# The reactivity of pigments composed of chromium in a porcelain glaze

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## Supporting information

### 1. Analytical methods

X-ray powder diffraction (XRD) data were collected using a PANalytical X'Pert PRO diffractometer with Cu Kα radiations ($\lambda_{Cu,K\alpha1}$ = 1.54056 Å, $\lambda_{Cu,K\alpha2}$ = 1.54439 Å). XRD patterns for the pigments were measured on powered samples, between 5° and 130°, with a step of 0.008° 2θ and a counting time of 25 s/step. For the glazes, XRD patterns were measured without specific preparation, between 10° and 130°, with a step of 0.016° 2θ and a counting time of 550 s/step. Rietveld and LeBail refinements were carried out using the FullProf Suite program[1].

Diffuse reflectance spectra were recorded using a Perkin Elmer Lambda 1050 spectrometer equipped with an integrating sphere, between 4000 and 36,000 $cm^{-1}$. The pigments were finely ground and the powdered samples were deposited on a support. A perfectly flat tablet of $BaSO_4$ was used as a white reference material. A Kubelka-Munk conversion applied to a diffuse reflectance spectrum enables to obtain the absorption spectrum[2].

Cross sections were cut from the porcelain shard with the glaze on the top. These fragments were embedded in a resin block, polished using diamond pastes down to 3 μm and carbon coated. Scanning electron microscopy (SEM) analyses were conducted with a Zeiss Ultra55 (Oberkochen, Germany), with an acceleration voltage of 15 keV, a working distance of 7.5 mm and a backscattered electron detector, associated with an X-ray Energy Dispersive Spectroscopy (XEDS) microprobe.

Electron transparent foils were prepared using Focused Ion Beam (FIB) on a FEI STRATA DB235 instrument. Sections were analyzed with a JEOL 2100F microscope operating at 200 kV. This microscope was equipped with a field emission gun, an ultra-high resolution (UHR) pole piece and a scanning TEM (STEM) device, which allowed Z-contrast imaging in the high angle annular dark field (STEM–HAADF) mode. Chemical analyses were performed using a JEOL detector with an ultrathin window by XEDS elemental mapping in the STEM-XEDS mode. Selecting area electron diffraction (SAED) patterns were acquired along two or three zone axis to identify unambiguously the structure of the crystal.

X-ray absorption near edge structure (XANES) spectra at the Cr K-edge were collected on the LUCIA beamline at the SOLEIL synchrotron facility in Saint-Aubin (France). The synchrotron operated with a storage ring current of 450 mA and an energy of 2.75 GeV. The layout of the LUCIA beamline is described in Vantelon et al.[3] XANES spectra were collected using an

Si(311) double crystal monochromator. The monochromator was calibrated against the maximum intensity of the first inflection of the first derivative of a metallic Cr standard (5989 eV). XANES measurements were performed in the energy range 5940 eV to 6200 eV. The energy steps were fixed to 2, 0.05, 0.2, 0.5 and 1 eV for energy ranges of [5940 - 5983] eV, [5983 - 5999] eV, [5999 to 6040] eV, [6040 - 6120] eV and [6120 - 6200] eV, respectively. Spectra were collected under vacuum at room temperature (around $10^{-2}$ mbar), in X-ray fluorescence mode using a 4-elements Silicon Drift Diode detector. Powdered samples (reference of $Cr_2O_3$, pigments 10100 and 10059) were pressed into pellets and were mounted on carbon tape. Two to four spectra were recorded for each sample with a counting time of about 1s per step. Multiple Cr K-edge XANES spectra recorded for each sample were merged to obtain average spectra before background subtraction and normalisation using the ATHENA software[4].

## 2. Solid solution $CoAl_2O_4$-$CoCr_2O_4$

The two end-members of the solid solution, i.e $CoAl_2O_4$ and $CoCr_2O_4$, were first synthesised. Reagent-grade chemicals CoO, γ-$Al_2O_3$ and $Cr_2O_3$ were weighted in the right stoichiometric proportions, mixed, ground in an agate mortar with ethanol and calcined in a platinum crucible at 1400 °C during 20 hours. Then, using the same procedure, nine compounds in the solid solutions $CoAl_{2-x}Cr_xO_4$ with *x* from 0.2 to 1.8 were synthesised from the end-members. The color of the sample varies from blue ($CoAl_2O_4$) to greenish-blue ($CoCr_2O_4$).

XRD diagrams acquired on each sample show the formation of a single spinel phase (figure S-1). Lattice parameter *a* was calculated by Le Bail refinement of the XRD pattern and plotted as a function of the Cr content *x* in the $CoAl_{2-x}Cr_xO_4$ series (figure S-2). A gradual increase in the lattice parameter is observed when substituting Al by Cr. A linear regression points out that this solid solution obeys Vegard's law with the following equation: a (Å) = 0.1153 *x* + 8.107 (Å). The lattice parameter found for $CoAl_2O_4$ is consistent with results previously reported in the literature[5].

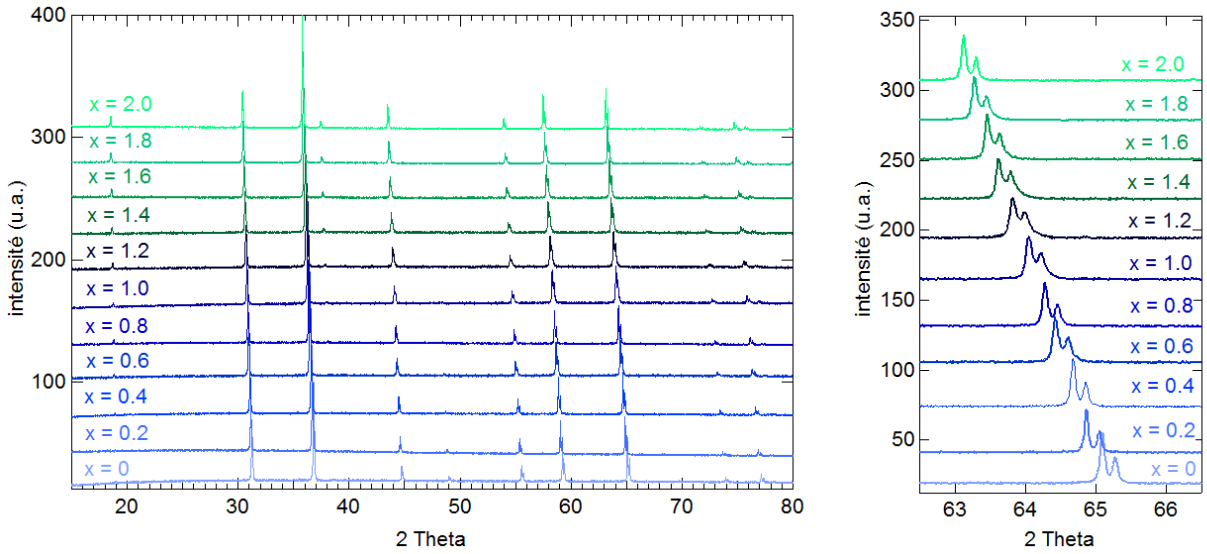


*Figure S-1: XRD patterns of the samples $CoAl_{2-x}Cr_xO_4$ with x between 0 and 2. The linear shift towards lower 2θ with the increase of chromium content x is due to the linear increase of the lattice parameters.*

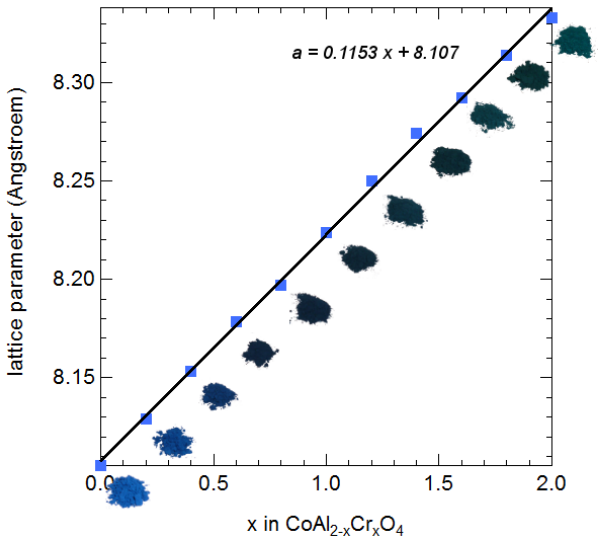


*Figure S-2: In blue, variation of the cubic lattice parameters a of $CoAl_{2-x}Cr_xO_4$ calculated with Rietveld refinements as a function of the chromium concentration x; in black the linear regression; for each composition the pictures of the powders is on the right.*

## 3. Modification of the thermal treatment applied on glaze g-10100

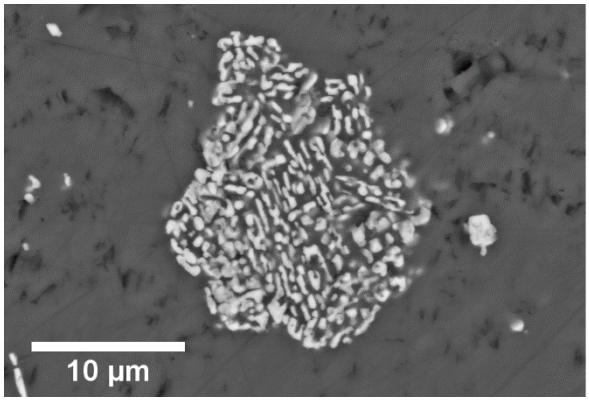


*Figure S-3: SEM image (signal ASB, EHT=15 kV) of a representative grain of pigment in g-10100 fired at 1280°C during 15 hours.*

## 3. References


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