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Original Article

Jun ware glazes: Chemistry, nanostructure and optical properties

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ABSTRACT

A set of the *Classic* and *official* Jun ware shards found at various kilns at Yuzhou (Henan) are analyzed. The blue color and *milky* appearance of the glazes subject of intense debate as being due to either the glaze nanostructure or chemistry. The presence of submillimetre areas showing different color and opacity gives to the glazes a three dimensional *cloudy sky* appearance. Nanostructure and chemistry of the glazes, oxidation state of iron and nature of the copper nanoprecipitates are studied at a submillimetre level. Images of the glaze nanostructures are obtained using a Focus Ion Beam and Scanning Electron Microscope with nanometric resolution. The size and volume fraction of the nanostructures determined by image treatment are related to the chemical composition of the glazes. Differences between kiln productions are found and the origin of the color and opacity of the glazes discussed in terms of the chemistry and nanostructure.

1. Introduction

Jun ware is one of the five famous wares created in the Northern Song dynasty (960–1126) in the first quarter of the 12th century [1–3] and which continued being produced during the Jin (1115–1234), Yuan (1271–1368) and early Ming (1368–1435) Dynasties. Jun ware is a high-fired grey-bodied stoneware with a subtle high temperature glaze of a pale bluish tone [1–3]. It is classified as Classic Jun (including monochrome and Splashed Jun) and Official Jun (also called numbered Jun) [1,2]. Although there is not much debate about the continuity in the production of the Classic Jun, there is still a lot of debate about the dating of Official Jun, either placing it in the early Ming dynasty [4] or in the Jin or Yuan dynasties [5]. The Classic Jun is characterized by an opalescent light blue glaze to which purple/red splashes are applied while the Official Jun is characterized by the presence of a purple/red glaze either mixed or applied over a darker blue glaze. However, looking more closely, the blue glaze contains submillimeter areas of different blue shade and opacity which give to the glaze a three dimensional *cloudy sky*-like appearance. Contrariwise to other glazes translucency, medium gloss and depth of appearance are the most sought after characteristics of these glazes. The origin of the opalescent blue colors shown by Jun wares has been the object of many studies and much debate [1,3,6–13]. Scattering due mainly to the presence of a glass nanostructure but also of small microcrystallites of wollastonite and cristobalite, of undissolved quartz grains and submillimeter bubbles are considered responsible for the opalescence. The formation of a glass nanostructure has been proved to be a consequence of the specific composition of the Jun glaze, that is, a lime glass with a high SiO_2:Al_2O_3 ratio (above 7:1) which, when fired at temperatures of about 1200 °C, undergoes a liquid-liquid separation [14]. Although it is known that the liquid-liquid phase separation depends primarily on the cooling rate for each specific composition within the immiscibility gap [6–11,13,14], the analytical models are not able to explain properly the final glass nanostructure and consequently, the mechanism of this process is still unsolved [15,16,13]. Finally, the presence of phosphorus and also magnesium have also been highlighted as favouring the development of the glass nanostructure and therefore for the enhanced opacity.

The presence of metal ions (iron and titanium) is also considered responsible for the blue color. However, the high amount of iron and titanium of the glazes (1.5–3 wt% Fe_2O_3 and 0.15–0.5 wt% TiO_2) should give a darker and more greenish color than the one shown [17,3]. Various studies highlighted the combined effect of iron and titanium in the glaze [17,3] and in good agreement with Chinese porcelain analysis and modern replications gave a consistent maximum content of about 0.2% TiO_2 to obtain a blue glaze [2].

Another characteristic of Jun ware glazes is that the reaction between the glaze and the stoneware ceramic gives rise to chemical interdiffusion, so that an Al_2O_3 richer and CaO and SiO_2 poorer dark olive-brown glaze is formed at the interface where anorthite (calcium feldspar) crystals develop [6–8,11,10,3,13]. Although this glaze color s seen in those areas showing a thinner glaze, in particular at the edges of

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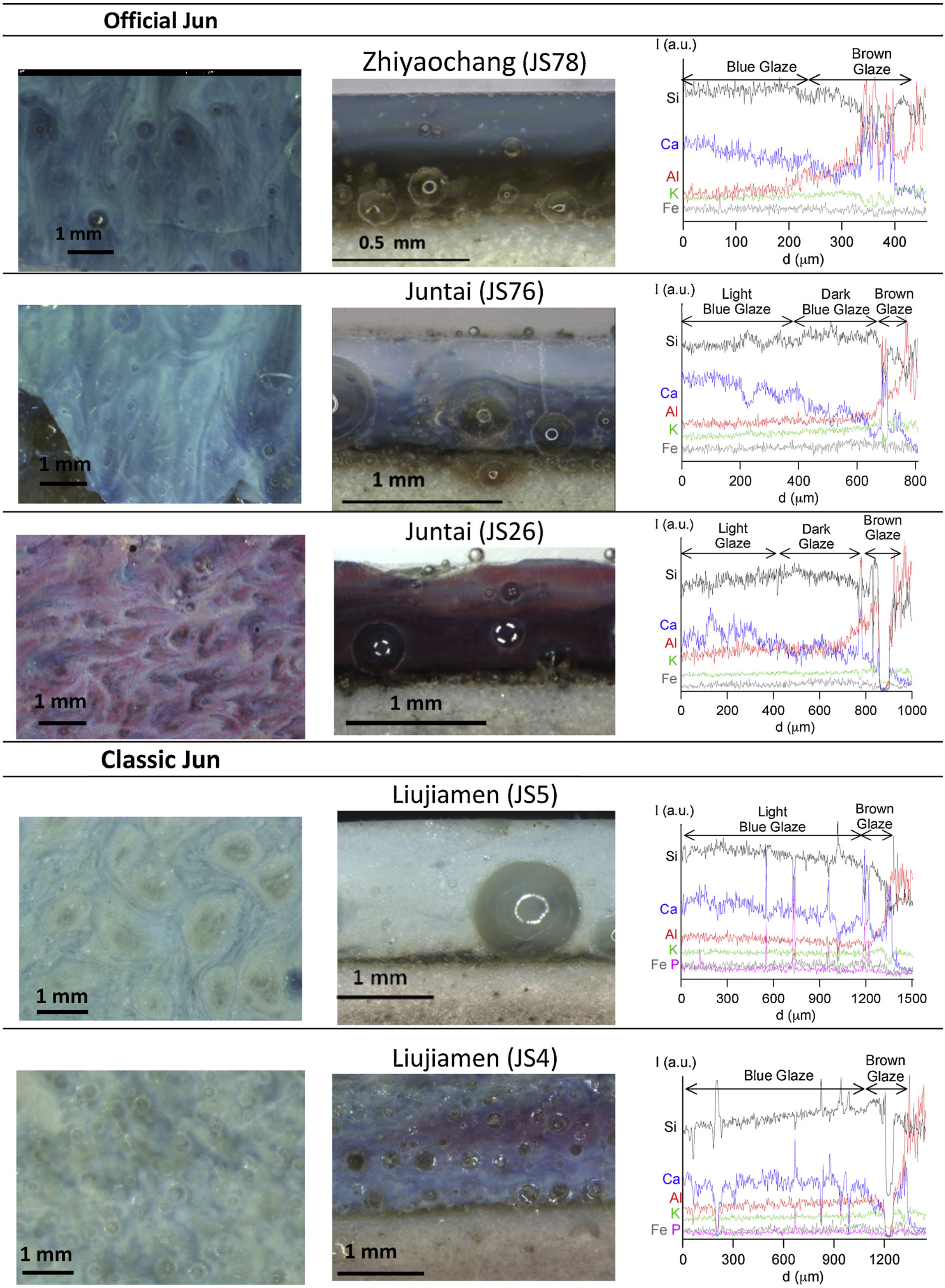

Fig. 1. (left) Surface, (middle) cross section image and (right) Si, Al, Ca, Fe and K cross section line scans corresponding to different color shards from the three kilns studied.