RAMAN MICROSCOPIC INVESTIGATION OF PAINT SAMPLES FROM BUILDINGS AT COPAN, HONDURAS

R.A. Goodall[1], J. Hall[2], R.Viel[2], H.G.M. Edwards[3] and P.M. Fredericks[1]

[1]School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, Qld 4001, Australia E-Mail: r.goodall@student.qut.edu.au
[2]School of Social Sciences, University of Queensland, St Lucia, Qld 4067, Australia
[3]Chemical and Forensic Sciences, University of Bradford, Bradford BD7 1DP, UK;

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Abstract: Paint samples from three buildings in the main acropolis group, Copan have been subjected to analysis by Raman microscopy to study both the stucco composition and the pigments used to paint these surfaces. Indications of repainting are identified.

At the height of the Maya civilization the temples and structures which formed the Copan acropolis were magnificently carved and painted. The samples come from, Tunnel 28, 'Clavel' building, Early classic AD450-550, 'The Jaguars' tunnel in the 'Ani' building, Middle classic AD550-600 and Temple 22, South east corner, Late classic, AD 730. Visual microscope investigation showed there are significant differences in the physical characteristics of the three samples. The samples from Tunnel 28 Clavel building, AD450-550, show a thick, 2 to 3 mm substrata of stucco covered by a fine grained stucco of approximately 0.1 to 0.2 mm thickness under a single painted layer, Figure 1. The stucco layers contain particles of various sizes interspersed in a fine matrix material. These grey and off-white particles vary between 0.05 to 0.2 mm diameter for the thick under layer and 10 to 58 µm in the fine material below the pigment. The later Jaguar tunnel and Temple 22 samples are similar in makeup with a much thinner under layer of 1 mm of coarse stucco with a thin layer of fine stucco 0.1 to 0.13 mm. The first painted layer is quite thick, up to 60 µm in some areas. Over this painted layer is a second fine stucco layer coated with a second fine pigment layer (Figure 2). The coarse stucco layer contains black particles and red particles of about 10 µm. The white and grey particles range from 20 µm to 0.3 mm. Typical particle sizes in the fine layer are 10 to 30 µm. The outer surfaces of all samples have white and yellow material crystalline material coating the painted surfaces. All samples were buried or covered in soil and vegetation over the last thousand years and these coatings are more than likely residues from this process.

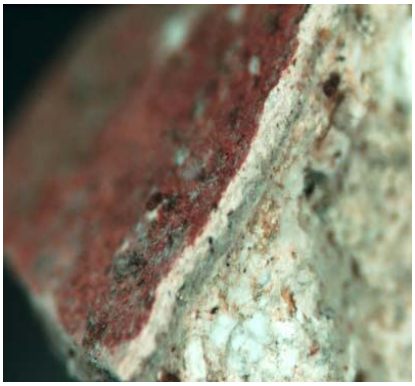

Figure 1 Side view of the Tunnel 28 stucco AD450-550

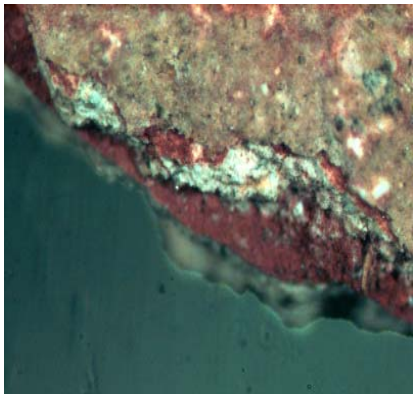

Figure 2 Jaguars tunnel showing two painting episodes

The red pigments on all samples contain iron oxide. Raman spectra of all red pigments display 7 distinctive bands at 225, 245, 293 with a shoulder at 299, 410, 500 and 612 cm^{-1} of hematite spectra [1] with the two magnon band at around 1320 cm^{-1} as well as broad bands at around 815 and 1100 cm^{-1}. A small band at around 660 cm^{-1} can be seen in most spectra, this band can be assigned to magnetite which has a distinctive feature at this position. This band is much large in the Temple 22, AD 730, sample. The colour of this sample is much lighter and brighter than the other samples. The magnetite has not been mixed with the hematite but is an impurity in the hematite as no separate

magnetite particles have been identified. This difference could indicate a different source material has been used to paint this temple. The pigment material in all samples is fairly homogeneous. There are some darker areas but these are also identified as hematite. A few small platey particles have been found and these are specular hematite.

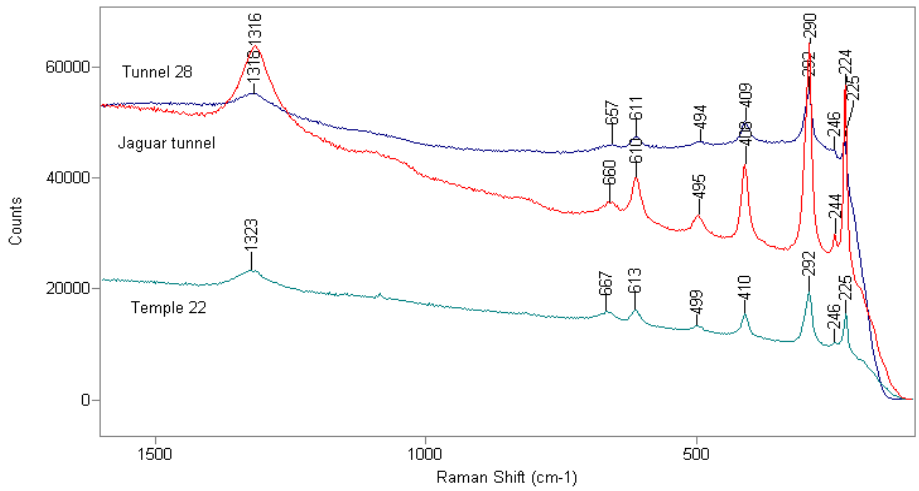

Figure 3 Raman spectra of red pigment from the three samples showing characteristic bands for hematite. Note the more intense band at 667 cm-1 for the Temple22 sample.

The particles and matrix material of the stucco layers had bands at 1086, 712 and 281 cm^{-1} belonging to calcium carbonate. These are characteristic of slaked lime preparations [2]. Evidence of gypsum bands has not been found on any of the samples, so it is unlikely that the Maya used gypsum in their stucco preparation. The burial of the buildings for much of their life would also preclude biodeterioration from organic growths. The calcium carbonate crystals in the surface contamination indicate that recrystallisation is occurring. The stucco layers have a large number of tiny red and black particles dispersed through the matrix. The black particles have bands at 1320 and 1590 cm^{-1} indicative of carbon [2]. The presence of small particles of wood in the plaster is due to the heating process in the preparation of lime. The red particles are hematite and are probably contamination from the presence of hematite pigments in the work areas. Small particles with Raman bands at 464 cm^{-1} indicative of quartz have also been identified in the matrix. Crush stone and quartz has been reported as an additive to reduce shrinkage on drying of the lime plaster [3].

FTIR-photoacoustic spectroscopy was recorded on each of the painted samples. Calcite was the major component of each spectrum with distinctive bands at 1435, 876 and 712 cm^{-1}. Small bands at 3697, 3620 and 915 cm^{-1} are indicative of clay minerals [4] and are commonly found in pigments used on rock art. Quartz bands at 779 and 798 cm^{-1} also confirm the presence of quartz in the samples. Examination of the reverse stucco only side of the samples gives only calcite bands.

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References:

1. V.C. Farmer, The infrared spectra of minerals, Mineralogical Society, London 1974.
2. H.G.M. Edwards, P.S. Middleton, S.E. Jorge Villar, D.L.A. de Faria, Analytica Chimica ACTA, **484**, 215 (2003).
3. R.J. Gettens and G.L. Stout, Painting Materials, A Short Encyclopaedia, Dover Publications, New York, 238, 1966.
4. V.C. Farmer, The infrared spectra of minerals, Mineralogical Society, London 1974, 335.