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The Grolier Codex: A PIXE & RBS Study of the Possible Maya Document

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Abstract. The Grolier Codex has been a controverted document ever since its late discovery in 1965. Because of its rare iconographical content and its provenience from non-authorized archaeology, specialists are not keen to assure its authenticity that would set it amongst the other three known Maya codes in the world (Dresden Codex, Paris Codex and Madrid Codex).
The document that has been kept in the Biblioteca Nacional de Antropología e Historia in Mexico City, since its exposure in 1971 at the Grolier Club of New York, is being now analysed by a set of techniques in order to characterise its forming materials; paper, preparation layer for painting and pigments.
This paper discusses the results obtained for PIXE and RBS studies carried out at the Pelletron Particle Accelerator of the Instituto de Física (Universidad Nacional Autónoma de México), the aim of which is to ensure the materials in the Grolier Codex match those found for other prehispanic documents and discard the presence of modern pigments that would appoint the document as a fake.

Keywords: *PIXE, RBS, codex, maya, Grolier, pigment.*

INTRODUCTION

The Grolier Codex is a document consisting of 11 pages of 125 cm length and 18-19 cm high in average. The pages were originally displayed as an accordion, though only some of them stay put together. It features some venusian calendar with gliphs and figures painted in red, black and bluish colours over a white surface and shows some remains of the preliminar drawings. It is accompanied by one separate sheet of paper with no painting or preparation layer on it.

The nature of the document is still unknown; neither scientific studies have been done to confirm the presence of bark *amate* paper, nor have they been carried out to characterise the materials employed for the paintings.

The Grolier Codex[1] (Fig. 1) was discovered in the Sierra de Chiapas y Tortuguero (Chiapas, Mexico) in 1965. Apparently it was shown for its purchase to an art collector, Dr. José Saenz and it was first exposed in the Grolier Club of New York in 1971. Its provenience from non-authorised archaeology and its iconographical content, sets it apart from the other three known Maya codes (Dresden, Paris and Madrid) that were discovered round the 18th and 19th century. Though radio-carbon dating of its latter free-standing sheet of paper placed it in 1230 ± 70 AD[1] matching the fall of the Maya civilization, when this culture was being absorbed by the Toltecas; detractors insist that despite the fact that the paper is antique, the painting might be the handcraft of an experimented copycat that has had access to the other three codes, particularly to the Dresden Codex.

We shall not know if this document was meant as an original calendar for auspicious war days, or a copy of the Maya stile by looking at its signs and drawings, but we might be able to identify its materials and thus find whether there are modern or synthetic ones that do not match the Maya period and would thus mark it as a fake.

From what curators can see, there might be some induced degradation; the missing parts of the sheets could have been torn and the darker shades in the preparation layer may be due to the application of some chemical product.

Unfortunately, the codex does not present much amount of the bluish colour; only some blue recipient can be found on its 11th page (Fig. 1). Maya people used a very characteristic blue (Maya blue) made of the colorant indigo fixed to clay (palygorskite) [1, 2, 3]. Though PIXE cannot identify organic molecules such as indigo, and there is quite an amount of clays and silicates that share palygorskite components, it can tell if non-usual modern pigments[1] such as smalt (potash-glass with cobalt oxide), cobalt blue ($CoO{\cdot}Al_2O_3$), cerulean blue ($CoO{\cdot}nSnO_2$) or Prussian blue ($Fe_4[Fe(CN)_6]_3$)for instance are present.

PIXE and RBS in-air analyses of the materials present in the Grolier Codex have been performed in the scope of throwing some light on the authenticity of this document.

EXPERIMENTAL

PIXE and RBS in-air measurements were carried out at the 3MV Pelletron Particle Accelerator of the Instituto de Física (Universidad Nacional Autónoma de México) using a 3 MeV proton beam of 1nA and 1mm in dia. (Tantalum collimator 140 µm in diameter).

The pages were placed on PVC stand rotated 60º from the horizontal plane (Fig, 2) and protected with PVC sheets on top that left uncovered just the analysed areas.

Pages analysed were 1, 2, 3, 5, 6, 8, 9 and 11. Measurements were taken in different points including fibre, preparation layer and pigments.

Two detectors were used in the PIXE set-up; a Si-Pin for the detection of light elements and a LEGe for the trace detection. The Si (Peltier) detector was placed 40º to the beam direction and supplied with a Helium flux of 0.85 sl/min in order to improve the detection of light elements. LEGe detector was also placed at 40º to the beam direction had an 8 µm Kapton window and a 63 µm aluminium absorber. For RBS a Si particle detector (Ortec R series) was used, placed at 45º to the beam direction.

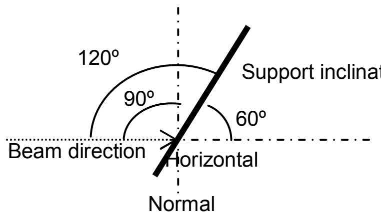

FIGURE 2. Sample geometry in the set-up.

FIGURE 1. The Grolier Codex

RESULTS AND DISCUSSION

The Preparation Layer

The preparation layer is the surface on to which painting is applied. Our results show the presence of hydrated $CaSO_4$ (14.9% S, 49% Ca, 32.4% O) with some amount of strontium (2%). This material –matching gypsum composition- has been known since antiquity as a support for paintings together with $CaCO_3$[6].

Minor components show variations from the darker to the lighter shades of the preparation layer in the content of iron and potassium. It is known for ferrogallic ink that the iron present in them contributes to the degradation of cellulose, thus changing the appearance of paper by casting a shadow on it. However no trace of ferrogallic inks has been detected in the code.

The Fibres

Fibres show a large amount of calcium (29.4 % against 49 % found for the preparation layer) but very little sulphur; there would be no presence of $CaSO_4$. Calcium may come from the paper fabrication process.

Amate paper[7] (coming from *Ficus Glabrata* or *Ficus Inspida*) as well as other vegetal papers, were made from bark. The obtention of paper included the treatment of the bark fibres with lime water (water and CaO) for its softening in a variable time (at least 3 hours when boiled). The process was completed by rinsing, drying and flattening the fibres with stones. It was and still is a general procedure for the manufacture of hand-made paper in Mexico.

As no phosphorous has been found, the presence of bone-ashes containing $CaPO_4$ is excluded. However, there is some potassium (3.5 %). Potassium, though present in plants, does not reach this concentration; some vegetable ashes do, and contribute to the softening of the fibres in the same way of the bone-ashes.

The Black Pigments

Black pigments showed the same composition as the preparation layer with the PIXE technique. No trace of elements responsible for black colour could be found. RBS however showed the presence of carbon (not present for the rest of the pigments or the preparation layer), thus indicating the use of carbon-based black pigments, that are typical of Mexican codes[¡Error! Marcador no definido.] (Fig. 3).

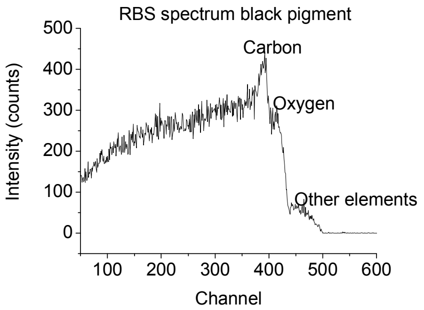

FIGURE 3. RBS spectrum of the black pigment.

The Red Pigments

The PIXE spectra of red pigments showed a great amount of iron (average 23.9 %), together with the elements present in the preparation layer (Ca, S, O, Sr). Also, some magnesium, aluminium, silicon, titanium and manganese could be found. Mexican pre-Hispanic red can be either an organic colorant (carminic acid) or an inorganic pigment

		Elements in preparation layer							Elements attributed to the pigments						
		O	Ca	S	Sr	Mg	Al	Si	K	Cl	Ti	Mn	Fe	Cu	Zr
	P1	33,3	49,3	13,3	1,14	0,32	0,25	0,59	1,02				0,67	0,082	
	P2	30,3	51	14,7	1,97		0,18	0,59	0,65				0,53	0,084	
	P6	33,5	48,2	15,1	1,33		0,27	0,48	0,56				0,35	0,19	
black	P11	31,7	49,5	15	1,36	0,12	0,2	0,5	0,98				0,54	0,064	
	P1	36,3	37,8	9,33	1,1		0,65	0,87	1,09		0,084	0,085	12,7	0,067	
	P2	30,6	26,9	3,62	1,19	0,17	0,54	1,15	0,67			0,129	35	0,048	
	P6	49,3	26,8	9,72	0,86	0,16	0,55	0,97	1,28	0,005	0,067	0,03	10,1	0,12	
	P8	55,5	12	2,11	0,65		0,43	0,88	0,21		0,089	0,089	28	0,049	
red	P11	27,1	22,8	3,66	0,76	0,05	1,07	2,23	0,69	0,034	0,187	0,061	33,8	0,041	
	P2	36,6	31,9	26	2,39		0,49	0,98	0,79				0,76	0,12	
	P6	40,8	27,9	5,24	0,76		1,12	1,71	0,4		0,146	0,08	21,7	0,095	
Previous drawing	P8	27,9	51,7	14,6	2,4	0,07	0,19	0,64	1,42	0,018			0,86	0,243	
blue	P11	29	54,6	8,15	1,38	0,87	0,52	2,7	0,98	0,049		0,014	1,52	0,26	0,012

TABLE 1. PIXE concentrations % (w-w) for the pigments present in the Grolier Codex. Errors are ±10%

(minium, cinnabar, red ochre) [6].

No mercury or lead has been found; the presence of iron and elements that are commonly found in soils, indicate the use of natural red ochre, also called hematite red (Fe_2O_3 plus soil material such as clay).

The previous drawings

In most pages of the code, there are traces of the drawings that were not followed for the executing of the painting. They are a thin red wash shade of red. However, the iron concentration in them resembles more that of the preparation layer than the one in red pigments. The fact that aluminium – always present in natural red ochre – shows proportionally higher concentrations for the previous drawing than for the red pigment in relation to the iron content (Al/Fe) means that there is no red ochre in the previous drawing.

The Blue pigment

Blue pigments in the Maya culture are usually "Maya Blue" pigments. Maya blue consists of colorant (indigo) fixed on palygorskite or other similar clay **¡Error! Marcador no definido., ¡Error! Marcador no definido., ¡Error! Marcador no definido., ¡Error! Marcador no definido.**. Indigo is an organic colorant extracted from the *Indigofera suffruticosa* plant and palygorskite is an ino-phyllosilicate that belongs to the sepiolite family. The Maya Blue appears in the 8th century a.D. and is used up to 1580[5].

Whilst Indigo - being an organic colorant- cannot be identified with PIXE, elements present in palygorskite are possible to detect with this technique. The PIXE spectra of the blue shade show in fact a composition that would match that of palygorskite: Mg, Al, Si, K, Cl, Mn, Fe, Cu, Zn.

However, as PIXE does not provide information of the compound but only of the elements present in it, and there are other materials also found in Mexican artefacts that should too be considered, it is not possible to assert the presence of Maya Blue.

Mexican artefacts have shown the presence of smalt (pigment used since the late 15th century), lapis-lazuli ($3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2Na_2S$) riebeckite ($(SiO_3)_4\ Fe_2\ Na_2\ (SiO_2)_4$), or blue clays such as montmorillonite and aerinite; the four last ones known since Antiquity [6].

It is feasible to exclude the presence of smalt and other cobalt pigments, as this element has not been found in the blue paint. The presence of lapis-lazuli cannot be neither discarded nor assured, for the sulphur that would distinguish it from the rest of the pigments would be masked by the preparation layer (hydrated $CaSO_4$).

The rest of silica-based compounds would match the elements present in the spectra as well as the palygorskite clay. Though the presence of palygorskite cannot ensured we are able to conclude that no modern synthetic pigments have been found in the blue paint. Furthermore, the composition of the blue pigment would match that of palygorskite clay.

CONCLUSSIONS

External PIXE and RBS analyses have been applied to the Grolier Codex. Results indicate no modern synthetic materials are present. The preparation layer consists of hydrated $CaSO_4$, carbon-based blacks have been evidenced by the use of RBS, red pigments are made of red ochre (Fe_2O_3) and blue shades do not show cobalt synthetic materials but some clay composition.

From what can be seen with these techniques, the Grolier Codex bears original pre-Hispanic materials, although the pattern of blue materials has not been observed in the studied codex. Further analysis needs to be done for the identification of this pigment.

We are however a bit closer to the determination of its authenticity, but other factors must be considered, such as deterioration patterns, content and context. Materials analysis is just one of the facts.

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