Wall painting materials and technique: The case of the famous iconographer Onoufrios

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In the 16th century, regarding the iconography in the former Byzantine area, besides the School of Crete, and besides Francos Catelanos and his school, a third artistic personality who created his own school too, Onoufrios, appeared in the central Albania and expanded his activity as a painter till northern Greece, the nearby areas, Ohrid etc. Inscriptions documenting the works of Onoufrios are found in some of the churches that he decorated with wall paintings: "St. Apostles" (1547) Kastoria Greece, "St. Nicolas" Shelcan Albania, "St. Paraskevi" (1554), Valsh Albania, while are attributed to him the church of "St. Theodores" in Berati, Albania (before 1547) and others. He is one of the best icon painters of the whole Balkan region and the best painter that had ever worked in Albanian territory. Onoufrios managed to combine the local painting tradition with the best tradition of the eastern (Paleologian) and western (Italian) schools, resulting in a realistic and natural drawing. He is the creator of the "Berati School" that expanded in other parts of the peninsula. Ground and paint layers were examined using micro-FTIR, Optical Microscopy, TXRF and SEM-EDS, to characterize materials and methods used by the artist to create these works. Our findings in each church are discussed and compared each other in order to understand how and with what material and resources the painter worked, and how he developed his technique.

Experimental details: A total number of 24 kind of samples that include plasters and pigments of different colours were collected from the three churches. In each of the sampling points, small pieces of pigment and plaster (about 5 mm^2) were removed with a scalpel and placed in small plastic vials with hinged caps to avoid contamination, these being the samples for FTIR, SEM-EDS and optical microscopy, while a small amount of material was also rubbed off the same spot of painted area by means of a dry cotton bud (a Q-tip) that was next placed in a clean plastic bag, these being the samples for TXRF. Due to the destructive nature of sampling, the samples were carefully chosen from areas that had no aesthetic or iconographic value for future reconstruction. A common characteristic of the wall paintings in the studied churches is related with their state of the preservation. Apart from the damages, the remaining fragments of the wall paintings seem to suffer –more or less- a colour change. Looking attentively it can be observed topically white areas as a thin layer. This phenomenon, related probably with the environmental pollution, is observed also in other churches and is discussed in the continuation.

Results and discussion: Plaster: In the FTIR spectra of all plasters, a common characteristic is the strong presence of calcium carbonate with a small participation of gypsum and silicon compounds. The existence of calcite is identified from the bands at 1445, 866 and 712cm^{-1}, while the bands at 602, 668, 1146, 3406 and 3550cm^{-1} are attributed to the bending and stretching modes of the SO_4 group of gypsum. The SEM-EDS analysis of plaster samples from all churches show that calcium is the element with the highest concentration associated with smaller amounts of magnesium, silicon and partially gypsum [1,2]. Therefore the FTIR and EDS results are in good agreement. Similar results were obtained from TXRF measurements of the plaster samples.

Deterioration: The surface of the wall paintings was covered topically by white areas having a crystalline texture. The analysis of the effected areas identified the presence of gypsum in all churches and calcium oxalate, except "St.Nikolaos". These results indicate the presence of two types of deterioration: (i) The alteration of calcite ($CaCO_3$) –which is in high amount in wall paintings- to gypsum ($CaSO_4 .2H_2O$) due probably to acid air pollution (sulphur oxides), (ii) Biodeterioration by lichens which cause -except of mechanical damages- and chemical damages by excretion of oxalic acid. [3,4]

Blue pigments: The presence of cupper in great amounts from the TXRF and EDS results of the blue specimen gives us a strong indication that the pigment is azurite (fig. 1). The comparison of the obtained FTIR spectrum of the sample, with the spectrum of azurite from the spectral library, confirms that the used blue pigment is azurite.

Green pigments: Green Earth could be recognized from the comparison of the results of EDS and FTIR methods. The presence of Fe, Si and Mg from EDS analysis of green samples, leads to the conclusion that the pigment can be attributed to Green Earth. From a detailed examination of FTIR spectra, the four narrow bands

OH stretching in the 3610-3530cm^{-1} region and the area 1100-900cm^{-1} of Si-O stretching lead us to characterize the green earth as celadonite.

Red pigments: Elemental analysis on the red coloured layers from St. Nikolaos and St. Paraskevi churches identified Fe along with Al and Si, indicating the existence of iron oxide as the possible material producing the red colour. Moreover the coexistence of the alumino-silicate materials guide to the consideration that the pigment is red ochre. This result is supported with the FTIR spectra of the above samples that are almost identical with the spectrum of the red ochre from the spectral library. The red samples from St. Theodori church present a difference referring to the use not only red ochre but also cinnabar, especially for the light red areas. The identification of cinnabar is based in the presence of Hg and S as major elements in the EDS results. Hg was also detected by TXRF.

	Saint Theodori	Saint Nikolaos	Saint Paraskevi
Green	Green earth	-	Green earth
Blue	Azurite	-	-
Yellow	Yellow ochre	Yellow ochre	Yellow ochre
Red	Red ochre +/or Cinnabar	Red ochre	Red ochre
Brown	Red ochre	-	Red ochre
White	Calcite	Calcite	Calcite
Black	Carbon black	Carbon black	Carbon black
Grey	-	-	Calcite + Carbon black

Table 1: The used pigments from the painter Onoufrios

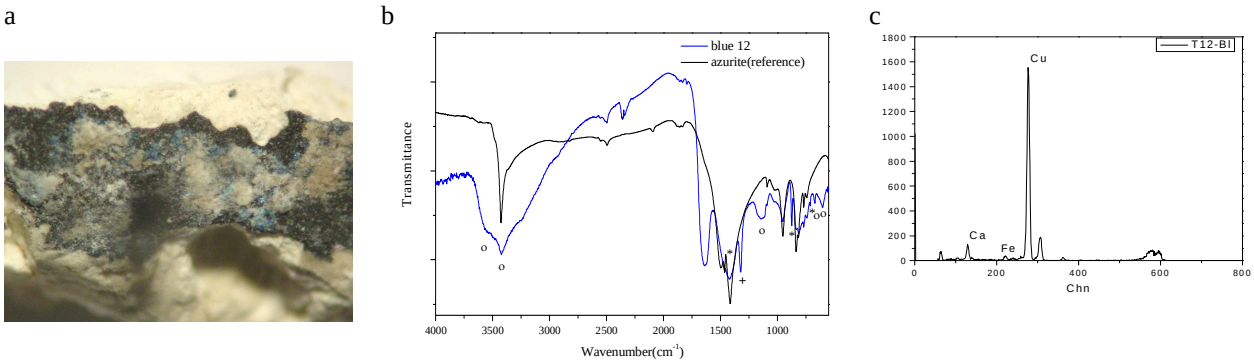

Fig 1: Sample T12-Bl (a) optical photograph, (b) FTIR transmittance spectra (o for gypsum, + for calcium oxalate and * for calcite), (c) TXRF

Conclusions:

The chosen analytical methods permitted the identification of plasters and pigments of the three monuments. The plaster of all the wall paintings, made with the fresco technique, was generally characterized by the strong presence of calcite with a small participation of gypsum and silicon compounds. Plaster samples from the churches of "St.Theodori" and "St.Nikolaos", taken from the wall-paintings of anonymous painters, showed more or less no participation of gypsum, leading thus to the conclusion that gypsum is a characteristic of Onoufrios' wall painting technique. As far as concerned Onoufrios' technique, he was using for the wall paintings the fresco technique while the inclusion of gypsum in the plaster is a characteristic of his way of painting. As it is testified from the Table 1, Onoufrios used the same type of pigments for the same colour shades in all three churches (azurite, green earth, red ochre, cinnabar, yellow ochre, carbon black, calcite) with the exception of cinnabar, for the rendering of red colour, detected only at the church of "St.Theodori".

Deterioration of the wall paintings was analyzed and the presence of gypsum in all churches and calcium oxalate, except "St.Nikolaos", was detected .

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