Structure of decorative layers in Changsha colored porcelains: role and physical properties of nano-crystallized metal oxides

French supervisors: Philippe Sciau and Chantal Brouca-Cabarrecq (CEMES-CNRS, Toulouse University)

Chinese supervisor: Tiequan Zhu (Archaeometry lab, Sun Yat-sen University, Guangzhou)

In partnership with the Archaeometry Lab of Sun-Yat-sen University, we are studying the glazes and decors of various types of Chinese ceramics and specifically the decors obtained at high temperature (>1000°C) based on metal transition elements such as Fe, Co or Cu1,2. Since several years3,4,5, we have developed a series of analytical tools, which allow us to study the structure and physical properties of materials on different scales (from nm to mm). They include: i) laboratory techniques such as optical microscopies and spectroscopies (colorimetry, reflectivity, Raman), electron microscopies (SEM, TEM5) and spectroscopies (SEM-EDX, TEM-EDX, TEM-EELS), X-ray diffraction and spectroscopy (XRF) as well as ii) synchrotron radiation based techniques in France (ESRF) and in California (ALS and SSRL) including X-ray spectroscopies (XRF, XANES, Full-Field XANES) and X-ray diffraction (powder µXRD, Laue µXRD4). This multi-scale analytical approach provided unprecedented results on Roman ceramics6 and more recently concerning blue and white porcelains1,2. These recent studies allowed us to go beyond the methodology development, take advantage of the sophisticated tools we developed (transmission electron microscopy, focused ion beam and full-field XANES), and apply them to complex and heterogeneous cultural heritage materials. A great part of valuable information on how these heterogeneous materials were created is embedded into their microstructures. This is precisely what we want to achieve concerning the decors of Changsha colored porcelains through this PhD proposal.

In history of Chinese ancient ceramic, Changsha kiln of Tang dynasty (A.D. 7-10th century) was one of the pioneers in the development of the high temperature poly-color technique. Tang’s productions are known for their polychrome decors but most of them were obtained at low temperatures (<1000°C) using lead glazes. The use of higher temperature (1150-1250°C) enhances the chemical reactions among the pigment mixture, the glaze and body, and requires adapted compositions to control the diffusion of chromogenic elements in the glaze. Depending of the way the pigment mixture is applied, the decor is called underglaze (applied on the body surface before glaze application) or overglaze (applied on the glaze after glaze application). A firing can be performed between the two steps, before glaze application (underglaze, seldom) or before pigment application (overglaze, often) to limit the diffusion. Usually, cross-section observation under...
optical microscope allows us to define the decor type but for Changsha production, it is a little more difficult. Some observations, such as the one shown in Fig. 1, seem to point out an underglaze technique with a higher concentration in chromogenic element at the interface between the body and glaze, while other observations are in agreement with the use of an overglaze technique. In many cases, the diffusion of chromogenic element is very high and it is very difficult to decide. In addition, if the chromogenic element given the green/bleu color was identified (Cu ions), the origin of red color is more discussed (nano-crystallized iron(III) oxides or Cu nanoparticles?)

In this PhD proposal we want to address this two main questions through the study of the distributions of the chromogenic elements, the determination of the crystallographic phases containing them and through the identification of the chemical mechanism at the origin of their formation. For this last point, we will try to consider the glaze layer as a set of sub-system taking into account the heterogeneity and local composition in order to be able to use the phase diagrams. Compared to our previous studies, this approach could be more difficult to implement because of the higher diffusion of some elements, which could complicate the identification and differentiation of sub-system. In the other hand, it is the possibility to test and improve the approach. Depending on the nature and the organization of various crystallized phases inside the glaze, we will try to link the structural data to the optical properties and the functions of this ware. A special attention will be focused on some rare polymorphs such as the \( \varepsilon \)-Fe\(_2\)O\(_3\) phase, which are very interesting for modern application but whose synthesis is not yet well mastered. The corpus will be chosen in order to be representative of the Changsha kiln productions and to cover both Tang and Ten Kingdoms periods. We hope that the set of results allow us to better understand the manufacturing process and to highlight possible changes but also provide new advances in material sciences concerning both methodological aspect and the use of some rare iron oxide polymorphs.

References


