## Macro and Micro-level X-Ray powder diffraction mapping of Giotto and Cimabue fresco fragments from Assisi Cathedral

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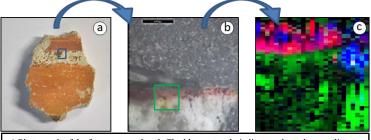
Cimabue (1240 – 1302) was an Italian painter and designer of mosaics from Florence. He is famous for breaking away from the Italo-Byzantine painting style. According to Vasari, he was the teacher of Giotto (1267 – 1337), the first artist of the Italian Proto-Renaissance. Cimabue went to Assisi to paint several large mural paintings at the new Basilica of Saint Francis and his pupil Giotto accompanied him.<sup>[1]</sup> The paintings of Cimabue in Assisi are generally in very poor condition. The white areas painted by the master today appear blackened as for example in the painting of the Crucifixion. In the 1997 earthquake, a portion of the vault of the Upper Basilica collapsed. Several fragments of the Cimabue mural paintings that show discolorations were collected after the earthquake and conserved.

Several fresco fragments of the Upper Basilica belonging to Cimabue and Giotto have been chosen for examination with the aim of explaining the conversion process that triggers the oxidation of lead white to plattnerite ( $\beta$ -PbO<sub>2</sub>). While in mural paintings, the blackening of lead white has been frequently noticed and attributed to the formation of plattnerite, the mechanism and primary cause of this oxidation process remains unclear.<sup>[2]</sup>

Experimental evidence suggests that chlorine is the main contributor in this blackening process. If Cl is present in the hypochlorite form, the following reaction may take place:

$$Pb^{2+} + OCl^- + 2OH^- \rightarrow Cl^- + PbO_2 + H_2O$$

An extensive investigation of the fresco fragments is being performed to confirm the starting hypotheses and provide insights into the painting techniques and material use of Cimabue and Giotto. Reflection mode MA-XRPD scans on the fragments themselves are combined with SR-based microscopic XRPD scans in transmission geometry to identify the different pigments and degradation products formed over the paintings. The discriminating capability of this method allows to collect highly specific distributions of the different crystalline compounds, as shown in the figure.



- a) Photograph of the fragments analyzed. The blue rectangle indicates where the sampling was performed
- b) Cross sectional micrograph of the scanned area
- c) RGB Distribution map Plattnerite β-PbO<sub>2</sub>, Laurionite PbOHCl & Calcite CaCO<sub>3</sub>

## References

- [1] G. Vasari: Le vite de' più eccellenti pittori, scultori e architettori, (1568)
- [2] M. Vagnini, R. Vivani, E. Viscuso, M. Favazza, B.G. Brunetti, A. Sgamellotti, C. Miliani: Investigation on the process of lead white blackening by Raman spectroscopy, XRD and other methods: Study of Cimabue's paintings in Assisi. Vibrational Spectroscopy, 98, 41-49 (2018).