ESRF	**Experiment title: In-situ XRD study of raw clays leading to the formation of brownware or blackware Chinese glazes**	**Experiment number**: HG 144
Beamline: ID22	**Date of experiment**: from: 03/03/2021 to: 07/03/2021	**Date of report**:
Shifts: 9	**Local contact(s)**: Catherine Dejoie	*Received at ESRF:*

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Report:

The experimental aim of this study was to obtain information concerning the chemical reactions occurring during the firing of the raw material used to make the glazes of black and brown ceramics. In particular this study focuses on the crystallisation of species that could be precursors to ε-Fe_2O_3; a phase that is recurrently present in ancient brown-ware.

For this, 4 different raw materials were investigated (out of 5 planned): 3 types of naturally sourced powdered minerals - one sourced in the Yaozhou site (Shaanxi), one in the Luhuaping site (Fujian) and one given by Sun Jianxing, artist and manufacturer of Jian-ware (Fujian) – and prepared raw material from the Yaozhou minerals. These were labelled respectively Jish1, Fuj1, Fuj2 and RZZJraw. An additional material sourced from Aveyron, France, labelled Mon4,1 was also brought for comparison but priority was given to the Chinese samples and we had not the time to study it.

Prior to this study, high-resolution diffraction patterns of the 5 raw materials were collected at room temperature (cf. Figure 1). These allowed a detailed identification of numerous phases presents in the materials, although some minor peaks remain to be determined. Indeed as naturally sourced raw materials, the huge diversity of mineral species present in the mixture, coupled with the complexity of the patterns of clay minerals, feldspar and micas present make it hard to interpret fully.

Rietwelt refinement was attempted on these measurements, however when compared to preparatory experiments implemented at CEMES-CNRS, it was found that the amount of quartz and calcite was significantly higher in the hight resolution diffraction patterns. This is

probably due to phase segregation during the filling of the capillary. This creates a biais in quantification using the high-resolution patterns.

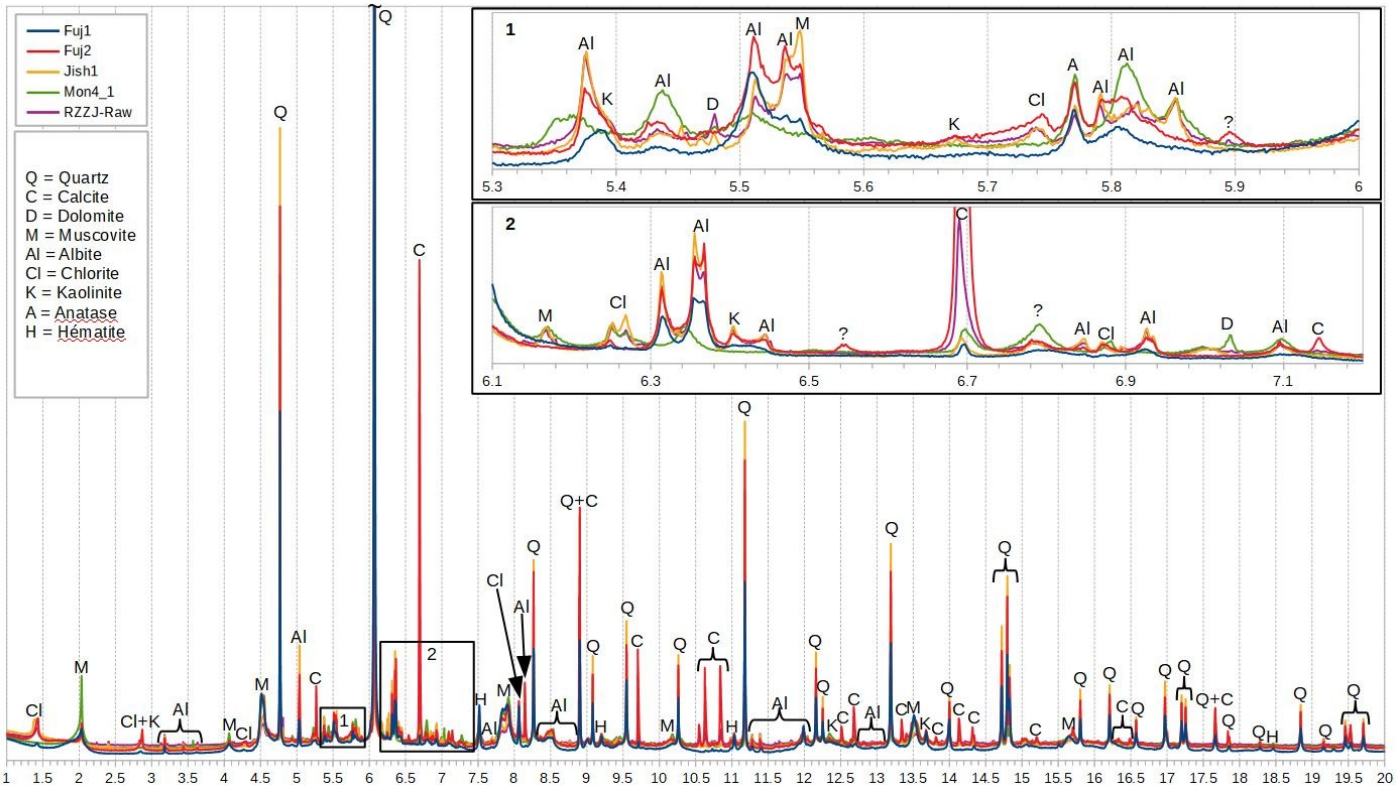

Figure 1: Raw material diffraction pattern with phase identification (unit=2θ)

The in-situ experiments were performed in quartz capillary in the furnace of ID22 beamline. Platinum powder was added in every capillary for temperature determination. Temperature was controlled by adjusting the power of the three lamps from 45 W to 270 W. 20 minutes diffraction patterns were recorded regularly during the heating and cooling of the material. At high temperature, melting of the capillary was often observed, making it necessary to reduce the number of recording at high temperature and to repeat experiments.

In total 7 firing were studied (2 for Fuj1, Jish1 and RZZJraw and 1 for Fuj2). Heating temperature were determined with platinum for Jish1_1, Fuj1_2 and Fuj2_1. However for the other recording, problems in the recrystallisation of platinum prevented from determining the temperature accurately (presence of 3 peaks instead of 1). Quartz was thus chosen as an internal temperature standard for other samples.

The in-situ experiments highlighted the growth of new crystalline species, such as indialite, a high temperature dimorph of cordierite, which were found on modern recreations and some ancient sherds (cf. Figure 2 left). Augite crystallisation and remelting, followed by anorthite crystallisation was also observed (cf. Figure 2 right). Peaks belonging to other species were also detected, in particular a series of four intense peaks that were not identified due to thermal shifts which prevented any phase identification.

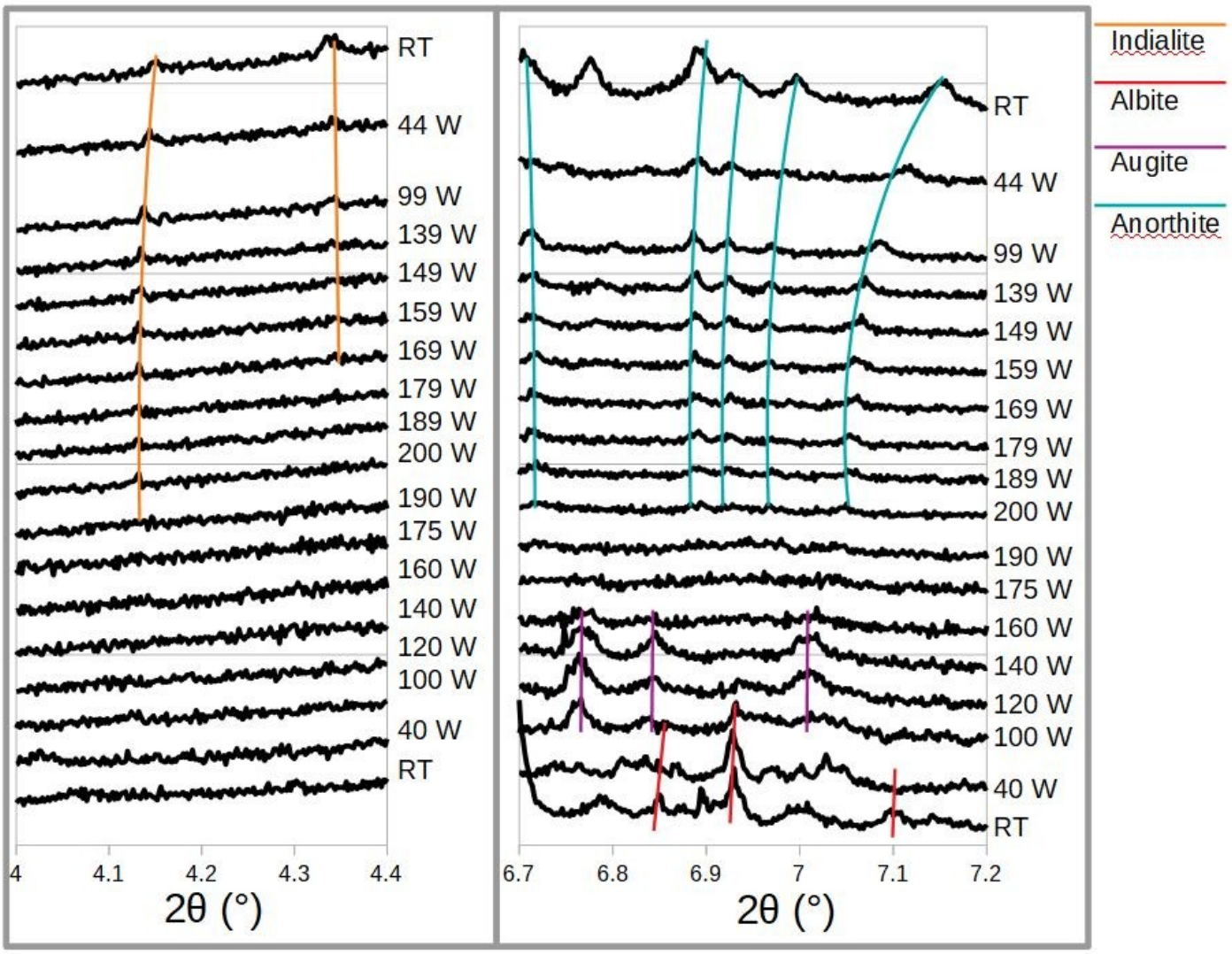

Figure 2: Following of phases in RZZJraw

It should be noted however that, due to the significant lack of clay minerals and feldspars compared to the raw material and the capillary conditions, the comparison with traditional firing should be taken very cautiously. The lack of clays/feldspars in particular may create a bias in the crystallising species. It should also be mentioned that no ε-Fe_2O_3 or other iron oxides were detected during the firing.

A more in depth analysis of those results will be presented in Clément Holé's PhD manuscript.