ISSN 1824-2707
Volume 6 (2010)

Archaeometry of rock art paintings: *La Piedra De La Cuadricula* (Soacha, Cundinamarca, Colombia). A contribution to the study of prehistoric art

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Abstract

This article is a part of the results of the master thesis, which aim was to improve significantly the studies of the conditions of pictorial elements in a rock art mural, that is, to know the materials that were used and their interactions with the open air. This academic exercise introduces new aspects in the research process concerning the materials present in these rock art works and leads up to the works about technology of pigments in the studied area, extending the descriptive possibilities of the conservation conditions of rock art. The study of the materials opens a route towards the conservation work, and constitutes an essential way for the projected studies on dating. In this work, pigments were analyzed, some accretions, the rock substrate and the possible raw material of the rock art paintings. This analysis was done using Spectrometry Infrared. This investigation process is set in the context that the research group GIPRI has developed, as an extension of the methodological model of record and documentation of rock art in Colombia, especially in the cundiboyacense highplateau. The rock chosen was "La Piedra de La Cuadrícula ", located in a set of 167 rocks in Tequendama's area, Soacha's Municipality, in Cundinamarca's department. This sector is one of the most important archaeological sites of the country. In this site cultural stratigraphic sequences between 12 500 B.P. and 2500 B.P. have been found. On the other hand, there have been developed very important studies of the Pleistocenic and Holocenic environment.

Keywords: Rock Art, Infrared Spectrometry, Mineral Composition, Pigments, Accretions, Conservation.

Introduction

The work exposes here does part of the Master thesis in Prehistoric Archaeology and Rock Art (Erasmus Mundus Program 2006-2008), which one of the authors (Trujillo) developed and she was supervised for the other three authors. This work must be understood as a specialized aspect inside the context of a very wide process of the study of the rock art in Colombia, which has been realizing the group of investigation of rock art GIPRI Colombia, from 1970. In this process, diverse types of activities have developed theoretical and practical for the documentation and the study of the aesthetic manifestations of the inhabitants of the zone named conventional as altiplane cundiboyacense (Andean oriental high plateau of Colombia), where rock art constitutes one of the matters fewer acquaintances and worked. In this dynamic, GIPRI organized in all this process a historical - critical perspective for the comprehension of the rock art studies, which not only were including the topics in Colombia and in America, also their roots in the European influences of the 20th century studies. For the nineties the studies were started organizing and recovering moreover on the alterations and the characteristics of the rock art in the open air. Even if it is true that the group had detected the problems, it was very difficult to accede to the technology that allow determining accurately and with a scientist level of the materials and the physical, chemical and biological dynamics that were there in game. So with these premises, this project of work directed to improve significantly the studies about the conditions in which the pictorial elements of a rock art mural meet with open air conditions. This means to extend the descriptive possibilities of the environment of conservation of the rock art in Colombia.

Today questions are focused on the operative chain, that is, on the possible process of production and on the existence of some of the stages in the manufacture of the paintings. In this dynamic of study the interest is on the location of the places where the raw materials should be had obtained. Likewise, in what periods the warming would be possible or not of the raw material for the manufacture of the pigments and which might be the relation among these processes and the development of the ceramics, provided that the pigment would behave as a ceramic structure, according to some of the results obtained in this work.

For these reasons, archaeometry analysis is considered essential in this research; as a matter of fact it is absolutely indispensable in the search and determination of the materials present in a specific rock art mural. The elements gathered correspond to one of the items considered within the research dynamics, the outline of work criteria to document rock art sites. The systems of deposits description (deposit files, conservation files, as well as area, history of transcriptions and digital manipulation files) should be understood in this study as an additional context, gained through GIPRI experience, but also as an organized proposal presenting methodological criteria in order to study any deposit in a detailed and accurate manner. Therefore, the accomplished activities in the Infrared Spectrometry Analysis merge into the dynamics of the used criteria in the notebook of general description of rock art sites.

Contexts

Geographically the rock art shelter "Piedra de La Cuadrícula" is located in the Ecological Park "La Poma" (Fig. 1). It is a project to recuperate the biodiversity and landscape of Andean Ecosystem of the zone. It is at the height of 2600m, under cold climate thermal floor, having a good facility to go towards warm and temperate climate thermal floor descending by the Bogota river basin.

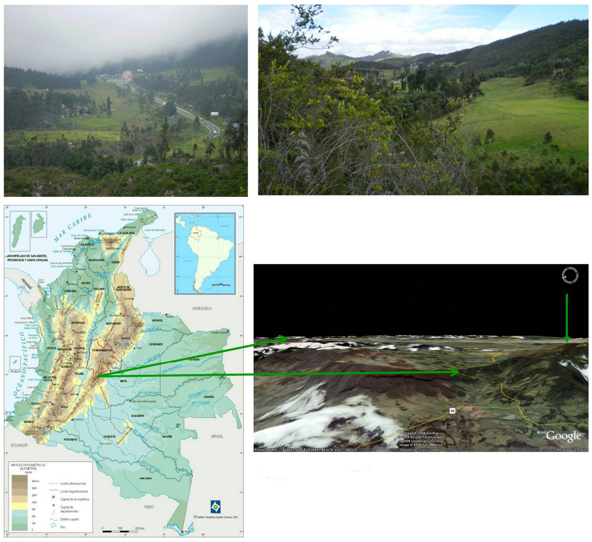

Fig.1. Location of the studied region. It is in the south-west of the Bogota's Savanna at 2600 m in cold weather. The vegetation in this area is specific to the Andean dry forest (bs-A). Also, an overview of the current landscape.

The vegetation in this area corresponds specifically to Andean dry forest (*bs-A*). This formation is part of the Oriental Mountains in the country, since beginning of Bogota Savanna, continues by all high plateau, that waters of the river Bogota spreads over the Duitama and Sogamoso valleys, until the north lands that are spread by the Suárez and Chicamocha rivers. The average temperature is between 12 y 18°C approximately, with an annual average of rains between 500 y 1000mm.

On the other hand, this area has been studied establishing the complete development of the climatic changes and the fauna variations and vegetation rigorously (van der Hammen, 1992). This process has been accompanied by the palinological studies, for the derived data of the excavations and finally, for the reconstruction of a crono-stratigraphy that it goes from early periods (12.500 B.P.) until the same moment that the Spaniards arrived in the XVI century to the highland.

With regard to the rock art in Colombia have met as much paintings as petroglyphs, and mobile art with rock art tradition, although until the moment they have not been found geoglyphs. It has news of the existence of rock art practically in all the departments of the country. In some places, there are references and in others have been carried out studies and rigorous documentations. In most of the cases the techniques of painting and engraving are very similar in the whole national territory. For the paintings there are different colors: white, yellow, black, but in their great majority they are of red tonalities. In the case of the petroglyphs, in their great majority they are dotted with stone tools. The rock art appear so much in low as high regions, in hillsides, valleys, next to currents of water, in places at the moment are desert, and even in rocks that are submerged in the rivers during a great part of the year. As for their styles, they are also diverse, from those that could call themselves naturalistic until those that their forms are quite synthetic. At the present time we have reference of a great quantity of rock art manifestations in the whole country (Muñoz, 2006), the rock art study area has been denominated as 3 A-B and it contains 44 rocks registered by GIPRI group. However, it is necessary to remember that inside the history of the investigation in Colombia there is not a clear relationship between the archaeological contexts and the rock art. Although, in the research of Los Abrigos Rocosos del Tequendama (Correal & van der Hammen, 1977), there is organized a complete crono-stratigraphy of the Savanna of Bogotá, there is an open road with the restlessness for the chronological investigation of the rock art, still for the rocks that were in the same place of the excavation. A fundamental step, to contribute to the development of this investigation, is the rigorous study of the materials and the composition of the same ones, to understand if they are natural or manufactured and, with it, to consent to elements and approaches that determine to what period of the total structure of the population these rock art vestiges correspond.

Methodology

The main objective of this work was to carry out certain laboratory analyses that until the present time the group of Colombian investigation GIPRI had not been able to perform, because it didn't have access to these procedures. These analyses were directed to respond questions about the type of chosen rock as place to do the rock art paintings, the mineralogical composition of the pigments used for the paintings and of the organic and inorganic materials that cause deterioration to the rock art drawings.

After having collected 9 samples of the *Piedra de La Cuadrícula* (Fig. 2), these were analyzed using *Infrared (IR) Spectrometry with Fourier Transformations in* the Centre de Spectroscopie Infrarouge du Muséum National d'Histoire Naturelle of París (CSIRMNHN), to identify the mineralogical composition of each one of them. This method allows establishing a correspondence between the frequencies of the bands of absorption and the molecular parameters (mass of atoms implied in the vibration, the type and angles of the connections and the vibration ways). The IRS gives this way access to an inventory of the constituents of the analyzed body (Fröhlich & Gendro-Badou, 2002), a sort of structural repertoire that has to be compared with a pattern, usually belonging to the lab's database of CSIRMNHN.

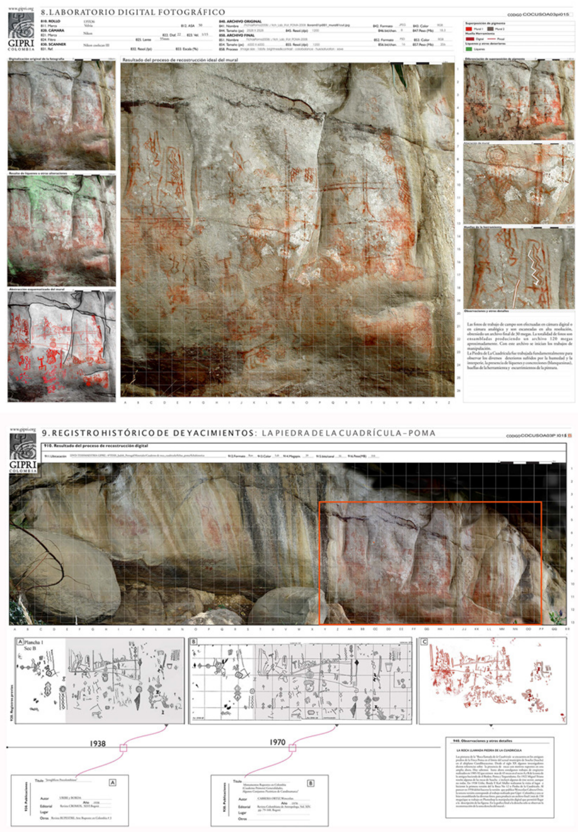

Fig.2. Registration and Documentation of "La Piedra de la Cuadricula" with the GIPRI Documentation's Model of Rock Art, which was designed and used for the registration of Colombian rock art sites. With the digital lab is made the first diagnosis of the current state of both the rock art paintings, and the rock itself. This digital photo process identifies important elements of the paintings and the site.

To determine minerals in IR spectroscopy it is necessary to start from the chemical family. The group bands indicate the functional group to which they belong and the specific bands help to define the mineral species. For the case of the spectra of mixtures of minerals it is necessary to know that they are compound for the sum of the spectra of all the constituents. But in the practice the constituents that have bigger importance are those that are detected. The characterization of a mineral species is possible if one or more specific bands appear. It is very common that different constituents share the same band or that they are overlapped. For example, the band of group 460-470cm^{-1} corresponds to several minerals: quartz, caolinite, montmorillonite, dolomite and hematite (Tab. 1a).

In this method, the sample is prepared in a solid solution of Bromide of Potassium (KBr) in form of pressed pill and it is possible carried out so much qualitative analysis, as quantitative. The KBr serves of transparent medium so that the sample is in solid dissolution, and as it is a halogen, the spectroscope it doesn't detect it. The use of the KBr has been standardized because its refraction index is very stable to each frequency, because this parameter is decisive when finding the transmittance coefficient or absorbance of the sample.

The preparation of this pill is carried out under a rigorous protocol (Fig. 3) and it has as objective to be able to carry out some calculations about the concentration of the samples that they are controlled by the denominated *Absorbance Law or Lambert-Beer Law* (Fig. 4). It is for this reason that the process of the preparation of the pills of KBr should fulfill the entirety of the protocol, to have a control especially of some of the variables that are in game, with the diameter, longitude and mass of the pill.

Results

The CSIRMNHN of Paris has a patron bank of graphs to carry out the analyses (Tab. 1b). In relation to the organic materials, these they were not determined because they didn't have the standards to make their precise identification. All the carried out analyses, such qualitative as quantitative, they were advised by the Professor François Fröhlich, coordinator of this Center.

Familia Química	Grupo funcional	Compuesto	Bandas del grupo Cm^{-1}	Bandas específicas (cm^{-1})
Silicatos	$[SiO_4]^{4-}$	Cuarzo	1095-1085(MF), 1170 (F), 798 (MF), 779 (F), 696 (F), 512, 478, 460 (MF), 436	696
		Sílice amorfa	1084 (MF), 800 (F)	800
Aluminosilicatos	$[Al_2SiO_3]$ $[SiO_2]$	Caolinita	3694, 3621, 1100, 1030, 1008, 913, 800, 694, 539, 471, 431	3694
		Montmorillonita (Esmectites)	3642*, 3624, 3420 (H2O), 1115-1090, 1038-1026, 915, 878, 845-835, 796-790, 623, 522, 467	3624
		Feldespatos	594-650 (Albitas), 578-625 (anortitas)	
Carbonatos	$[CO_3]^{2-}$	Calcita	1780-1790, 1160, 1432-1438 (MF), 878 (F),845, 713-712 (M) 315 (F)	712 (M)
		Dolomita	1810, 1620 (H2O), 1437 (MF), 879 (F),797-778, 693, 552, 509, 460 350 (F)	729 (M)
		Aragonita	1476 (MF), 851 (F)	712 (M), 700 (F)
Óxidos	Fe_2O_3	Hematites	551 (MF), 540 (F), 470 (F),463, 425, 390 (F), 345 (F)	551
Hidróxidos	FeO.[OH]	Goethita-Limonita	3140-3100 (M), 900-800 (F), 798 (Q M), 630 (M),	3125, 405
Sulfatos	$[SO4]^{2-}$	Yeso	1150 (MF), 1120 (MF), 673 (M), 461, 428,605 (M)	3560 (MF), 3420 (MF), 1685 (D), 1620 (F)
		Anhidrita	1160 (F), 1130 (M), 676 (F) y 616 (M)	579 (F)
Fosfatos	$[PO_4]^{3-}$	Apatito	1050 (MF), 1085 (M), 605 (M) y 580 (M)	
Nitratos	$[NO_3]^{1-}$		384 (v3), 728 (v4)*	

Intensidad de las bandas de absorción: Muy Fuerte (MF), Fuerte (F), Media (M), Débil (D)

Colección/ Publicación	Patrón	Banda Absorción (cm^{-1})	Absorción Media
CSIR-MNHN	Hematite ref: 02319	551,593	1,0307
CSIR-MNHN	Goethita ref: 02320	3125,37	0,5057
CSIR-MNHN	Calcita ref: 01080T	712,568 875,524	0,2415 0,9869
CSIR-MNHN	Dolomita ref: 04091T	728,06	0,2371
CSIR-MNHN	Cuarzo KBR2	798,46 696,211	0,0389 0,0165
CSIR-MNHN	Caolinita UK T	3691,91	0,6018
CSIR-MNHN	Montmorillonite	3627,45	0,1904
Mina St. Pierre, Alsace, France	Monohidrocalcita ref: IR2753	3319 3232	

No.	Material	Código	Carbonatos Calcita	Silicatos Cuarzo	Aluminosilicatos (Arcillas) Caolinita	Hematites	Goetita	Fosfatos
1	Sustrato	5-08307		76%	6,5%		10%	
2	Ocre	1.2-08301		27%	35%		10%	
3	Pigmento + Pátina*	1-08303		✔	✔	✔		
4	Pigmento*	7-08309		✔	✔	✔		
5	Pigmento	2-08302		14%	20%		10%	
6	Líquen + Pigmento	3-08304		73%	✔	✔		
7	Concreción 1+ Pigmento	4-08305		✔	✔			
8	Concreción 1	4.1-08306	✔					
9	Concreción 2	6-08308						✔

Tab.1. a)Some absorption bands of functional groups. b) Patterns Collection of Centre de Spectroscopie Infrarouge of Muséum National d'Histoire Naturelle, Paris (CSIRMNHN) and publications. c) Qualitative and quantitative results of the samples analyzed by IR spectroscopy (KBr pellet method). * There was not enough sample material to quantify the results.

The analysis that is made of the materials allows finding the components (compositional) that registers in percentages and they are calculated with the Lambert-Beer Law. Approximately they should add 100%, percentage that is interpreted as the quantity of components that has the sample of organic or inorganic materials. Starting from the spectra, it has been identified the presence or absence of carbonates (calcite and dolomite), silicates (quartz), aluminosilicates (caolinite and montmorillonite), oxides and iron hydroxides (hematite and goethite) and organic materials. In the results of the spectra the sum of the total of the percentages of the samples usually, never arrives to 100% and it is due to that some substances, like the atmospheric CO_2, the H_20 of the environmental water, organic matter, make part of bands which have a minimal presence in the sample, or they don't present absorption in IR and don't reach to be registered inside the bands of absorption that the spectrometry manages (Tab. 1c).

Fig.3. *Initial steps in the preparation of the samples.* a) Extraction b) Storage and Codification c) Manual crushing of the sample to homogenize and shrink the size of the grains, less than 2.0 µm. *Pills Preparation.* d) precision balance for weighing 2.5 mg of powdered sample and homogenization of the sample with KBr. *Pressing the Pill.* e) Introduction of the mixture into the mold. f) Mechanical press with the mold connected to a compressor, checking the pressure gauge that is 11 ton/cm^{2}g) The process of drying of the tablets at a temperature of 110 ° C for subsequent analysis in the IR spectrometer.

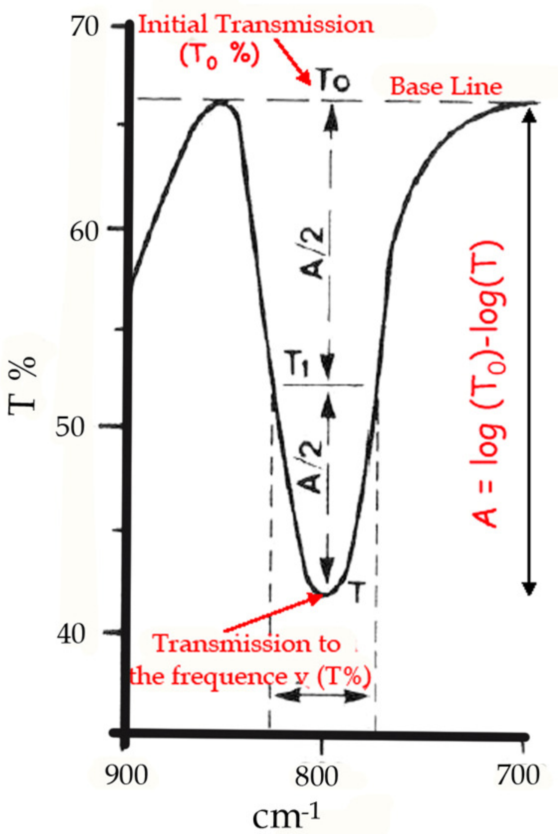

Fig.4. Graph representing the relationship of transmittance or IR absorption. (Obtained from Fröhlich, 2008). There is observed as the transmittance *To* (initial transmission), the transmittance *T* at a frequency ν given. That is, the transmittance T (expressed in %) or intensity of the IR which is a function of frequency or wave number ν (expressed in cm^{-1}), resulting in the absorption A, called the *Law of Absorption or Lambert-Beer A = log (To) - log (T).*

Sample 1: Substrate

With the spectrometric analyses, it was found that the substrate was a sandstone hard rock, rich in iron, because it presents 10% of Goethite (FeOCOM), this show their yellowish color, with 76% of Quartz, and 6.5% of Caolinite. They are also observed organic materials and H_20 (Fig. 5a). The sandstones are generally sedimentary rocks with a consolidation of sand granules silts between 0,02 to 2 mm. The quartzite composition confers them a high resistance to the abrasive waste. According to the Hardness Scale of Mohs, it would be 7. These results coincide with the classification of rocks of the study area that regularly, they are sandstone blocks of great size that are denominated shelters, because they have a roof with eaves, the whole group of rocks of the sector was favorable for the hunter gathering groups that frequented and lived in this region.

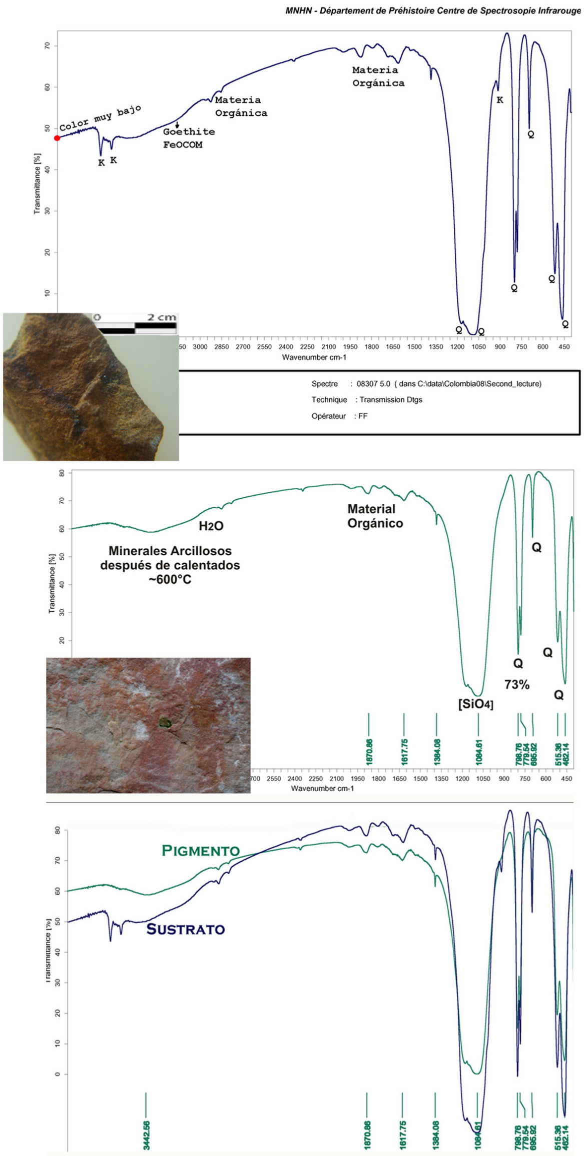

Fig.5. a) IR spectrum diagram for the sample of the rock. There are absorption bands corresponding to the most important components of the substrate. b) IR analysis of sample 6, consisting of pigment, bedrock and algae. There is a large amount of quartz, which corresponds to the rock, presence of heated clay minerals, possibly as in samples 3 and 4, and a large amount of organic material associated with the presence of algae. c) Comparison of the graphs for the sample 6 to sample 1, it is important to note the presence of organic material in the two samples and the high amount of quartz.

Sample 2: Raw Material

This sample consists of reddish mineral clays beside the rock. It is easily founded in any part of the world and it is a constituent of the clay sediments due to the meteorization of igneous, metamorphic and sedimentary rocks. It is known that it is compound mainly for silica, alumina and water; also containing other substances like fragments of rocks, moisturized oxides of iron, alkalis and colloidal materials (Foucault & Raoult, 1985).

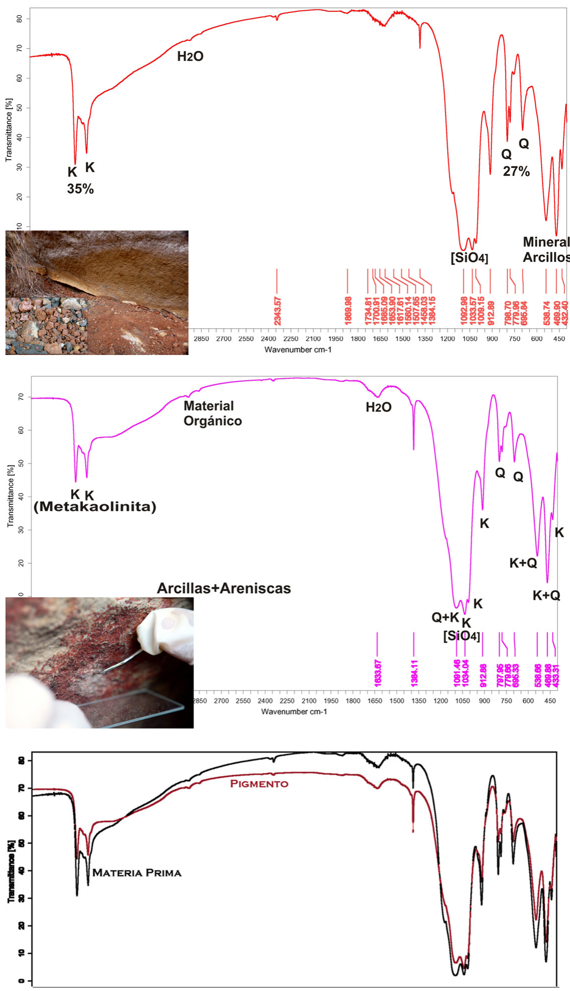

Fig.6. a) IR spectrum diagram of the assumed raw material used to make the rock art pigments. . b) Sample pigments, along with the rock of support. There is a dehydration of kaolinite, but is not evidence that the natural product had been heated. It seems that this pigment came directly from the clay soils. c) Comparison of Figures 6a and 6b, ie, raw material and pigment, respectively. Their characteristics are quite similar. This leads to the conclusion that quite possibly the raw material was used without any previous calcinations to obtain another type of red.

The results show (Fig. 6a) that its base transmission line is near to 70% what confirms its red color, it is near to the base line of IR (60%), and therefore with a low energy of initial transmission. It also contains 35% of Caolinite, and 27% of Quartzite, a typical caolinitic mineral. The rest of components were not quantified, but interfacial H_2O was identified around the band of 2950 cm^{-1} that shows the high humidity of the sample. Amorphous Silica was also identified [SiO_4], and in the last bands of the graph, between 600 and 430 cm^{-1}, the presence of ferrous oxides is observed (hematite) that can be interpreted as the causing of the reddish color of the sample. Bands of absorption associated to organic materials were identified, but with a very low presence. These can be in the sample like part of the contamination to be outdoors and in contact with water and microorganisms.

An overwhelming aspect to imagine that it could be the raw material of the pigments it is that, near temperatures at the 550°C, the mineral clays lose the caolinite, it is destroyed to this temperature. This can be observed in the results obtained for the samples of pigments. All this makes think that indeed they could be heated to obtain different tonalities of red, frequently used in the rock art paintings of other regions of the world (Pepe et al, 1991; Santos et al, 2007; Tosello, 2005).

Samples 3, 4, 5 & 6: Pigments

These samples were obtained of three parts different from the rock. The samples 3 and 4, correspond oneself place, unfortunately, the quantity of sample 3 only corresponds to 2,10 mg circumstance that affects the exact parameters of the protocol to build the pill of KBr, because they are needed minimum 2,50 mg of brute sample. So the carried out analysis was only qualitative. The sample 3 corresponds to pigments and mineralogical elements of the patina that cover the painting. The sample 4 only corresponds to an inferior layer of pigment. For this sample, just 1,00 mg was obtained, for this reason, quantitative analysis could neither be made.

In the graph of sample 3 (Fig. 7a) we can observe a base line of quite low transmittance, approximately 38%, that is, a low energy corresponding to a not very intense red color with tendency to the yellow. In the first bands of absorption one can observe great quantity of water that it associates to the mineral clays. So this quantity of water can be associated to the same material, clay minerals, the same situation to the water that can register for the bands of 2200 and 1633 cm^{-1}. Around the frequency of 2925 cm^{-1} organic material appears that were not identified. The band in 1088 cm^{-1} shows the presence of Oxygenated Silicone, associated to the Silica molecule; this band appears in all the silica minerals. Followed by one of the bands associated to the presence of Quartz in 798 cm^{-1}, although their transmittance is low, what means that it is not characterized completely the quartz; it associates rather to Aluminosilicates [SiO_2]. This characteristic is emphasized with the band of 695 cm^{-1} that shows the presence of Quartz, but it is also very weak and it should appear in 780 (like it was the case of the first sample that it contains 27% of this mineral).

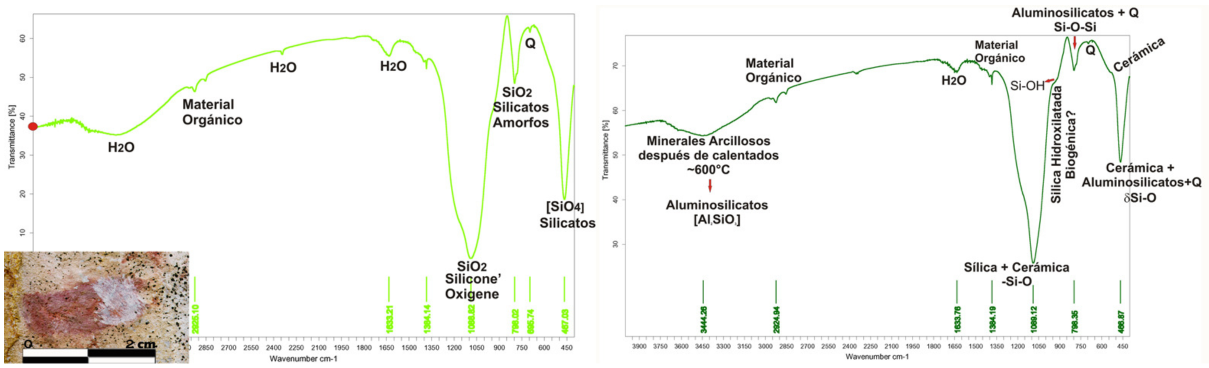

Fig.7. IR spectrometry graphics of samples of pigments in the same painting. a) It corresponds to the first layer of pigments. As was covered by a kind of transparent cement, it was very difficult to remove. b) This graph will have detailed each of the elements associated with the absorption bands of pigments found in the inner layer. The two graphs show a similarity in the loss of Kaolinite, due to anthropogenic warming processes between 500 and 600 °C, the raw material.

With this information we can conclude that, in the first place, the sample is not a primary product or raw material rather is a product that has suffered some changes in its initial components of Quartz and now it has become Aluminosilicate. A very usual form of creating these changes in the clay minerals is subjecting them to an increase of moderate temperature, around 500 at 600°C, as it is generally made with the ceramic. In this way, the presence of the Quartz becomes very weak and it changes its frequency. Secondly, the raw material could be oxidizing ferrous clay, namely, with goethite presence that transformed into hematite when being warmed. It is known that with a small quantity of heated, goethite can easily be gotten the change of initial color to a red one in the end. (Personal conversation with Professor Fröhlich).

For the inferior layer of pigment, sample 4; its base transmittance line is 58% (Fig. 7b). The obtained results of the qualitative analyses show that the composition of this is very similar to the previous one (Fig. 7a). The differences among two samples are in the percentage of the transmittances. In general, the characteristics of the pigment, in the sample 4, reflect to be the treatment of the raw material when increasing the temperature.

The sample 5 was obtained from a fragment of the mural that would seem to be the representation of a hand. It is observed in the graph (fig. 6b) that the base transmittance is around 70%, i.e., a higher energy transmission. For this sample it was possible to carry out quantitative analysis. It was 20% of Metakaolinite, it is a dehydration of the Caolinite, because the bands of absorption are weaker. On the other hand, 14% of Quartz is existent in its more characteristic band of absorption 696 cm^{-1}. The last bands correspond to the components of ferrous oxides, caolinite and typical quartz of the clay minerals. Similarly, it can be observed the typical absorption bands of Aluminosilicates.

All these characteristics drive to the conclusion that this pigment had a treatment very different to the previous ones, because a clear evidence of heating is not observed. Caolinite continues existing in the sample, as it is observed in the bands 3696 and 3620 cm^{-1}. Although the transmittance is a little weaker, it shows that the dehydration was not total, because it is necessary an approximate temperature of 550°C to be destroyed the caolinite. The rest of characteristics have just confirmed that this pigment has likeness with the raw material, in this case, with the sample 2 (Fig. 6c). It seemed that this material was used directly to get the pigments without calcinations, that is, the color of the pigment would correspond to the color of the clay minerals in the raw material.

The sample 6 is composed by rock substrate, pigment and lichens. The IR (Fig. 5b) shows some important aspects. For instance, the sample was composed by great quantity of Quartz, 73% that would correspond to the rock substrate, in agreement with the results of the sample 1 analyses. The interesting thing is that it doesn't observe the presence of Caolinite, at least weak transmittances doesn't subsist in the characteristic band of absorption, 914 cm^{-1}, of this mineral. That makes think, it was destroyed as in the samples 3 and 4. On the other hand, if it can observed the presence of clay minerals heated in the absorption band of 3442 cm^{-1}. Also the hydroxides represented the presence of Goethite. Additionally, water and organic material associated to these minerals, as it has been verified of all samples. Although, this circumstance, in the graphs of the samples 6 and 1, allow to see a bigger quantity of this material among the bands 1870 and 1615 cm^{-1} that it is not so visible in the other samples. It seemed then, that the rock substrate is affected by microflora so external, as internally. This is completely evident in the last sample, because at first sight, the lichens can be observed stuck it, but in the sample 1 was not easy to perceive their presence.

The previous characteristics of the sample 6 allow observing the great likeness between their graph and the graph of the rock substrate sample (Fig. 5c). Their difference, it is the presence of Caolinite in sample 1, while in the other one hydroxides are observed. This situation can be explained if we think that the sample 6 was also composed by pigments, with the same behavior as in samples 3 and 4, it would be the product of the clay mineral calcinations to obtain different tonalities of red.

Samples 7, 8: Accretions

These samples correspond to certain whitish blooming that exists on a great percentage of the pictorial mural. They are deteriorations that they have gone destroying great part of the paintings that seemed to be there a long time ago for their hardness and concentration. It was taken two samples of the same place, one to move away the superior layer that should contain pigments, and the other one to move away a second layer that it only contained the accretions and that it was not on the surface of the location.

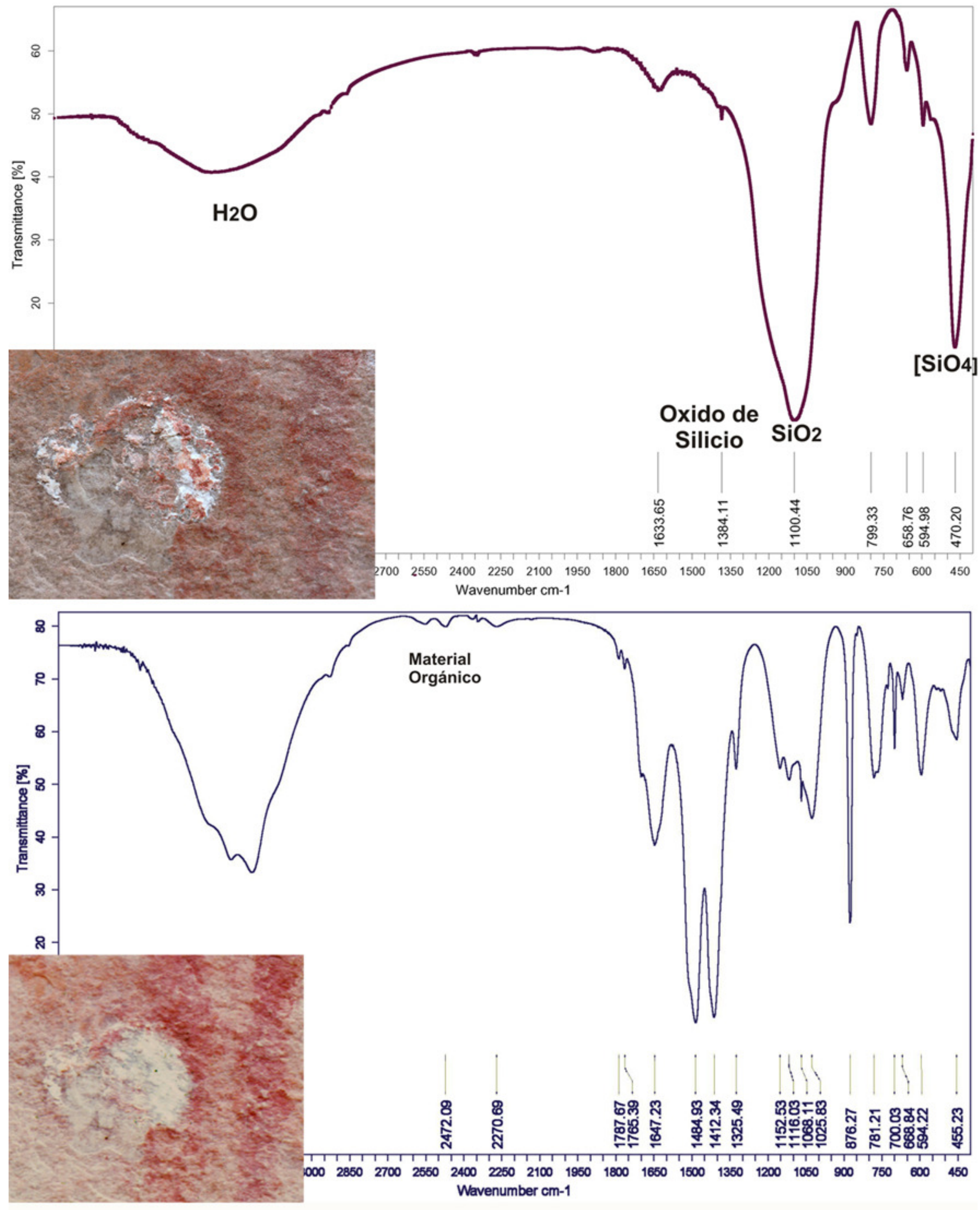

Fig.8. a) IR spectrometry analysis for the sample 7. The mineralogical composition of this material corresponds to silicon oxide, related to the existence of hydrotermal, or unicellular microorganisms such as phytoliths or diatoms. b) IR spectrometry of the sample 8. This material is basically composed by monohidrocalcita and organic materials.

For the graph of the sample 7 (Fig. 8a) we can observe that the components are very different from the previous ones. The absorption bands of this material correspond to an amorphous solid, which is mean, it doesn't have order of long reach or crystalline structure, and they don't have a periodic organization, as for example, glass and certain plastic materials (Foucault & Raoult, 1985). This amorphous material is the silicon oxide (SiO_2), or hydrated dioxide of silicon, the high presence of water is identified through the absorption band of 3381cm^{-1}. Bands corresponding to the Quartz are not presented, but Aluminosilicates are presented around the band of 470cm^{-1}.

This kind of accretions can appear for biogenic reasons, associated to the presence of microorganisms that when being in permanent contact with the water, they have been mineralizing. The precipitation of a mineral as a result of the metabolism or cellular activity of living organisms is denominated biomineralization. These organisms are denominated bioliths. They are sometimes identifiable as fossil plants (phytoliths) or fossil animals (zooliths) (Bertoldi, 1985). The other reason can be the presence of diatoms, algae unicellular, which are in any watery atmosphere, marine or sweet. These cells are in charged to do the photosynthesis, for this reason, they are so important in the phytoplankton. These unicellular organisms present a very special characteristic, they have a covered with silica that is denominated frustules (Jones et al, 1999).

The sample 8 correspond to the materials attachés to the rock in the inferior layer to the sample 7. The results of their analyses are also very interesting. Almost all the bands of absorption correspond to a mineral that is not very frequent, which is denominated monohydrocalcite ($CaCO_3H_2O$) (Fig. 8b). As the sample presents, such organic material, as inorganic coal and monohydrocalcite, has a high concentration of Carbone in general, giving to the sample possibilities of being dated in the future.

The monohydrocalcite is also a biogenic mineral; it is formed due to an organic effect taken place by algae in a high humidity. This mineral can end up becoming Calcite (Jones et al, 1999). As this process is carried out with changes of temperature, it could be possible to measure the time in it carries out this change. It would also give the possibility, in a future, to investigate this type of analysis to be able to date this type of accretions.

Sample 9: Excrement of Birds

This sample was obtained of residuals of bird excrement that are deposited in the wall of the rock. The rock shelter presents some very capable concavities so the birds can be protected of the rain and very possibly to make their nests. It is not known accurately that type of birds is those that frequent the place, but for the size of these holes, they cannot be very big.

The IR spectrometry graph doesn't easily show mineral components, the components are organic in their majority. It allows suggesting that these materials are quite recent. However, bands of absorption could be associated to phosphates, oxide of carbon (CO), but it is not easy to assure it. It is reached to distinguish respectively in the bands of absorption 2962 and 2926cm^{-1} the presence of a Carbone and two hydrogens. Unfortunately, the picked up sample was very recent and the mineralogical components could not be analyzed that leave the excrements on the mural when spending of the years. Since these materials are also producing withy stains that are covering the rock art paintings and causing an irreparable deterioration on them.

Conclusions

The use of Infrared Spectrometry Analyses in this Archaeometry project was really helpful. We could find interesting results about the mineral composition of the pigments and accretions of the rock art paintings in this mural. It contribute to organize a first diagnosis on the state of conservation of the paintings and the rock, as station pilot that allows to observe the interactions among the pigments, the substrate, the humidity and the climatic conditions. Aspects that not all are developed in depth, but they are fundamental for the construction of a model that can come to be developed in diverse phases. Now it can be companied by the conservation record that began with GIPRI (Methodological Model) many years ago (Muñoz & Trujillo, 2009).

The outcomes in what concerns the pigments are: two out of three samples show similar manufacturing techniques to those used in ceramics, this means that the raw material must have been subjected to changes in temperature in order to obtain distinct tonalities of red. This could be observed by the destruction of kaolinite, regularly present in argillaceous minerals. Considering that the last sample of pigments has similar characteristics to argillaceous minerals of tropical areas, it may be inferred that the raw material must have been applied directly without any transformation, besides being crushed and used in the mural.

In what concerns the samples of rock surface accretions of the studied mural, their chemical composition reveals their biogenic origin and the high interaction between microorganisms, substrate, paintings and climate conditions of the site. An entire set of conditions that influences rock art conservation. On the other hand, their overall composition opens new possible ways to a relative dating of the rock art paintings through these associated elements.

With relationship to the obtained results of the ochre, found in the base of the rock it was observed that are made up of clay minerals that could be the raw material for the production of the pigments of the studied mural. It will also be necessary to look for other possible sources of matter ocher near to the mural and to locate the relative concentrations of the pigments in the geologic strata of diverse areas, where paintings were also made. The purpose will be enlarging the options to demonstrate in conclusive form if all and each one of the pigments was or not subjected to heating processes.

This study equally could allow some periodicity of the technological activities and present techniques in the rock art painting. If the different chronologies already existent they find some correspondence with the studies and variations of the materials, the studies of the rock art would contribute additional aspects to the amplification of the knowledge of the cultures, which inhabited the territory.

In this context, the work that here is presented constitutes an additional contribution to the understanding of the operative chains of production of the art, and in that mark in particular, to the analysis of the raw material, to the pigments, to the accretions and the studies of the rock substrate, relative to the paintings in the highland Cundiboyacense in the sector of Tequendama, place in which the most rigorous studies in the Colombian archaeology have been made, from the seventies. The study also suggests different moments of composing the panel, the motives produced with heated pigments corresponding to a different moment from the others.

Acknowledgements

The authors would like to acknowledge support of:

- Erasmus Mundus Program;
- Indigenous Rock Art Research Group, GIPRI Colombia;
- Instituto Colombiano de Antropología e Historia, Parque Ecológico La Poma Colombia;
- Centre de Spectroscopie Infrarouge del Muséum National d'Histoire Naturelle, Institute de Paleontologie Humaine and Musée de l'Homme, París France;
- Universidade Trás-os-Montes e Alto Douro, Instituto Politécnico de Tomar, Museu da Arte Pre-Histórica and Instituto Terra e Memoria de Mação, Portugal.

References

Bertoldi de Pomar, H. 1975. Los silicofitolitos: Sinopsis de su conocimiento. Darwiniana 19: 173-206.

Correal Urrego G. and van der Hammen Thomas. 1977. Investigaciones arqueológicas en los Abrigos Rocosos del Tequendama. 12 000 años de Historia del Hombre y su Medio Ambiente en la Altiplanicie de Bogotá. Fondo de Promoción de la Cultura, Banco Popular, Bogotá.

Foucault,A. and Raoult J.F. 1985. Diccionario de Geología. Barcelona. Edit. Masson S.A. pp.316.

Fröhlich F. and Gendron-Badou A. 2002. La spectroscopie infrarouge, un outil polyvalent. In: Miskovsky, J.C. (Ed.), Géologie de la Préhistoire: Méthodes, techniques, applications. Association pour l'étude de l'environnement géologique de la préhistoire, Paris, pp. 663-677.

van der Hammen Thomas. 1992. Historia Ecología y Vegetación. Corporación Araracuara, FEN de Colombia, Fondo de Promoción de la Cultura, Bogotá.

Jones, M.S. Wakefeld, R.D. Forsyth, G. 1999. Presencia de minerales poco comunes en la roca alterada de un edificio medieval escocés colonizado por organismos biológicos. In Rev: Materiales Construccion, Edición, Vol. 49 (256):3-14).

Muñoz C. Guillermo. 2006. Rock art in Colombia. Zone2: Colombia In: Rock art of Latin American and Caribbean. Thematic study. ICOMOS. June. Paris France http://www.icomos.org/studies/rock-latinamerica.htm

Muñoz C., Guillermo; Trujillo, Judith. 2009. Inventarios Gráficos y Geográficos: un proyecto de registro y conservación. del arte rupestre en Colombia. In: Rock Art Data Base. New methods and guidelines in archiving and cataloguing Proceedings of the XV World Congress UISPP 30 (Lisbon, 4-9 September 2006).

Pepe, C. Clottes, J. Menu, Walter, M. P. 1991. Le liant des peintures paléolithiques ariégeoises. In: C.R. Acad. Sci. Paris, t. 312, Série II, pp 929-934.

Santos, L.M. Filho, B.B. Fontes, L.M. Cavalcante, L.C.D. Lage, M.C. Fabris, J.D. 2007. Análise Química de Pigmentos e Produtos de Alteração do Sítio Pedra do Castelo. 47 Congreso Brasilero de Quimica. Septiembre, Natal, Brasil.

Tosello, G. 2005. Alguns elementos sobre as Técnicas das Pinturas de Santa Elina. In: Pré-História do Mato Grosso. Cidade de Pedra. Vol. 2. Edusp, Brasil.