	Experiment title: Study of the manufacturing processes of blue decors of Chinese Yuan porcelains from the analysis of micro-structure and micro-composition by FF-XANES and SR-µXRF	**Experiment number**: HG 97
Beamline: ID21	**Date of experiment**: from: 21/09/2016 to: 27/09/2016	**Date of report**:
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Report:

The first study concerning Qinghua porcelain fragments produced during Ming Dynasty (1378-1644 AD) was a success and allowed us to define both an efficient sample preparation and measurement strategy [Wang 2016][1]. Also, in the light of these results, we wanted to study Qinghua porcelain of Yuan Dynasty (1269-1378 AD), which is considered as the heyday of this type of ceramics by historians. The elemental composition of the two types of productions is quite close except that Yuan blue colour contains no Mn and more Fe.

The cross-sections thin samples for measurements were prepared as previously [Wang 2016, HG44 report] but as Yuan fragments are much rare, the choice of interest areas was more limited and difficult.

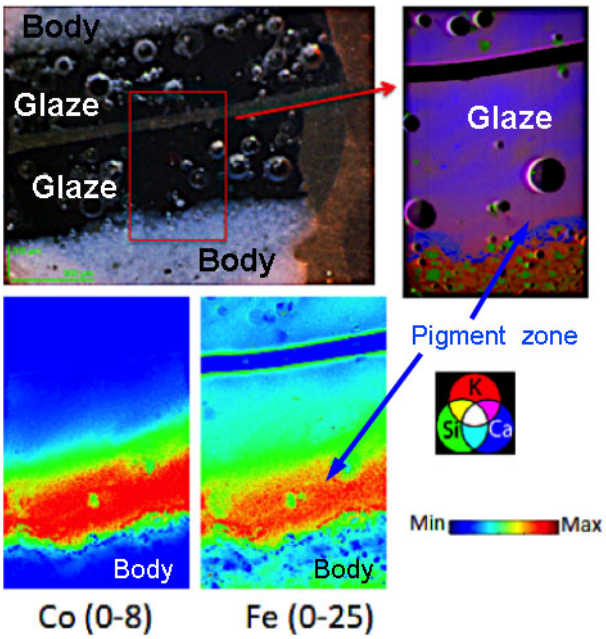

Fig. 1 typical elemental maps obtained for a Yuan sample. The transition elements (Co, Fe) are concentrated in the pigment zone

[1] Microstructure of blue decor of Qinghua porcelain, Beauty of science ESRF site, juillet 2015

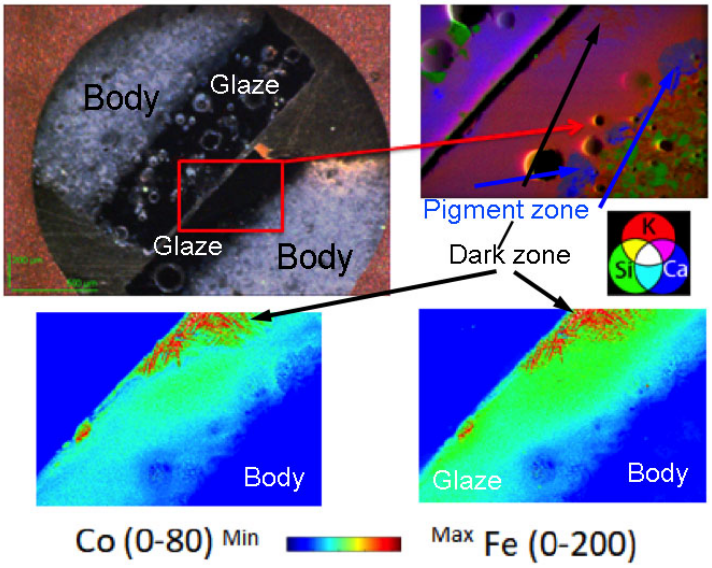

Fig. 2 Elemental maps obtained from a dark zone showing the $CoFe_2O_4$ dendritic crystals.

As a first step, SR-µXRF mappings were carried out by using the Scanning X-ray Microscope of ID21 beamline on the most concentred blue colour of 10 Yuan samples. A typical result is shown in Figure 1. The spatial distributions of the main glaze and body elements (Al, Si, K, Ca) are similar to the ones observed for Ming samples. However, the distribution of transition elements (Fe, Co) is very different. The higher concentration of Co appears in the pigment zone is close to the body/glaze interface, but this distribution is quite homogeneous unlike for Ming samples, which display punctual high Co concentration. The Co distribution is more diffuse and it is similar to the one of Fe. High punctual Co content were only observed close to the surface and always associated to high Fe content as shown in Figure 2. These zones correspond to the dark spots visible the surface of blue decorations. This situation did not allow us to perform FF-XANES investigations at Co K-edge as previously. The measurements are performed in transmission and the absorption before the Co K-edge is too high because of the iron absorption. A decreasing of sample thickness allows a decreasing of the Fe-absorption but it decreases also the Co-absorption making it unmeasurable. However it was achievable at Fe K-edge and allowed us to study the Fe high content zones as the one of Figure 2.

The difficulties to perform FF-XANES investigations at Co K-edge, led us to reduce the shift number for these investigations and to use more shifts for XANES studies from fluorescence measurements by using Scanning X-ray Microscope. XANES spectra recorded in the Co/Fe concentred zones close to the body/glaze interface (pigment zone) are typical of Co^{2+} dispersed in a glass. Only the spectra recorded in the dark zone (Fig. 3) revealed a different speciation corresponding to the $CoFe_2O_4$ structure and in agreement with the records at the Fe K-edge. XRD measurements confirmed the identification while FF-XANES allowed us to image the dendritic network of these crystals with a sub-micrometre resolution.

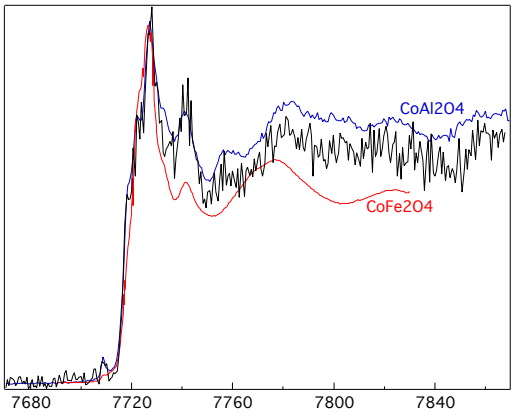

Fig. 4 Co XANES spectrum recorded in dark zone

In conclusion the experiment was a success, even if the FF-XANES at the Co K edge was not achievable. However the differences between the first investigations on Ming samples and these ones on Yuan samples are so significant that we must be very careful. In both cases, it is Co^{2+} but it seems mainly diffused in the glass matrix in the Yuan samples, while in Ming samples, it should be mainly integrated in cobalt aluminate crystals ($CoAl_2O_4$). The differences could indicate an evolution in the blue pigment preparation. We are working on the question through both archive researches (supervised by historians) and the study of chemical reactions likely to occur during the firing.