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Physics and arts / Physique et arts

## Reactivity of chromium-based pigments in a porcelain glaze

*La réactivité des pigments composés de chrome dans un décor de porcelaine*Louisiane Verger<sup>a,b</sup>, Olivier Dargaud<sup>b,\*</sup>, Gwenaëlle Rouse<sup>c,d</sup>,  
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## ABSTRACT

This paper presents a comprehensive investigation at the microscopic scale of various pigments composed of chromium from the French 'Manufacture de Sèvres' to establish the origin of color in glazes. Electron microscopy coupled with X-ray diffraction allows the determination of the microstructure and composition of the crystalline phases after firing. X-ray absorption spectroscopy reveals subtle changes in the medium-range ordering around Cr with high spatial resolution, in the pigment grain or at the pigment/glass interface. Principal results indicate systematic and common changes whatever the pigment types: (i) Cr-enrichment for the final crystals, that controls the coloration of the glaze, (ii) migration of specific elements such as Al or Zn from the pigments to the amorphous part of the glaze, and (iii) crystallization of anorthite in the near proximity of the altered Cr-bearing crystalline pigments.

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## R É S U M É

Divers pigments composés de chrome et synthétisés à la Manufacture de Sèvres sont étudiés dans cet article pour comprendre l'origine de la couleur des décors de porcelaine. La microscopie électronique couplée à la diffraction des rayons X permet de déterminer la microstructure et la composition des phases cristallines présentes après la cuisson du décor. Des mesures d'absorption des rayons X spatialement résolues révèlent des changements subtils de l'environnement du chrome, dans le grain de pigment et à l'interface pigment/verre. Les résultats montrent un mécanisme commun et systématique de réactivité des pigments au cours de la cuisson du décor de porcelaine : (i) enrichissement des cristaux en chrome, contrôlant la couleur finale du décor, (ii) migration spécifique de cer-

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tains éléments tels que Al et Zn du grain de pigment vers la partie amorphe du décor et (iii) cristallisation d'anorthite à proximité des grains de pigment altérés.

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## 1. Pigments and glazes from the French 'Manufacture de Sèvres'

A porcelain decoration, or glaze, is composed of one or several partially vitrified layers on the porcelain surface. Colored glazes are obtained by the mixture of an uncolored component with pigments. The uncolored component can be a glass frit, or a crystallized mixture that will vitrify during the firing of the porcelain decoration. Pigments can be simple oxides composed of transition metals (chromium, cobalt, iron, for example), or can require a synthesis step prior to the formulation of the glaze. The French porcelain factory named 'Manufacture de Sèvres' is famous for the delicacy and the colors of its porcelain decoration since its creation in 1740. Every step of the porcelain manufacturing is conducted at the 'Manufacture'. In particular, the laboratory is in charge of pigments synthesis and preparation of glazes [1].

During the 19th century, the variety of colors obtained at the *Manufacture de Sèvres* was substantially developed. This period starts with Alexandre Brongniart [2], introducing chromium in the laboratory, an element recently discovered by Louis-Nicolas Vauquelin [3,4]. Green glazes especially stable at high temperatures were obtained with this new element, and subsequently replaced glazes obtained from copper oxides [5]. In 1845, Brongniart hired a young scientist, Jacques-Joseph Ebelmen, as deputy director of the factory. Ebelmen conducted research on the synthesis of minerals. Drawing its inspiration from solution chemistry, Ebelmen initiated the flux growth method for preparing crystals: precursors (solutes) are heated at high temperatures in platinum crucibles with a flux, typically boric acid or borax, acting as a solvent. This innovative technique allowed Ebelmen to synthesize new crystalline compounds, including spinels [6]. After Ebelmen's death (1852), his work was continued by his co-worker Alphonse Louis Salvétat, chemist at the 'Manufacture de Sèvres' [7]. Ebelmen and Salvétat obtained tiny crystals (less than one millimeter in their largest dimension) that were perfectly suited to be used as pigments. These syntheses paved the way for new coloring agents containing chromium. Eventually, a palette of 138 pigments numbered between 10001 and 10138 was established at the Sèvres laboratory, among which 76 pigments are composed of chromium oxides. Our previous work [8] identified five different groups of pigments in this set of 76 Cr-pigments, based on the main crystalline phases present: (1) eskolaite ( $\text{Cr}_2\text{O}_3$ ), (2) uvarovite ( $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ ), (3) eskolaite-corundum ( $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ ) solid solution, (4) Cr-doped cassiterite ( $\text{SnO}_2$ ) and malayaite ( $\text{CaSnSiO}_5$ ), and (5) spinels.

Once a new pigment is synthesized, it is tested in several porcelain decorations types, and applied on thin porcelain slabs. More than eight different types of porcelain decoration were created at the 'Manufacture de Sèvres', depending on the porcelain nature and on the number of partially vitrified layers. All tests conducted are stored at the laboratory, and they are a unique trace of a pigment's history. Since 1882, laboratory note books have been kept to follow the production (Fig. 1A–B). To test a new pigment, the porcelain decoration is applied with various thicknesses. Interesting visual effects can arise from this process, as illustrated in Fig. 1C. The pigment used to decorate this slab is composed of a gahnite with chromium pigment  $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$  synthesized on October 8th, 1893. The slab was decorated using this pigment a few years later, on December 25th, 1896 (we can note that production at Sèvres did not stop at all through the year!). As the thickness of the glaze decreases, we observe a gradient of color from pink to green hue. Interestingly, a vase produced at the same period, in 1899, is characterized by the same shading from pink to green (Fig. 1D). In this case, there is no evidence that the shading is only due to a difference of thickness. This reflects a reactivity of the pigment during the firing of the glaze, which is yet to be understood. It also exemplifies the direct use of the research conducted at the laboratory for the production of the 'Manufacture'.

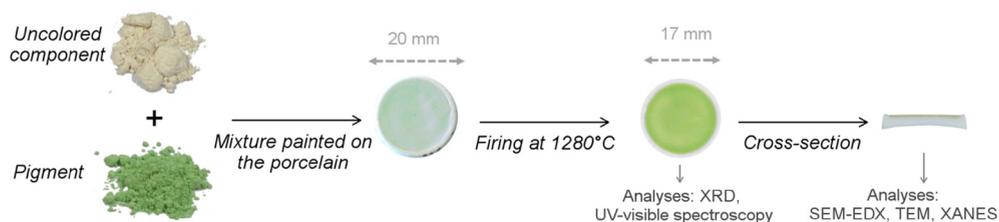
The uncolored component vitrifies during the firing of the porcelain decoration, and can be described as a glass. The interaction between the pigment grains and the melt can be accounted for by two opposite phenomena: the pigment grains can simply be embedded within the glass and preserve their crystallinity or, on the contrary, they can react and dissolve in the glass. The reality is usually more complex, as already emphasized on a corundum type ( $\text{Fe,Al}$ ) $_2\text{O}_3$  pigment [9,10]. Color change can occur during the thermal treatment, which degrades or modifies the initial color of the pigment. These color modifications highlight a reactivity of the pigments, usually poorly understood, and empirically controlled in industrial and craft processes. In our previous works [11,12], we showed that the pigment 10045 mainly composed of the spinel phase  $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$ , is not stable in one of the most used uncolored components from the 'Manufacture', preventing its use and depriving the palette of decoration from the interesting salmon color given by this pigment (see Fig. 1C). In this article, we investigate the reactivity of two pigments composed of spinels with different divalent ions ( $\text{Mg}^{2+}$  and  $\text{Co}^{2+}$ ), and we compare the results with pigment 10045. In a second part, we will focus on a pigment belonging to the eskolaite group, which apparently does not undergo color modification during the firing of the glaze.

## 2. Preparation of modern samples

The pigments used in this study belong to the collection of the Sèvres laboratory. Most of them are prepared by a classical ceramic route: metallic oxides are mixed, ground, and then calcined at 1280 °C or 1400 °C in porcelain crucibles. The



**Fig. 1.** From laboratory tests to the production of objects. (A–B) Extract from the laboratory notebooks of the years 1893 and 1896, referring to the synthesis of a gahnite with chromium type pigment on October 8th, and its test in a porcelain decoration on December 25th, respectively. (C) Porcelain slab composed of the porcelain decoration prepared on December 25th, 1896. The reference of the sample appears on the back of the slab (not shown). (D) Vase de Chagny A (1899) from the collection of the “Cité de la céramique”, MNC12652, dimensions: 120 cm (height), 55 cm (diameter). ©RMN-Grand Palais.



**Fig. 2.** Protocol to obtain modern glazes. The pigment is mixed with the uncolored frit, and the mixture is painted on a porcelain mount. The porcelain is then fired at 1280 °C. X-ray diffraction (XRD) and UV-visible spectroscopy measurements are performed directly on the glaze. The cross section is cut from the sample and observed by SEM, to carry out XANES spectroscopy at the Cr K edge, and to prepare a FIB cross-section for TEM.

synthesis protocol is known [1], and the phases obtained were characterized in a previous work [8]. Porcelain decorations, or glazes, were prepared at the ‘Manufacture de Sèvres’, following its savoir-faire (Fig. 2). They are obtained by mixing 0.5 g of pigment with 4.5 g of an uncolored crystallized component named CI. The uncolored component is composed of feldspar, kaolin, quartz, and chalk, in proportions specific to the porcelain of Sèvres. The mixture of the pigment and the uncolored component is painted on a round porcelain mount, designed for this study. The edge allows controlling the amount of glaze deposited and their shape enables to adapt the sample to a wide variety of characterization techniques. The sample is then fired following a typical heat treatment for porcelain artifacts at the Manufacture: 1000 °C is reached in 10 h, then 1280 °C is reached in 5 h 30. Once 1280 °C is reached, the furnace is immediately turned off and slowly cooled down to room temperature. The atmosphere of the electric powered furnace is not controlled for the preparation of this kind of decoration. In this article, the indexing of pigments respects the one in use at the ‘Manufacture’ (number between 10001 and 10138) [1]. The corresponding glazes are named with the letter g in prefix.

Table 1 is a summary of the selected pigments for this study, and their visual aspect in the porcelain decoration after firing. A systematic change of color between the pristine pigment and the resulting glaze is observed for the spinel group: glazes made from pink pigments 10024 and 10045 become brown after firing, while a green hue appears after firing of the glaze made from blue pigment 10094. Concerning pigment 10100, no color change is observed. To understand the change of color occurring with pigment 10024, 10045 and 10094 on the one hand, and to compare the results obtained with pigment 10100 on the other hand, a multi-analytical approach combining UV-visible spectroscopy, scanning and transmission electron microscopies, X-ray diffraction (XRD) measurements, and X-ray absorption spectroscopy was conducted. All experimental conditions can be found in Supplementary Information.

**Table 1**

Summary of the samples studied. Pigments are indexed using the numbering of the 'Manufacture de Sèvres'.

Eskolaite	Spinel		
Cr <sub>2</sub> O <sub>3</sub>	ZnAl <sub>2-x</sub> Cr <sub>x</sub> O <sub>4</sub>	MgAl <sub>2-x</sub> Cr <sub>x</sub> O <sub>4</sub>	CoAl <sub>2-x</sub> Cr <sub>x</sub> O <sub>4</sub>
	<i>x</i> =0.41	<i>x</i> =0.44	<i>x</i> =0.59
10100	10045	10024	10094
			
g-10100	g-10045	g-10024	g-10094
			

### 3. Spinel: a systematic modification of color between the pigment and the resulting glaze

#### 3.1. Characterization of the pigments and the glazes

Pigments mainly composed of three different types of spinel solid solutions were investigated,  $\text{MAl}_{2-x}\text{Cr}_x\text{O}_4$ , where M = Zn, Mg, and Co for pigment 10045, 10024, and 10094, respectively. The composition of the phases is determined through Rietveld refinements of their XRD patterns (Fig. 3A). The majority phases are all indexed in the cubic  $Fd\bar{3}m$  space group, characteristic of the spinel system. The solid solutions studied here follow Vegard's law. The lattice parameters  $a$  of phases  $\text{MAl}_{2-x}\text{Cr}_x\text{O}_4$  are linked to the chromium occupancy  $x$  by the following linear equations:

$$a(\text{\AA}) = 0.1215x + 8.086 (\text{\AA}) \quad \text{M} = \text{Zn} \quad (1)$$

$$a(\text{\AA}) = 0.1210x + 8.083 (\text{\AA}) \quad \text{M} = \text{Mg} \quad (2)$$

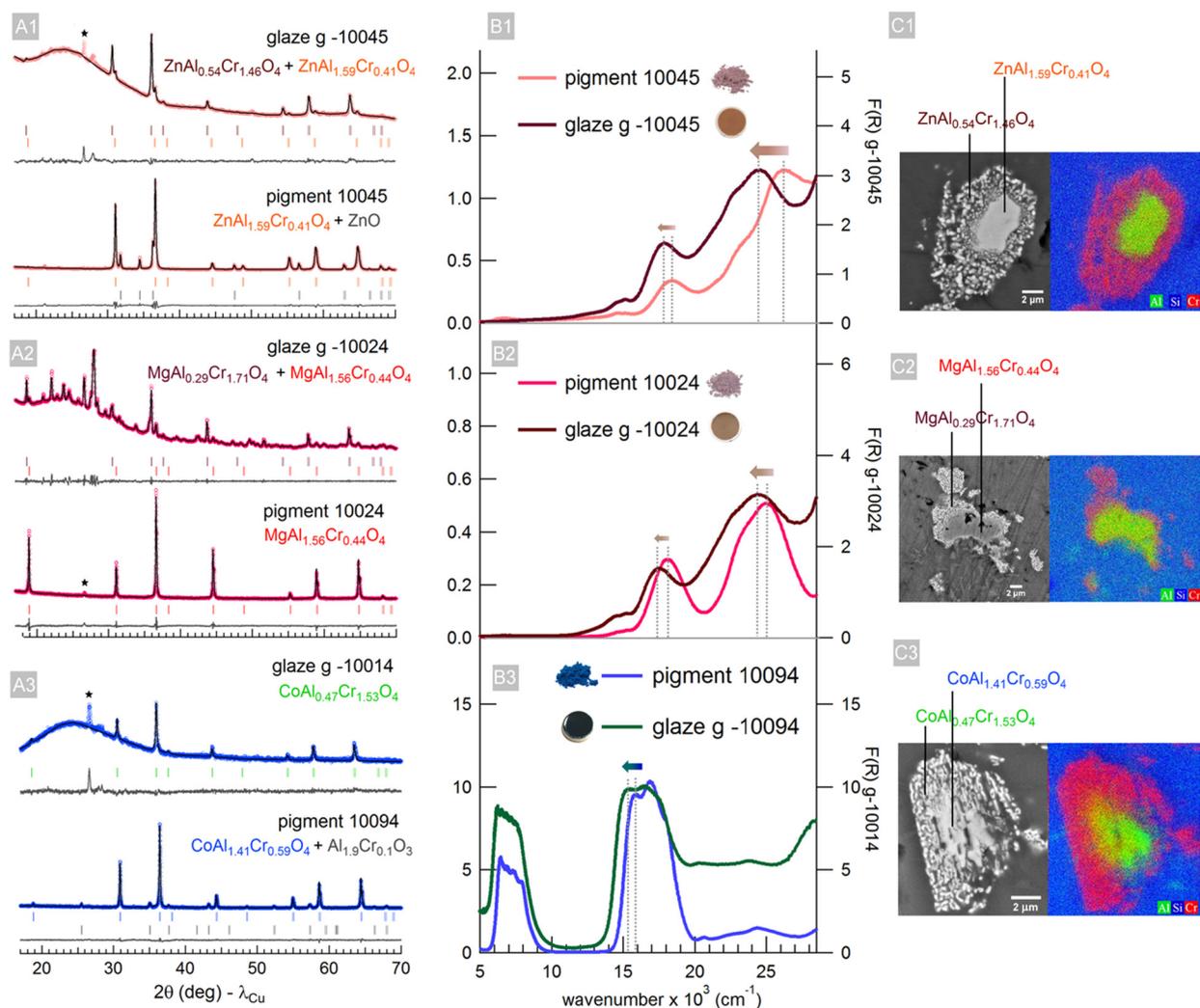
$$a(\text{\AA}) = 0.1153x + 8.107 (\text{\AA}) \quad \text{M} = \text{Co} \quad (3)$$

derived from our previous XRD investigation (see reference [13] and Supplementary Information) and the work of Prim et al. [14]. Both lattice parameter and chromium occupancy are fitted during the refinement and they are in good agreement. Since  $a$  and  $x$  are nicely correlated, we prefer to use equations (1)–(3) to obtain  $x$  from  $a$ . Chromium is in octahedral environment along the three solid solutions, due to the large octahedral ligand field stabilization of  $\text{Cr}^{3+}$  [15].

Pigment 10045 is mainly composed of spinel  $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$ , with a small amount of ZnO (Fig. 3A1 – bottom). The presence of ZnO can be explained by the fact that reagents are usually not introduced in stoichiometric amounts during the synthesis of the pigment. The crystalline purity of a pigment is not necessarily a criterion at the 'Manufacture', but rather its coloring properties in a glaze. The amount of Cr in the phase gives a pink color to the spinel [13]. Pigment 10024 is slightly more concentrated in chromium: it is mainly composed of spinel  $\text{MgAl}_{1.56}\text{Cr}_{0.44}\text{O}_4$  (Fig. 3A2 – bottom), which also presents a pink color [16]. The impurity of quartz is detected, as usually observed in pigments synthesized at the 'Manufacture' [8]. Pigment 10094 is composed of spinel  $\text{CoAl}_{1.41}\text{Cr}_{0.59}\text{O}_4$ , with a small amount of  $\text{Al}_{1.9}\text{Cr}_{0.1}\text{O}_3$  (Fig. 3A3 – bottom). It is characterized by a blue color.

A systematic modification of color is observed when glazes are fired. The three pigments and their respective glazes were characterized by UV-visible spectroscopy (Fig. 3B). The color of pigments 10045 and 10024 is due to the presence of  $\text{Cr}^{3+}$  in octahedral environment. A shift towards lower wavenumbers of the two main absorption bands of  $\text{Cr}^{3+}$  is observed between pigments 10045 and 10024, and their resulting glazes g-10045 and g-10024 (Fig. 3B1–B2). The optical extinction coefficient is smaller in octahedral environment than in tetrahedral environment. The two large absorption bands visible on the spectra of pigment 10094 (Fig. 3B3) are then mainly due to  $\text{Co}^{2+}$  in tetrahedral environment [17,18]. The effect of  $\text{Cr}^{3+}$  and  $\text{Co}^{2+}$  in octahedral environment in the spinel is not discussed here. On glaze g-10094, the band centered at  $17,000 \text{ cm}^{-1}$  is shifted towards lower wavenumbers.

XRD measurements were performed directly on glazes (Fig. 3A). The presence of a diffuse background common to the three samples near  $2\theta \approx 26^\circ$  is due to the formation of a calcium aluminosilicate glass resulting from the vitrification of the uncolored component. The melting process is, however, not completely achieved, since Bragg peaks due to quartz are



**Fig. 3.** Multi-analytical study of glazes composed of spinel type pigments. (A1) Rietveld refinements of pigment 10045 composed of ZnO and spinel  $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$  and glaze g-10045 composed of spinels  $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$  and  $\text{ZnAl}_{0.54}\text{Cr}_{1.46}\text{O}_4$ . (A2) Rietveld refinements of pigment 10024 composed of spinel  $\text{MgAl}_{1.56}\text{Cr}_{0.44}\text{O}_4$  and Le Bail refinement of glaze g-10024 composed of spinels  $\text{MgAl}_{1.56}\text{Cr}_{0.44}\text{O}_4$  and  $\text{MgAl}_{0.29}\text{Cr}_{1.71}\text{O}_4$  and anorthite  $(\text{Ca}, \text{Na})(\text{Al}, \text{Si})_4\text{O}_8$ . (A3) Rietveld refinements of pigment 10094 composed of spinel  $\text{CoAl}_{1.41}\text{Cr}_{0.59}\text{O}_4$  and  $\text{Al}_{1.9}\text{Cr}_{0.1}\text{O}_3$  and glaze g-10094 composed of spinel  $\text{CoAl}_{0.47}\text{Cr}_{1.53}\text{O}_4$ . The colored dots and black lines show the observed and calculated patterns, respectively. Vertical tick marks indicate Bragg reflections in space group  $Fd\bar{3}m$  for spinels,  $P6_3mc$  for ZnO and  $R\bar{3}c$  for  $\text{Al}_{1.9}\text{Cr}_{0.1}\text{O}_3$ . The peaks indexed with a star correspond to quartz ( $\text{SiO}_2$ ) impurities. (B1–B3) Remission function  $F(R)$  calculated from diffuse reflectance spectra of pigments 10045, 10024, 10094, and their respective glazes g-10045, g-10024, and g-10094. (C1–C3) SEM images (signal ASB, EHT = 15 kV) of a representative grain of pigment embedded in the glassy matrix in glazes g-10045, g-10024, and g-10094 (left) and composite images built from elemental EDS maps of Cr, Al, and Si (right).

detected. Glaze g-10045 is composed of two other phases containing Cr bearing spinels. The phase present in the initial pigment,  $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$ , is still detected in a low amount in the glaze. Interestingly, a phase belonging to the same solid solution, but with a higher Cr content is detected as a majority phase:  $\text{ZnAl}_{0.54}\text{Cr}_{1.46}\text{O}_4$ . The same observation is made on the sample g-10024: the initial pigment phase is only present in a low amount,  $\text{MgAl}_{1.56}\text{Cr}_{0.44}\text{O}_4$ , while the main phase detected is richer in Cr,  $\text{MgAl}_{0.29}\text{Cr}_{1.71}\text{O}_4$ . In sample g-10094, only the Cr-rich phase is observed,  $\text{CoAl}_{0.47}\text{Cr}_{1.53}\text{O}_4$ . Moreover, the sample g-10024 is characterized by the presence of anorthite  $(\text{Ca}, \text{Na})(\text{Al}, \text{Si})_4\text{O}_8$ .

Polished cross sections of glazes appear heterogeneous under the scanning electron microscope (SEM): they are composed of bubbles and aggregates of crystallized grains, embedded in the glassy matrix. Two main populations of aggregates are observed. Figs. 3C1 to C3 show representative SEM images of the first type of aggregates observed in the three different samples (left), with composite images built from elemental EDS maps of Cr, Al and Si (right). The morphology of the aggregate is common to the three glazes: while the center of the aggregate looks homogeneous and composed of a single grain, the periphery is fragmented and composed of several grains. The chemical composition is different as well, with the periphery enriched in Cr for the three samples. EDS analysis is in good agreement with the Cr-rich phases detected by XRD. The second population of aggregates is composed of smaller grains, completely fragmented, with a higher chromium content

compared to the periphery of the first population. In sample g-10024, a third phase is present, which seems to diffuse from the center of the aggregate to the silicate melt. This phase has been identified as anorthite  $(\text{Ca, Na})(\text{Al, Si})_4\text{O}_8$  according to EDS analysis. In sample g-10045, this phase is also detected, but only around large aggregates of grains [12].

### 3.2. A common mechanism of reactivity

In our previous works [11,12], we showed that pigment 10045, mainly composed of spinel  $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$ , is not stable in the uncolored component used. During the firing of the glaze, a Cr-rich phase belonging to the same solid solution forms from the periphery of the pigment grain:  $\text{ZnAl}_{0.54}\text{Cr}_{1.46}\text{O}_4$ . The second population of grains observed under SEM corresponds to fully reacted grains of pigment. The formation of this phase explains the color change. Indeed, the color of samples along the solid solution  $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$  varies with the chromium content  $x$  [13]. The introduction of a few ppm of chromium in the colorless gahnite ( $\text{ZnAl}_2\text{O}_4$ ) leads to a pink color. This color intensifies with Cr concentration  $x$ . From  $x = 1$ , a brownish hue appears, which intensifies until  $x = 1.6$ . The powder at  $x = 1.8$  appears brownish green and the zincchromite  $\text{ZnCr}_2\text{O}_4$  is green [19]. The formation of the Cr-rich phase can be explained by the gradual migration of Al from the pigment towards the surrounding silicate melt during firing. As a consequence of the Al rich layer near the pigment/melt interface, the system can pass through the stability field of anorthite in the ternary  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$  [20,21]. Observations through a transmission electron microscope (TEM) on a FIB cross section at the interface confirm the formation of anorthite around some grains, although in a low amount that is not detectable by XRD [12]. The mobility of Al from the pigment to the melt is enhanced by the chemical composition of the latter and, more specifically, the large content of alkali or alkaline-earth cations in the melt. The vitrification of the uncolored component results in the formation of mainly a calcium aluminosilicate glass. In such a glass, calcium cations ensure charge compensation of  $(\text{AlO}_4)^-$  tetrahedra. The peraluminosity of the uncolored frit ( $R = n_{\text{Al}_2\text{O}_3} / (n_{\text{Na}_2\text{O}} + n_{\text{K}_2\text{O}} + n_{\text{MgO}} + n_{\text{CaO}})$ ) before the thermal treatment is equal to 0.50, meaning that enough alkali or alkaline-earth cations (mainly  $\text{Ca}^{2+}$ ) can be used to stabilize Al in tetrahedral environment.

Interestingly, the same behavior for the spinel phase is observed when the divalent cation is modified in the spinel solid solution  $\text{MAl}_{2-x}\text{Cr}_x\text{O}_4$ : both pigments 10024 ( $M = \text{Mg}$ ) and pigment 10094 ( $M = \text{Co}$ ) react with the uncolored component, leading to the formation of a Cr-enriched spinel. For pigment 10024, the formation of  $\text{MgAl}_{0.29}\text{Cr}_{1.71}\text{O}_4$  is detected, together with the crystallization of anorthite. The color variation from pink to green with the Cr content is also observed on the solid solution  $\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$  [22], and the formation of Cr-rich phase explains the color modification. In the solid solution  $\text{CoAl}_{2-x}\text{Cr}_x\text{O}_4$ , the color varies from blue [23] ( $x = 0$ ) to greenish blue [24] ( $x = 2$ ). The formation of the Cr-enriched spinel  $\text{CoAl}_{0.47}\text{Cr}_{1.53}\text{O}_4$  in glaze g-10094 also explains the color change.

In the solid solution  $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ , the relative quantity of Al extracted from the spinel phase towards the melt varies moderately with the initial content in Cr  $x$ : 67.5% for  $x = 0.4$ , 68% for  $x = 1$  and 73% for  $x = 1.4$  (calculated from our previous work [11]). In the case of pigments 10024, 10045 and 10094, the initial  $x$  values are close enough to compare the three samples and to assess the effect of the divalent cation. While 66% and 67% of the initial Al amount present in the grain migrates in the melt for pigment 10045 and pigment 10094, respectively, 81.4% migrates for pigment 10024. This difference explains the large quantity of anorthite formed in glaze g-10024 that is even detected by XRD and present around most of aggregates of grain observed under SEM. The diffusion of Al is then enhanced by the presence of Mg in the spinel structure. This might be explained by the fact that  $\text{Mg}^{2+}$  cations are mobile and can adopt versatile environments, which promote the diffusion of Al and its stabilization in tetrahedral environment during the alteration of the pigment.

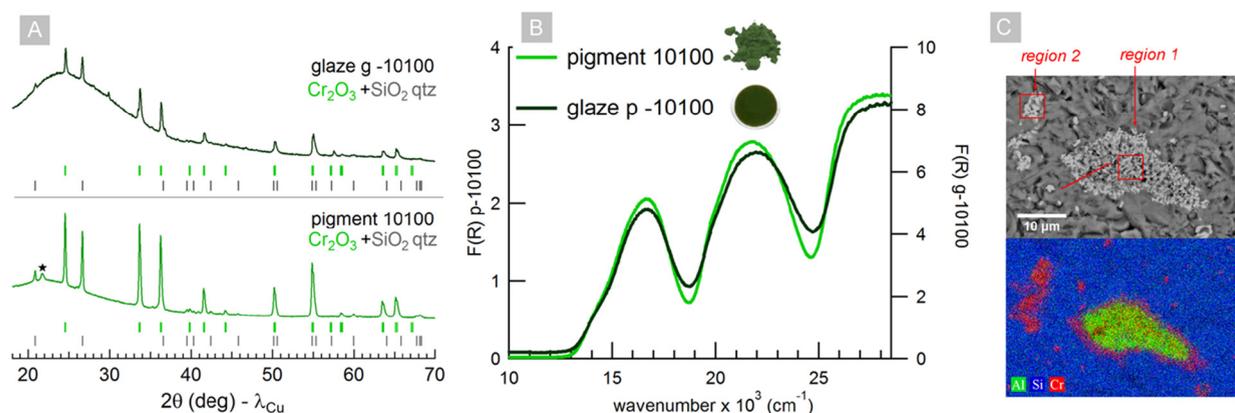
This mechanism is similar to the partial dissolution of a mineral with the simultaneous or subsequent precipitation of a different phase that takes place whenever a chemical disequilibrium exists between a melt and a crystal [25,26]. Elements are detached from the crystal and compositional gradients appear due to a continuous decrease in the concentration of the diffusive species with increasing distance from the melt/crystal boundary. These compositional gradients lead to dissolution and transport of matter into the melt and/or precipitation of a new phase. As a result, the chemical composition of the crystalline phase can vary as a function of time during the reaction. Dissolution models for solid solution exist [27,28], but a complete set of phase equilibrium data and transport properties is needed, which requires further studies.

## 4. Pigment mainly composed of eskolaite $\text{Cr}_2\text{O}_3$ : no visible change of color

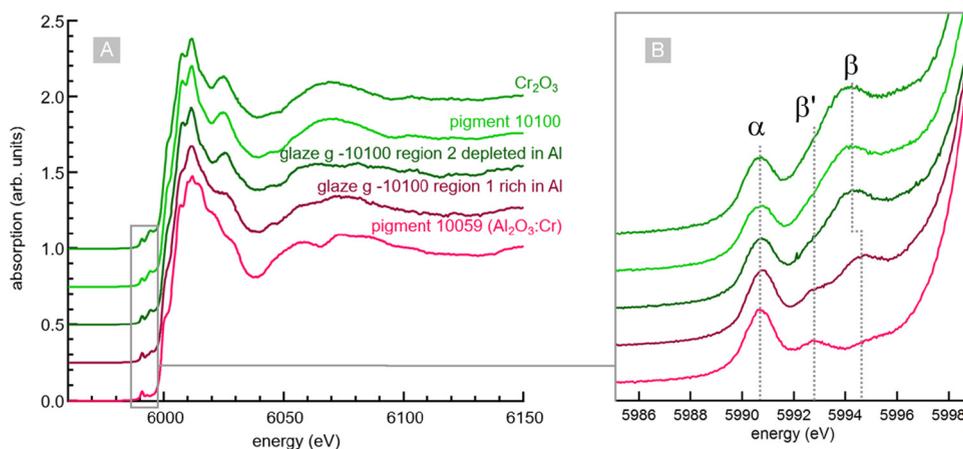
### 4.1. Characterization of the pigment and the glaze

Pigment 10100 is characterized by a forest green color. It is obtained at the laboratory of Sèvres by mixing eskolaite with quartz and pegmatite extracted from the area of Marcognac in France (rock mainly composed of quartz and feldspar). The purpose of this process was certainly to lighten the green color of eskolaite. The resulting pigment after thermal treatment contains crystalline phases,  $\text{Cr}_2\text{O}_3$  and  $\text{SiO}_2$ , mixed with a glass formed by the partial vitrification of the quartz and pegmatite (Fig. 4A). The characteristic peaks of eskolaite on the XRD pattern of pigment 10100 are asymmetric. In the glaze composed of pigment 10100,  $\text{Cr}_2\text{O}_3$  and  $\text{SiO}_2$  are still detected (Fig. 4A). A more pronounced contribution from the amorphous part is observed, due to the vitrification of the uncolored component, similar to glazes g-10045, g-10024, and g-10094.

UV-visible spectra of pigment 10100 and glaze g-10100 are compared in Fig. 4B. They are both characteristic of  $\text{Cr}^{3+}$  in eskolaite  $\text{Cr}_2\text{O}_3$ , without a significant modification of the peak position, resulting in a limited modification of color.



**Fig. 4.** Multi-analytical study of glaze composed of eskolaite pigment. (A) XRD diagram of pigment 10100 (bottom) and glaze g-10100 (top) composed of mainly  $\text{Cr}_2\text{O}_3$  and quartz  $\text{SiO}_2$ . The peak indexed with a star corresponds to cristobalite  $\text{SiO}_2$ . (B) Remission function  $F(R)$  calculated from diffuse reflectance spectra of pigment 10100 and glaze g-10100. (C) SEM image (signal ASB, EHT = 15 kV) of the two different kinds of grains population in g-10100 (top), with a composite image built from elemental EDS maps of Cr, Al and Si (bottom). The red squares represent the area analyzed by XANES, and the line corresponds to the FIB cross section.

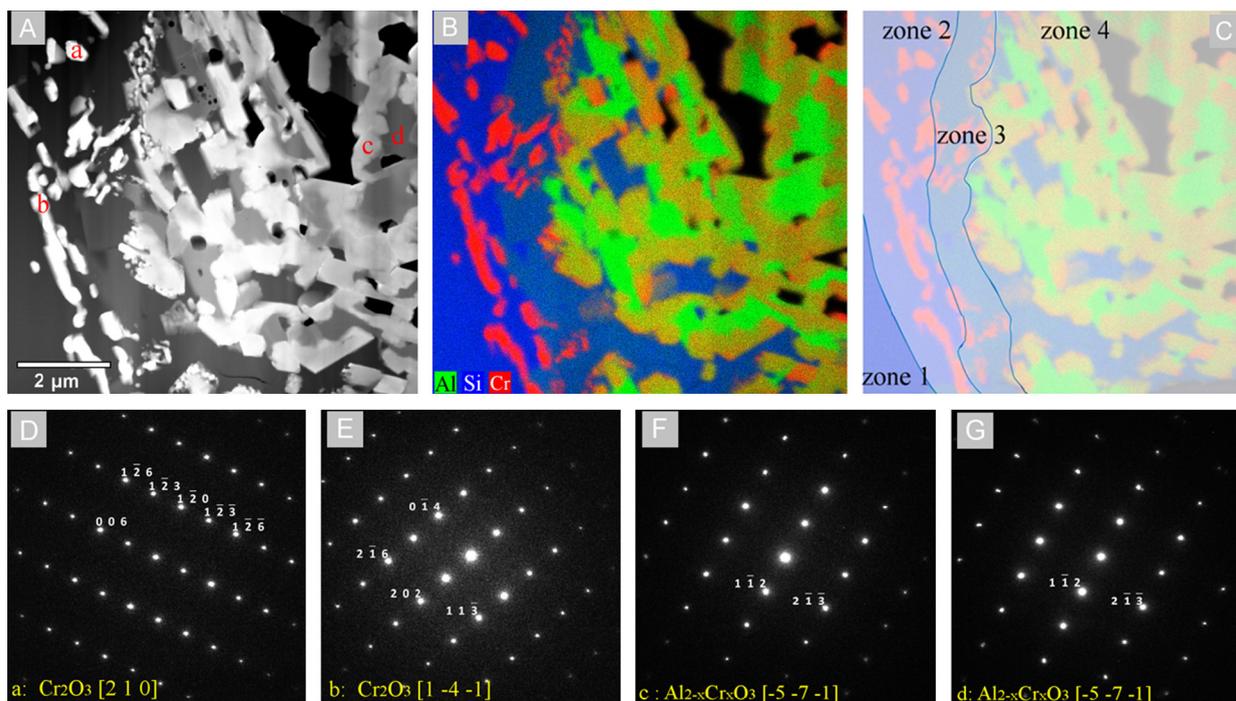


**Fig. 5.** (A) XANES spectra at the Cr K edge of the grain from population 1 and the center of the grain from population 2 in glaze g-10100. These spectra are obtained with a  $\mu$ -focused beam. They are compared with XANES spectra at the Cr K-edge obtained with an unfocused beam of initial pigment 10100, a reference of  $\text{Cr}_2\text{O}_3$ , and pigment 10059 composed of  $\text{Al}_{1.9}\text{Cr}_{0.1}\text{O}_3$ . (B) Focus on the pre-edge area.

Observations of polished cross sections of glaze g-10100 under SEM reveal the presence of two populations of grains (Fig. 4C). The first one is composed of grains with a size inferior to  $1 \mu\text{m}$ , with a composition that corresponds to  $\text{Cr}_2\text{O}_3$ . The second minority population is composed of larger heterogeneous grains, with a typical size of  $10 \mu\text{m}$ . The center of the grain is rich in Al, while the periphery is depleted in Al and enriched in Cr.

X-ray absorption near edge structure (XANES) measurements at the Cr K-edge with a micro-focused beam were performed to probe with high spatial resolution the local environment of Cr in typical grains. The positions of the probed areas are reported in Fig. 4C, the size of the squares corresponds to the spatial resolution ( $4 \times 4 \mu\text{m}^2$ ). The size of the beam being larger than the thickness of the periphery of the grain, the area on the left of the main grain with the same composition than the periphery was selected to probe the Cr environment in an Al-depleted area. Spectra are compared with those obtained for references ( $\text{Cr}_2\text{O}_3$  and the initial pigment 10100) in Fig. 5. The XANES spectrum acquired on region 2 exhibits similar XANES features between 6000 and 6020 eV than  $\text{Cr}_2\text{O}_3$  and pigment 10100. The pre-edge areas (Fig. 5B) are also similar, with the presence of two structures  $\alpha$  and  $\beta$  characteristic of  $\text{Cr}^{3+}$  in  $\text{Cr}_2\text{O}_3$ . On the contrary, the spectrum acquired at the center of the grain differs in the XANES region (structures less defined) and in the pre-edge. The pre-edge is characterized by the presence of the two structures  $\alpha$  and  $\beta$ , with  $\beta$  shifted toward higher energies, and a third structure  $\beta'$ . The pre-edge of the region 1 is similar to the one for the pigment 10059 composed of the  $\text{Al}_{1.9}\text{Cr}_{0.1}\text{O}_3$  phase: the structure  $\beta'$  is at the same energy as the one in  $\text{Al}_{1.9}\text{Cr}_{0.1}\text{O}_3$ . We can conclude that the XANES spectrum of the grain center corresponds either to an average between the two end-members  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ , or to an intermediate composition along the solid solution  $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ .

To address this issue, a FIB cross section was cut at the interface of the grain and the glass, and then observed under a TEM. Its position is reported in Fig. 4C. The analysis of the FIB cross section reveals a microstructure whose complexity



**Fig. 6.** (A) STEM image of a FIB cross section at the interface pigment/uncolored glass in g-10100. (B) Composit image built with STEM-XEDS elemental mapping acquired using windows related to SiK $\alpha$  (blue), AlK $\alpha$  (green), CrK $\alpha$  (red). (C) Map of zone 1 to 4. (D–G) SAED patterns corresponding to eskolaite (D and E) and corundum (F and G).

did not appear under SEM. STEM-HAADF images acquired at the interface are presented in Fig. 6A, with a STEM-XEDS composite image built from elemental mapping achieved using SiK $\alpha$ , AlK $\alpha$ , and CrK $\alpha$  lines (Fig. 6B). Several areas can be distinguished, numbered from 1 to 4 and schematized in Fig. 6C. According to the SAED electron diffraction patterns, zone 1 is amorphous and due to the vitrification of the uncolored component. Zone 2 is composed of single crystals, with a composition closed to Cr<sub>2</sub>O<sub>3</sub>, embedded in the amorphous part. SAED patterns (only two patterns are shown in Fig. 6D and E) acquired on different crystals, confirmed that they correspond to Cr<sub>2</sub>O<sub>3</sub>, oriented along different axes. Zone 3 is also composed of single crystals of Cr<sub>2</sub>O<sub>3</sub>, but they are embedded in a matrix with a chemical composition different from that of the amorphous part. This matrix is crystallized, with a composition close to that of anorthite CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>. These two latter areas most likely correspond to the area depleted in Al observed under SEM. Zone 4 corresponds to the center of the grain previously described under SEM. The presence of holes in the FIB cross section (black irregular shaped regions) shows a porosity in the center of the grains. It is composed of several grains exhibiting different concentrations in Al and Cr. SAED analysis shows that they are single crystals belonging to the solid solution Al<sub>2-x</sub>Cr<sub>x</sub>O<sub>3</sub>. Two juxtaposed crystals with different Cr concentration, such as crystal c and d, are oriented along the same direction (Fig. 6F and G). The small difference in lattice parameter between Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> does not enable us to distinguish them unambiguously from only the electron diffraction pattern.

#### 4.2. A complex microstructure resulting from Al migration

In the glaze g-10100, a complex microstructure was evidence by TEM analysis of the FIB cross section, at the interface between the pigment and the uncolored vitrified component (zones 2 and 3), and in the pigment itself (zone 4). The thermal treatment applied to fire a glaze (see section 2) was modified to follow the evolution of the different areas: once 1280 °C is reached, a plateau of 15 h was applied. SEM observations show that the small grains of Cr<sub>2</sub>O<sub>3</sub> are still present. However, the larger heterogeneous grains previously characterized by XANES and TEM appear homogeneous, entirely composed of Cr<sub>2</sub>O<sub>3</sub> crystals (see Supporting Information, Fig. S3). Annealing allows an evolution of the grains towards Cr<sub>2</sub>O<sub>3</sub>, leading to the gradual dissolution of zones 3 and 4 to zone 2. This is due to the gradual diffusion of Al from the initial grain of pigment towards the glass. This result is confirmed by the crystallization of anorthite in zone 3. Zone 4 is then present in the initial pigment, and zones 2 and 3 result in a reaction between the crystallized grains and the melt during firing of the glaze.

The initial pigment is composed of Cr<sub>2</sub>O<sub>3</sub> crystals (population 1), in majority, and grains with diverse compositions along the solid solution Al<sub>2-x</sub>Cr<sub>x</sub>O<sub>3</sub> (population 2). While the first one is stable in the uncolored component, the second one reacts, leading to the formation of Cr<sub>2</sub>O<sub>3</sub>. The presence of Al<sub>2-x</sub>Cr<sub>x</sub>O<sub>3</sub> grains can explain the asymmetry towards higher 2 $\theta$  observed on the XRD diagram of the pigment (Fig. 4A).

The reactivity highlighted here follows the same mechanism than the one involved for the spinel group, although the impact on the color is limited in this case because the majority of the grains present in the sample (population 1) imparts color to the glaze g-10100, while the altered grains are minority. The reactivity of pigment 10059 mainly composed of  $\text{Al}_{1.9}\text{Cr}_{0.1}\text{O}_3$  with the same glaze was investigated in a previous study [12]. We showed that the Al diffusion from the grain of pigment to the glaze led the formation of  $\text{Cr}_2\text{O}_3$  grains, following the same mechanism of reactivity than the minority grains in pigment 10100.

## 5. Conclusion

The color of the decoration on porcelains is strongly dependent on the reaction during firing between the pigment or the chromophore and the melt giving the glaze. We have investigated the role of Cr in various pigments synthesized at the 'Manufacture de Sèvres', revealing that this element remains in crystalline phases derived from the initial pigment. The environment of Cr in these crystals imparts the color properties to the glaze. Though Cr remains in the trivalent state and six-fold coordination, the positions of the optical absorption bands slightly change, affecting the final hue. The glazes have been investigated by coupling X-ray diffraction and electron microscopy to unveil the reaction of the initial pigments with the melt. We have studied three spinel pigments and an eskolaite pigment as representative compounds of the vast color palette available at the 'Manufacture de Sèvres'. We have observed an important reaction of all these pigments with the melt that results in crystals enriched with Cr. This enrichment and the presence of Cr–Cr neighbors detected by X-ray absorption spectroscopy is probably responsible for the color changes observed for spinels. The initial eskolaite pigment, which belongs to the solid solution  $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ , also shows a Cr-enrichment, but this does not affect significantly the coloration. Whatever the pigment types, important reactions occur at the microscopic scale, requiring advanced characterization tools to understand the interaction mechanisms. Chemical mapping indicates the migration of specific elements (such as Al) from the initial pigments towards the glazes, with the formation of anorthite crystals that do not alter the coloration. These findings point out a remarkable similar mechanism operating for all investigated pigments. These reactions modify the color by stabilizing phases with the surrounding amorphous part. The composition of the uncolored component is crucial in the crystal/glass equilibrium and a procedure to control the reactivity of the pigment is to adjust the content of Al/Zn in the uncolored component. Preliminary results have thus been obtained to stabilize gahnite with Cr by adding Al or Zn to the uncolored component. The addition of Al requires, however, a higher firing temperature to melt the glaze. A way to obtain the unique color of gahnite with Cr phase without modifying the firing temperature is to crystallize this phase by the addition of ZnO in the uncolored component and using  $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$  ( $x < 0.3$ ) as a starting pigment [29]. A more profound knowledge of the reactivity of pigments in glazes can contribute to optimize and better tune the color properties of the final products, thus improving traditional procedures.

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## Appendix A. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.crhy.2018.09.008>.

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