ANALYSIS OF PIGMENTS FROM ROCK PAINTING SITES IN RIO NEGRO AND CHUBUT PROVINCES

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Chemical and microscopical analyses were undertaken of samples from the rock painting sites Azcona (El Bolsón) in Rio Negro Province and Campo Moncada 1(Valle de Piedra Parada) and Cerro Pintado (Cholila) in Chubut Province, Argentina by the Canadian Conservation Institute. Representative microsamples were removed from rock paintings and substrate rock to investigate the pigments and any mineral accretions present. Analysis by x-ray microanalysis (scanning electron microscopy) and x-ray microdiffraction revealed the presence of hematite, lepidocrocite and green earth (celadonite or glauconite) pigments as well as calcium oxalates (whewellite structure).

Introduction

As part of an Argentina-Canada collaborative rock art conservation research project to study rock art sites in Argentina *(Documentación y Preservación de Arte Rupestre Argentino),* the authors undertook sampling and analyses of eight (8) samples from rock painting sites in Rio Negro and Chubut Provinces, Argentina. The samples were taken during a field trip of in 1995 by the study team from the sites *Azcona-El Bolsón* in Río Negro Province and *Campo Montada 1 (Valle de Piedra Parada)* and *Cerro Pintado (Cholila)* in Chubut Province. (see Table I) as part of the project *Comarca* [District] *Andina del Paralelo 42: investigaciones arqueológicas en arte rupestre.* This project has been carried out, since 1995, with the Subsecretaría de Cultura of Chubut Province. Analysis of microscopical samples by x-ray microanalysis (scanning electron microscopy) and x-ray microdiffractometry was undertaken by the Analytical Research Laboratory, Canadian Conservation Institute.

Methods of Analysis

X-ray Microanalysis

A Hitachi S-530 scanning electron microscope incorporating a Tracor Xray x-ray detector and a Noran

Table I. Samples

Sample name	Sample type	Site/Sector/Motif	Colour
CA1	rock painting	Azcona; El Bolsón; Río Negro, Argentina	orange
CA2	rock painting	Azcona; El Bolsón; Río Negro, Argentina	black (possibly with some orange)
CA3	rock painting	Azcona; El Bolsón; Río Negro, Argentina	yellow-orange
CA4	rock painting	Azcona; El Bolsón; Río Negro, Argentina	dark red
CA5	rock painting	Azcona; El Bolsón; Río Negro, Argentina	green and dark red
CA6	rock painting	Campo Moncada 1; Valle de Piedra Parada; Chubut, Argentina	green
CA7	red pigment	Cerro Pintado. Cholila; Chubut, Argentina	red
CA8	green pigment	Cerro Pintado. Cholila; Chubut, Argentina	green

Voyager x-ray energy spectrometer was used to obtain a qualitative determination of the chemical elements present in the samples. Using this technique, elemental analysis of volumes down to a few cubic micrometers can be obtained for chemical elements from sodium (Na) to uranium (U) in the periodic table with a sensitivity of about 1%. Analysis was carried out using an accelerating voltage of 20 kV and a working distance of approximately 20 mm. The chemical elements detected were categorized as *"major",* "minor" or "(trace)", based on relative peak heights, with no corrections for atomic number, absorption or fluorescence matrix effects.

X-ray Diffraction

In order to determine the crystalline components present, particles of pigment and other materials were removed from the fragments and analyzed by x-ray diffraction (XRD) using a Rigaku instrument equipped with a 12 kW rotating anode generator with a cobalt anode, operated at 45 kV and 160 mA.

Samples were mounted with silicone grease on a glass fibre and placed in a sample holder on a goniometer head for analysis by microdiffractometry. The detector, which has an angular range of 20 = 3° to 147°, is a position sensitive proportional counter with a position analysis device and is interfaced to a multichannel analyzer and a computer. Counting time was 7200 seconds. The mineral phases were identified by computerized searching of x-ray powder diffraction patterns from the International Centre for Diffraction Data PDF-2 database (sets 1-45, 1995) on a computer equipped with a CD-ROM drive. The software employed for the computerized searching was Micro Powder Diffraction Search Match (μ-PDSM) developed by Fein-Marquart Associates.

Results

The combined results of the x-ray microanalysis and x-ray diffraction are listed in Table II. No results by x-ray diffraction were obtained for samples CA1 and CA2 indicating the pigment concentration is either too low for characterization by x-ray diffraction or the pigments are amorphous.

The presence of manganese in the black sample (CA2) suggests that the pigment pyrolusite (ß-MnO_2) is present.

Results of particular interest are the presence of
-hematite (CA4; CA5b)
-lepidocrocite (CA3)
-green earth (glauconite/celadonite) (CA5a; CA6; and CA8)
-calcium oxalate hydrate (whewellite structure) (CA3; CA4; CA7)

Summary and Discussion

Hematite

The mineral hematite (Fe_2O_3), or red iron oxide, is the red colorant found in red ochres used for rock paintings throughout the world. Ochres consist of a mixture of hematite and other minerals such as quartz and clay minerals.

Lepidocrocite

Goethite, a yellow to brown iron oxide hydroxide with the formula α-FeOOH, is the most commonly identified iron compound in yellow earth pigments and their synthetic analogues (Buxbaum and Printzen 1993). Goethite belongs to the orthorhombic crystal system. The oxygen and hydroxyl atoms are hexagonally close packed with half of the octahedral sites filled by ferric ions (Schwertmann and Cornell 1991). Lepidocrocite and akaganeite are polymorphs of goethite with the formulae (γ-FeOOH and (β-FeOOH) respectively. Lepidocrocite belongs to the orthorhombic crystal system and has cubic close packing within each layer of octahedra; akaganeite belongs to the tetragonal crystal system. In both, half of the octahedral sites are filled by ferric ions.

Along with goethite, lepicocrocite is a common component of rust (Schwertmann and Cornell 1991). Lepidocrocite has occasionally been identified in earth pigments on rock paintings (Hyman *et al.* 1996, Zolensky 1982, Scott 1993, Watchman *et al.* 1990b). Lepidocrocite is also present in some synthetic, orange iron oxide pigments (Buxbaum and Printzen 1993:88-90).

Green Earth

The pigment "green earth" was found in two samples, one from the *El Bolsón* site, the other from the *Campo Moncada 1* site. Green earth pigments are composed of either of two minerals, *glauconite* or *celadonite.* It is not possible to determine which of the two specific mineral is present based on this analysis. Analysis of green pigments at other sites in Argentina are currently underway by the authors to determine how widespread was the use of "green earth" in this region. Green earth has not been observed at rock painting sites in Canada (which are almost all executed in red or orange-red pigments) however it has been found on First Nations artifacts including a Tsimshian stone mask in the collection of the Canadian Museum of Civilization (Wainwright *et al.* 1993).

Oxalates

A calcium oxalate hydrate phase with whewellite structure was found in several samples from both the Río Negro and Chubut sites. Oxalates has been observed at rock painting, wall painting and other cultural sites and the exact mechanism by which they are introduced is still a subject of research and speculation. (Moffatt *et al.* 1985, Russ *et al.* 1999, Wainwright *et al.* 1997; Wiedemann and Bayer 1989). For example, oxalates-usually whewellite and weddellite- can be produced by the reaction of calcium carbonate with the oxalic acid produced by lichens, fungi, or microorganisms (Saiz-Jimenez 1989). Their presence could indicate that the microclimate at the rock painting sites was at one time very humid or damp.

Table II. Results

Sample Description	XRD	SEM/XES*
CA1 red; thin layer, very firmly bound to rock beneath; not possible to separate completely from substrate	- small sample, no peaks in pattern	*sample area 1:* Si, Ca, Fe (Al, K, S, Mg, P) *area 2:* Si, Fe, Ca, Al (S, K, Mg)
CA2 black; thin layer, very firmly bound to rock beneath; not possible to separate completely from substrate	- small sample, no peaks in pattern	*sample area 1:* Si, Mn, Ca (Mg, S, Cl, K, Fe) *sample area 2:* Mn, Ca, Si (Al)
CA3 yellow-orange; powdery	- calcium oxalate hydrate (whewellite structure) - lepidocrocite	Ca, Si, Fe, Al (S, K, Ti)
CA4 red	- gypsum - hematite - calcium oxalate hydrate (whewellite structure)	Ca, S, Fe, Si (Al, K)
CA5b dark red; white crust present on parts of surface	- hematite	*sample area 1:* Fe, Si, Al, Ca (S, K) *sample area 2:* Fe, Si (Ca, K)
CA5a green; white crust present on parts of surface	- green earth (glauconite/celadonite)	Si, Al, K, Ca, Fe (Mg)
CA6 green	- green earth (glauconite/celadonite) - quartz - possible trace gypsum	Si, Al, S, K, Ca, Fe (Mg)
CA7 red powder scraped from surface of rock	- calcium oxalate hydrate (whewellite structure) - probably dioctahedral mica	Si, Al, K, Ca, Fe, Mg (Ti)
CA8 green powder scraped from surface of rock	- potassium feldspar - green earth (glauconite/celadonite)	Si, Al, K, Fe (Ca, Ti, Mg)

* *major elements,* minor elements, (trace elements); SEM/XES is an acronym for x-ray microanalysis in a scanning electron microscope using an x-ray energy spectrometer

Conclusions

Eight samples from rock painting sites in Río Negro and Chubut Provinces, Argentina have been analyzed by x-ray microdiffractometry and x-ray microanalysis to detemine their composition. Hematite, lepidocrocite, and "green earth" were found in the samples. Lepidocrocite has been found at rock art sites in other countries; hematite is the red mineral most commonly found at rock painting sites wordwide. Further studies into occurrences of green earth at rock painting sites in Argentina are currently underway. Oxalates were found at sites from both regions studied and coudl result from an earlier period of dampness which promoited the growth of lichens, fungi or microorganisms at the sites.

The number of samples analyzed and reported here is small. This is typical of many rock art studies where the first concern has to be the safe and unobtrusive removal of material. Samples are both extremely difficult to remove and can be difficult to analyze for several reasons including extremely small particle size, lack of crystallinity, and often heterogenous nature. For these reasons, several samples could not be completely characterized. As more analytical results are accumulated within the broader Argentinean rock art context a clearer picture of the use and distribution of pigments and other materials will undoubtedly be drawn.

Resumen

El Canadian Conservation Institute realizó el análisis químí-

co y microscopico de las muestras obtenidas de las pinturas rupestres de los sitios Azcona (El Bolsón) en la provincia de Río Negro y Campo Moncada1 (valle de Piedra Parada) y Cerro Pintado (Cholila) en la provincia del Chubut. Micromuestras representativas fueron removidas de las pinturas y del soporte para investigar los pigmentos y las acreciones minerales presentes. Los mircroanálisis por rayos x (SEM) y la microdifracción de rayos x revelaron la presencia de hematita, lepidocrocita y tierra verde (celadonita o glauconita) así como oxalatos de calcio (estructura whewellite).

Résumé

On a procédé aux analyses chimiques et microscopiques d échantillons prélevés des sites dart rupestre Azcona (El Bolsón) de la province Río Negro, et Campo Moncada 1 (Valle de Piedra Parada) et Cerro Pintado (Cholila) de la province Chubut. Des microéchantillons représentatifs ont été prélevés des peintures rupestres et du roc sous-jacent afin d étudier les pigments et les accrétions présents. La microanalyse aux rayons X (microscopie électronique á balayage) et la microdiffraction des rayons X ont révelé la présenee de pigments d´ hématite, de lépidocrocite et de terre verte (céladonite ou glauconite) aisni que d'oxalates de calcium (whewellite).

Resumo

O Canadian Conservation Institute fez a analise químico e microscópico das amostras obtidas das pinturas rupestres dos sitios Azcoca (El Bolsón) na provincia de Río Negro e Campo Moncada I (valle de Piedra Parada) e Cerro Pintado (Cholila) na provincia del Chubut. As microamostras foram extraidas das pinturas e do suporte para conhecer a composicao dos pigmentos e dos agregados minerais. A microanalise por raios X (microscopio de barrido elêtronico) revelou a presenta de hematite, lepidocrocite, terra verde (celadonite ou glauconite), e oxalates de calcio (estrutura whewellite).