	Experiment title: In-situ structural study of phase transformations leading to the formation of blue decors of Qinghua porcelain	**Experiment number**: HG 122
Beamline: ID22	**Date of experiment**: from: 28/06/2018 to: 02/07/2018	**Date of report**:
Shifts: 12	**Local contact(s)**: Catherine Dejoie	*Received at ESRF:*
Names and affiliations of applicants (* indicates experimentalists):		

GROENEN Jesse * (CEMES-CNRS, Toulouse)
PINTO Ariane * (CEMES-CNRS, Toulouse)
SCIAU Philippe * (CEMES-CNRS, Toulouse)
SHEN Bailin (Archaeometry Lab, Laboratory Sun Yat-sen University, China)
ZHU Tiequan (Archaeometry Lab, Laboratory Sun Yat-sen University, China)

Report:

The experimental aim was to obtain information concerning the chemical reactions occurring during the formation of the blue decors of Qinghua porcelain and, in particular to determine if $CoAl_2O_4$ and/or Co_2SiO_4 could be formed from chemical reactions between the glaze and cobalt oxides. We also wanted to verify that cobalt aluminate was well stable in the glaze at high temperature.

To do so, 3 types of cobalt source ($CoAl_2O_4$, Co_3O_4, 19th century pigment painting) were mixed with ~~a~~ raw glaze used currently at the ceramic institute of Jingdezhen and close to the composition of ancient glazes. At first, the whole high-resolution diffraction patterns of raw glaze and 19th century pigment painting were collected at room temperature. The high-resolution patterns allow us to identify their complex compositions[1] and thus confirm the presence of 2 different feldspaths (albite and microcline) in the raw glaze (Fig. 1). Then, the phase transformations of (Co_3O_4 + raw glaze) and ($CoAl_2O_4$ + raw glaze) were followed from

[1] 19th pigment painting contains: gypse ($CaSO_4.2H_2O$), aluminate de cobalt ($CoAl_2O_4$),quartz (SiO_2), calcite ($CaCO_3$), kaolin ($Al_2Si_2O_5(OH)$), lazincite (ZnO) and cobalt oxide trace. Raw glaze: quartz (SiO_2), calcite ($CaCO_3$), microcline ($KAlSi_3O_8$), albite ($NaAlSi_3O_6$), dolomite ($CaMg(CO_3)_2$)

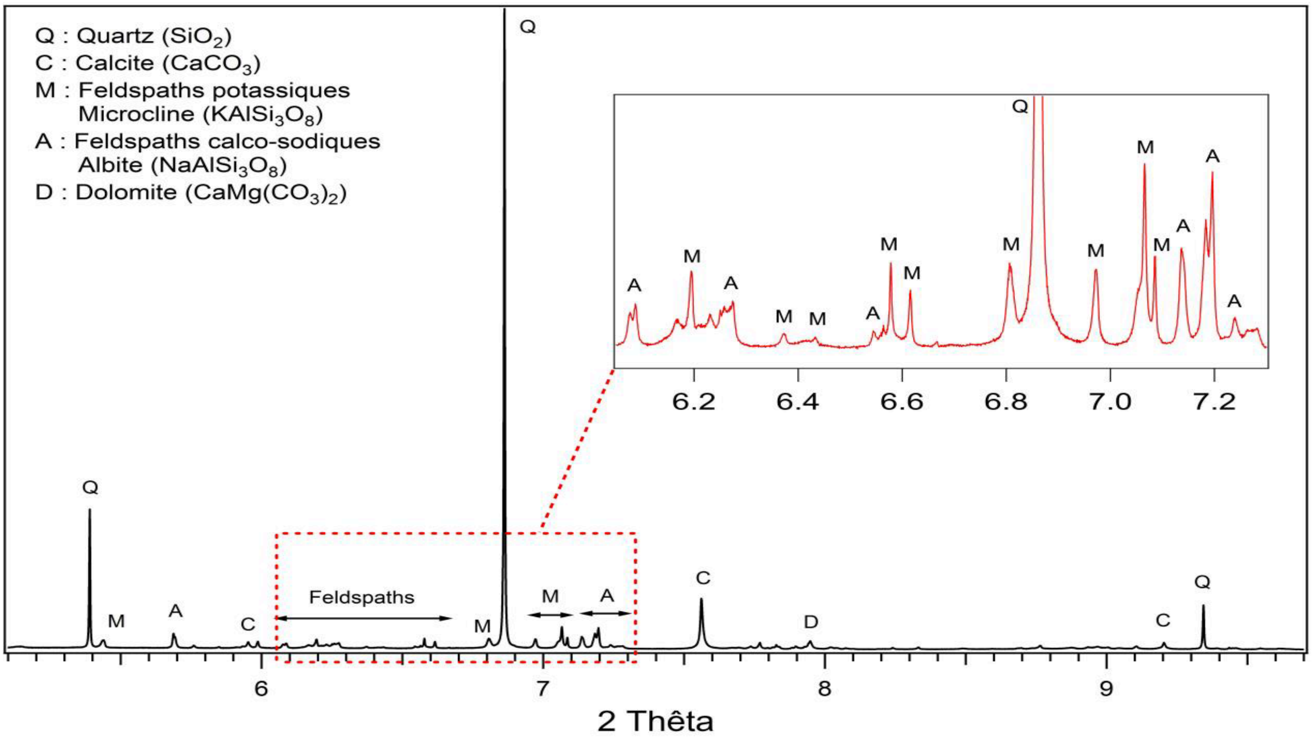

Fig. 1 XRD pattern of raw glaze recorded at roon temperature (λ= 0.40026659 Å)

room temperature to 1340°C. We started with the 2 simpler mixtures, and we did not have time to study the third one.

The in-situ study was performed using the mirror furnace of ID22. After having tried to use Pt capillaries, we realized that it was difficult to observe the minority phases, so we chose to use quartz capillaries. Pt powder was added to the mixtures for temperature calibration.

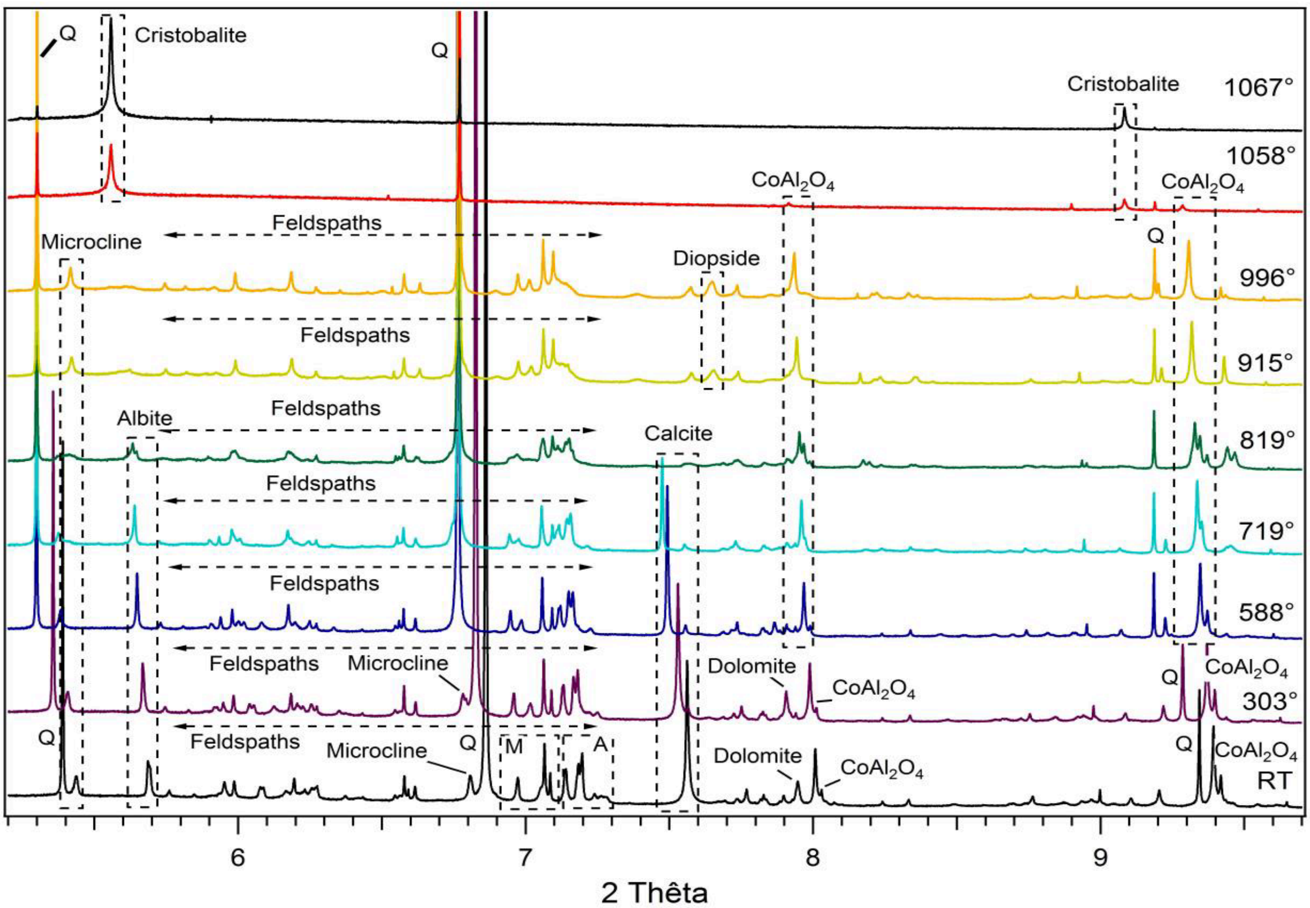

Fig.2 Evolution of the XRD patterns of (CoAl2O4 + raw glaze) mixture during the heating (λ= 0.40026659 Å)

The heating and cooling phases were controlled by controlling the power of the lamps from 50 to 300 watts. 9 and 5 patterns were recorded during the heating and cooling phases, respectively. The temperatures needed being quite high for quartz capillary (occasional loss of capillary) and the suitable lamp power being difficult to anticipate, the experiment was repeated several times for each mixture.

The study of (Co_3O_4 + raw glaze) mixture confirmed the dissolution of Co_3O_4 in the glassy matrix without formation of $CoAl_2O_4$. On the other hand, the study of ($CoAl_2O_4$ + raw glaze) mixture showed that the $CoAl_2O_4$ was more stable in the glassy matrix, but also eventually dissolves at higher temperature. In the two mixtures the phases of raw glaze showed the same evolution, i.e the disappearance of carbonates, the appearance of diopside and cristoballite as well as the transformation of albite in anorthite by substitution Ca /Na. No modification was observed during the cooling phase. These experiments showed that cobalt oxide did not react with the Al of the glaze to form $CoAl_2O_4$. It dissolves in glassy matrix. Al reacts in priority with Ca and Si to form anorthite, pyroxen and wollastonite. $CoAl_2O_4$ crystals are stable enough to be included in the glassy matrix, and theirs dissolution occurs at higher temperature.

The set of results is presented and discussed in term of pigment elaboration process in the Ariane Pinto's theses, which can be downloaded from open Hal archive (tel-02427084, version 1).