moganite has a monoclinic symmetry with space group I2/a (Götze et al., 1998). In high-temperature ceramics, they could be found and contain varying percent ratios of moganite to quartz depending upon their source (Pretola, 2001).

**Microscopic investigations of the Celadon bodies and glazes**

Thin sections of Celadons were observed under a polarizing microscope in order to identify the fabrication as well as the types of additives in the matrix. The body of the wares has a fine-grained fabric (Figure 6A). The porosity of the Celadons is too low due to the firing process. Quartz aggregates are the common additives within the ceramic matrices. The appearance of quartz as additives in the antiquity is mostly highlighted due to its durability effect on the clayey matrix (Kilikoglou et al., 1998). As a matter of fact, to consider the quartz as a justified temper in ceramic ecology two points must be considered, accordingly. Quartz is naturally altered non-plastic materials have been accumulated in many sedimentation basins (raw material availability) and best functionally experiences to work with this material not accidentally, but indeed experimentally (Giurgiu et al., 2017). Quartz aggregates are identified by their low birefringence and typical undulatory extinction effect. The grain size of quartz aggregates is estimated around 0.1-1 mm. Compact matrix with secondary calcite is observed due to the burial condition after the manufacturing process (Emami and Trettin, 2012) (Figure 6B). The CaO content

![Figure 6. A) The body of the CHK1 is classified as a clayey matrix with a very compact fabric. B) Dense matrix with fine secondary calcite. C) Quartz grain with its typical undulatory extinction structure. D) Recrystallization of calcite as secondary formation around the pores.](image-url)
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is observed in a very fine aggregate. Quartz grain with its typical undulatory extinction structure is being visible only with great magnification and is most difficult to identify with magnification by 40x or 100x (Figure 6C). In sample CHK7 the recrystallization of calcite as new formed secondary calcite around the pores is noticeable (Figure 6D). Mullite needles exist within the fabric in all samples with low birefringence and colorless but only can be detected in high magnification (unsharp crystals under a microscope).

Thermal analysis of the Celadon samples

Firing temperature of 7 ceramics has been estimated by STA (simultaneous thermo-analysis). The mineralogical decomposition and crystallization occur in four important parts; dehydration, dihydroxylation, carbonization, recrystallization (new formation) and sintering during the heating process (Emami and Trettin, 2010, 2012). The DSC curves indicate the same firing temperature till 1050 °C for these Celadon wares (Figure 7).

Data on the thermal behavior of seven Celadons supported the conclusion in the DSC curves, that the Celadons can be roughly classified into a single category. Celadon samples show a very similar thermal behavior (Figure 7). Such thermal behavior is characteristic of ceramics sintered in one time at a high temperature (Colomban et al., 2004). By increasing the temperature, an immediate one-step exothermic behavior is seen in the DSC curve of the sample. However, from this, it may conclude that the phase composition of Celadons fired at a high temperature is quite comparable to each other.

DISCUSSION

Seven pieces of Celadon wares from Kish Island have been investigated in order to explain their possible trends. They have mostly similar colors on the body as well as in the matrix of ceramics. The gray color of the body indicates the usage of ferruginous red clay, fired under reducing conditions (Pollard and Hatcher, 1986; Kerr et al., 2004). The bulk chemical composition of the Celadons showed a low amount of CaO versus enrichment of SiO$_2$+Al$_2$O$_3$ within them. As a matter of fact, concentrations of CaO (in a very low amount) can be associated with secondary calcium-rich phases (new formed calcium-rich phases) via burial conditions. The high amount of Al$_2$O$_3$ (>19%) is probably related to the high quality of kaolinite clayey raw material which have been used (Zhu et al., 2011). CaO and K$_2$O are the major oxides with the ability of fluxing agents in the kiln. However, the more ratios of K$_2$O contents lead to a greater increase of firing temperature. The variation of K$_2$O depends also on the source of clayey raw materials which had been used in the manufacturing processes (Kerr et al., 2004; De Rosa et al., 2012).

The iron constituents varied from 1.45 to 2.27 w%. The investigation of Pollard and Hatcher (1986) on green-ware indicated similar compositions except for the lime contents (less than about 0.5%). Potassium constituents vary between 2.69-5.42 w%. High SiO$_2$, Al$_2$O$_3$, CaO, and K$_2$O contents and low concentrations of MgO, MnO, Na$_2$O, and Fe$_x$O$_y$ (as Flux) are well documented in the china proto-Celadon glaze and body in antiquity (Li et al., 2012; Hao et al., 2013). The amount of TiO$_2$ (0.15%-0.22%) and Fe$_2$O$_3$ (1.63%-2.10%) in the Middle Ming dynasty (Zhu et

Figure 7. STA diagram of the analyzed Celadons from Harirah, Kish Island.
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The presence of mullite indicates a firing temperature above 980 °C (Gonzalez-Garcia et al., 1990). Mullite formed from a non-calcareous kaolinitic clay reservoir based on the dehydration reaction of kaolinitic clay which has been followed by decomposition to metakaolinite (± Al-Si spinel) and at least the formation of mullite above 980°C (Noll and Heimann, 2016). Mullite and morganite are the phases which could be the thermobarometer minerals in this study. Mullite appears in a firing temperature > 980°C (Figure 8B and C) (Heimann and Maggetti, 1981; Gonzalez-Garcia et al., 1990; Rathossi and Pontikes, 2010). Presence of mullite (3Al₂O₃·2SiO₂) (also in 15th-century Vietnamese porcelain) via high temperature and morganite (which has not yet reported in Asian literature) via high temperature as well as, is the considerable points for adjusting the raw materials for developing such wares.

The crystallization of high-temperature phases such as mullite and sillimanite and their disappearance up to 1100°C indicate a firing temperature up to 1050 °C for the samples (Daghnehchi et al., 2016). The compact structure of the bodies also corroborates a firing temperature above 1000 °C (Hao et al., 2013). The investigated Celadons vitrification has proceed about 1000 °C via secondary mullite formation out of liquid phase (Tite et al., 2012; Singh and Kumar, 2017). The pre-sintering occurred at 977°C probably due to the stability of mullite till 1100 °C.

CONCLUSION

The crystallite and chemical compositions of the 7 pieces of Celadons body and glaze were comparatively analyzed by XRD, XRF, STA, SEM-EDX and thin section petrography. The Celadon wares of Harirah Island suggest similar external appearance and chemical composition. The body of Celadon has lower Fe₂O₃ and higher K₂O. However, the existence of thicker glaze and the presence of knowingly more bubbles might be used as secondary structures allowing the similarity of Harirah Celadon to those reported from China. The ceramics proved to have high siliceous contents. The fabric of all investigated samples contains the same chemical composition. The microstructure of the material is very dense and well vitrified. The crystallite and chemical constituents in the body of Celadon are not compatible with the geological setting of the Island. The XRF analyses of the Celadons show a little amount of CaO as a flux. Anorthite is detected in the glaze and considered by CaO, Al₂O₃ and SiO₂ constituents. Morganite and mullite are also characteristic phases in these Celadons. DSC and XRD analyses indicate a firing temperature around 1000-1050 °C due to the crystallization of high-temperature phases. The glaze on the both internal as well as the external surface is very constant and seems to be covered with the same raw materials during the manufacturing process. The result shows that a lithoclastic source enriched in fibrolite were used as raw materials.
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This is also responsible for the different color of the body under different firing conditions and temperature. The presence of Moganite could be either due to its deliberate addition as part of the manufacturing process or as traces of raw material employed via technological features. These argumentations are mainly related to the suggestion of a local material, as well as production technology somewhere beyond the Iranian border.

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Figure 8. A) The boundaries and face interface areas between the glaze and the body of Celadons in sample CHK7, characterized by scanning electron microscope. Very homogeneously glaze surface is created and proved to have a well uniform layer above the body. B) the structure and distribution of mullite crystals in the samples as tiny prismatic crystals. C) Chemical composition of the mullite crystals by EDX. All pictures are from the sample CHK5.
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