

Unusual Pigments Found in a Painting by Giotto (1266-1337) Reveal Diversity of Materials Used by Medieval Artists

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The work of painters from the twelfth - fifteenth centuries is often discussed in the context of a short treatise on painting materials and methods written by an artist, Cennino Cennini, around 1390. His manual guides us to knowledge of how artists worked, but this very useful text tends to constrain our understanding of the potential richness and diversity of materials available to artists. Microanalysis of the pigments and binders used in one early panel paintings serves to broaden our view of the range of colorants and mixtures used by early painters. This paper will focus on the recent discovery of an unusual blue and yellow colorant found in the panel painting, *Madonna and Child*, painted by Giotto around 1320/1330.

Minute samples of the painting were obtained by scraping the surface with a surgeon's scalpel. The particulate matter was mounted in Cargille Meltmount ($n_D = 1.662$) on glass microscope slides. Cross sections were obtained by prying out small samples adjacent to small losses of paint using a pointed surgeon's scalpel. The samples were mounted in Bioplastic (Ward Scientific) and cut, then polished wet on SiC PSA papers or dry on micromesh cloths. The particulate samples were examined in transmitted polarized light and the cross sections in bright field, dark field, and fluorescence on a Leica DMRX microscope. Images were captured using a Canon EOS 1D camera in cr and jpg formats.

The samples were examined using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) using a Hitachi S3400-N microscope equipped with an Oxford Aztec spectrometer and an Oxford Xact SDD detector (80 mm²). Cross sections as described above were placed onto a double sided carbon sticky tab adhered to an Al stub. Particles were spread on a double sided carbon sticky tab which was adhered to a carbon stub (Pella). Samples were examined uncoated using 20 kV at 20-30 torr.

A cross section sample from the brilliant yellow lining of the Virgin's mantle has several layers of blue and yellow paint over a traditional gesso ground. One of the yellow pigments is a yellow ferruginous earth of high purity. The second is lead tin yellow. This name has been applied to a class of pigments based on a binary lead tin oxide. Some of these are glassy materials and recently the diversity of these materials has become better appreciated. In this instance, backscatter mode in SEM-EDX revealed cubic particles of lead tin oxide agglomerated around a glassy matrix containing lead, calcium, silicon, tin and oxygen. The proportion of glass to colorant makes this material appear to be similar to the pigment found in a crucible in Merovingian Switzerland [1].

The blue pigment is azurite of fine color and purity. It is mixed with a green blue colorant which is a ternary oxide of copper, bismuth and arsenic. Minerals of this sort are known for their unusual and interesting colors. In the BSE image the hexagonal habit of the crystals of the mineral is evident. With the current information, a likely identification of the colorant is the rare mineral mixite [2]. We do not know if the mixed oxide mineral was an impurity in the azurite blue, with which it has been observed, or purchased as a separate pigment.

These two findings of unexpected materials in a single sample from one painting impel us to review our perceptions about the range of materials employed by early Renaissance artists, particularly in our notion that artists had access to only a relatively narrow range of colorants, and show that microanalysis reveals a great deal of information which is a catalyst for deeper studies of early technology and trade in and beyond painting [3].

References

- [1] M Heck, T Rehren and P Hoffmann, *Archaeometry* **45** (2003), p. 33-44.
- [2] <http://www.mindat.org/min-2730.html> (accessed February 17, 2014).
- [3] I am grateful to my colleagues at the National Gallery of Art, especially those in the scientific research department, for their support.

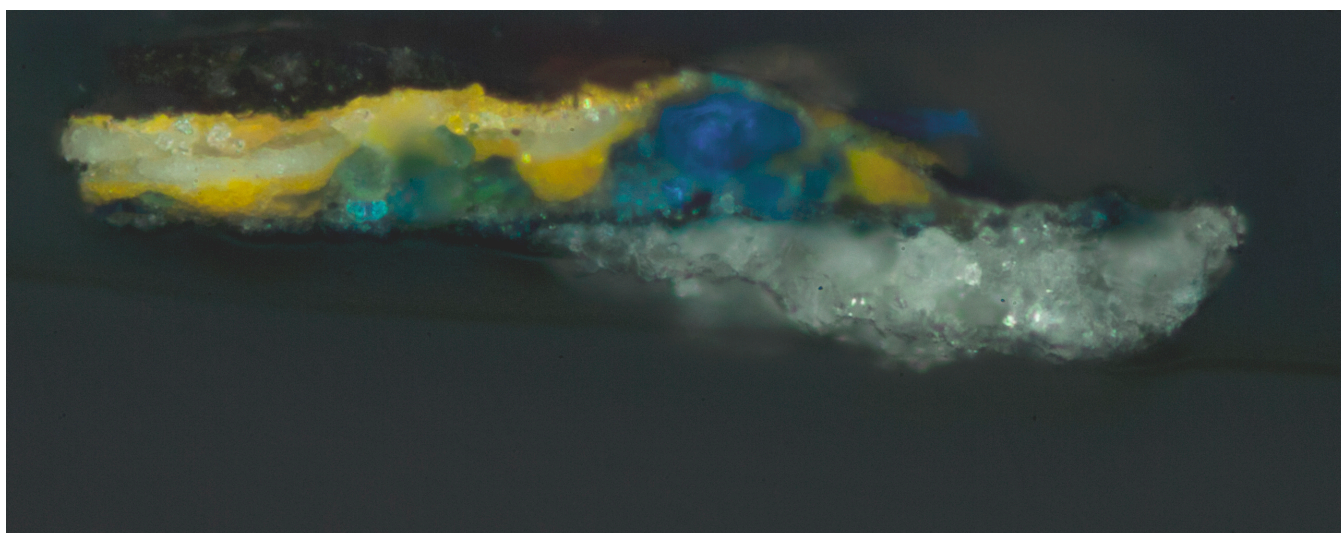


Figure 1. Cross section from the yellow lining of the Virgin's mantle in Giotto, *Madonna and Child* (1320/1330). The white gesso ground has several layers of blue and yellow lying on it. The yellow paint contains the glassy pigment lead tin yellow (type II). The blue paint contains deep blue azurite and green blue particles (seen just above the ground, left of center) which are a rare ternary oxide of copper, bismuth and arsenic. The total thickness of all the paint layers is c. 50 μm .