In order to identify organic substances in patinas taken from old villages and, therefore, to understand the reasons which cause the formation of oxalate, IR and Uv-Vis analyses were carried out.
The results of IR, performed in the range between 4000 and 250 cm^{-1} show for all patinas absorption bands (2925-2910-2820 cm^{-1}) due to the stretching C-H of saturated groups, absorptions (3095-3030 cm^{-1}) typical of the stretching of the oleifinic and aromatic groups C-H, absorption (1660-1610 cm^{-1}) of the stretching C=C.
The Uv-Vis spectra show always the same behaviour: a peak at 280 nm and a broadening at 245 nm.
Basically, the spectrophotometric analyses carried out on organic extracts show evidence of substances of aliphatic nature with chromophores having absorption at 245 and 280 nm, which would imply the presence of double bonds.
The information gathered about the nature of organic compounds in patinas of old villages do not allow an adequate identification of the compound itself. Therefore, considering the results obtained and the need of identifying the compounds, further laboratory researches and analyses are in progress. It should be noted that the eluent can be collected (in fractions corresponding to separated components) and analyzed by other analytical techniques, such as gas chromatography-mass spectrometry, FTIR, and nuclear magnetic resonance. Thus, a clear identification of the single organic components, may be possible.

4. CONCLUSIONS

The results achieved proved that it is possible to use the HPLC technique for the quantitative determination of the content of calcium oxalate in a patina.
The technique makes use an internal standard and extremely low sample amounts (maximum 5-10 mg). Furthermore, it is possible to work at low flow rates and obtain the acid separation in short times (retention time 2.48 minutes). Using both samples taken from various works and samples manufactured in the laboratory, high instrumental sensitivity and good precision of measurements were obtained.

Further researches are in progress for the separation and the identification of the organic components observed in the patinas.

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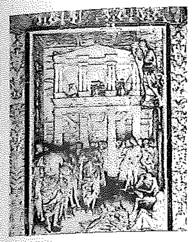

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MICRO-STRATIGRAPHIC ANALYSES OF LAMINATED OXALATE CRUSTS IN NORTHERN AUSTRALIA

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MICRO-STRATIGRAPHIC ANALYSES OF LAMINATED OXALATE CRUSTS IN NORTHERN AUSTRALIA.

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Abstract

Sandstone and limestone walls of rock shelters in northern Australia often contain a fabulous array of prehistoric engravings and red, yellow, white and black paintings that have been painted over, and partly obscured by, thick, dark brown dust and salt encrustations (crusts). Examinations of cross-sections of these strongly cemented brown deposits reveal sequences of finely laminated mineral accumulations consisting of varying proportions of whewellite, gypsum, polyhalite, gorgëyite, whitlockite, kaolinite, quartz, charcoal and other salts and minerals. Preliminary accelerator mass spectrometry radiocarbon age determinations, using carbon in charcoal and in oxalates, show that these naturally deposited oxalate-rich crusts have been forming continuously from terminal Pleistocene times.

Keywords: Rock art; Mineralogy; Dating; Australia.

1. SITE DESCRIPTIONS

1.1

Samples of hard, dark brown rock surface crusts were collected from a sandstone rock shelter in the Kakadu National Park, Northern Territory (Angbangbang), a sandstone shelter near Laura, Queensland (Sandy Creek 2) and from a limestone rock shelter near Chillagoe (Walkunder Arch, Figure 1). These three prehistoric painting and engraving sites, typical of many northern Australian rock shelters with thick gypsum-oxalate rich encrustations[Watchman 1990], are located in a tropical zone where annual average rainfall exceeding 750 mm comes principally in pre-monsoonal storms and torrential rains between December and March (the 'wet' season).

1.2

The aims of this research are to document the mineralogical variations in the crusts as part of a long-term project to examine evidence of palaeo-climatic changes in rock shelters, to establish the time period over which the crusts have formed, to determine the antiquity of remnant prehistoric paintings, and to make comparisons between rock surface data and archaeological material excavated from floor deposits. The specific focus of this paper is to document the inorganic mineralogical variations and to establish the ranges in age of each of the crusts. We have work in progress which is examining the organic components of crusts from the Walkunder Arch site with the view to establishing the source(s) of carbon contained in the oxalate salts.

2. ANALYTICAL METHODS

2.1 *Polished cross sections*

2.1.1

Permission to collect samples was obtained from the respective Aboriginal communities, local land holders and various Government

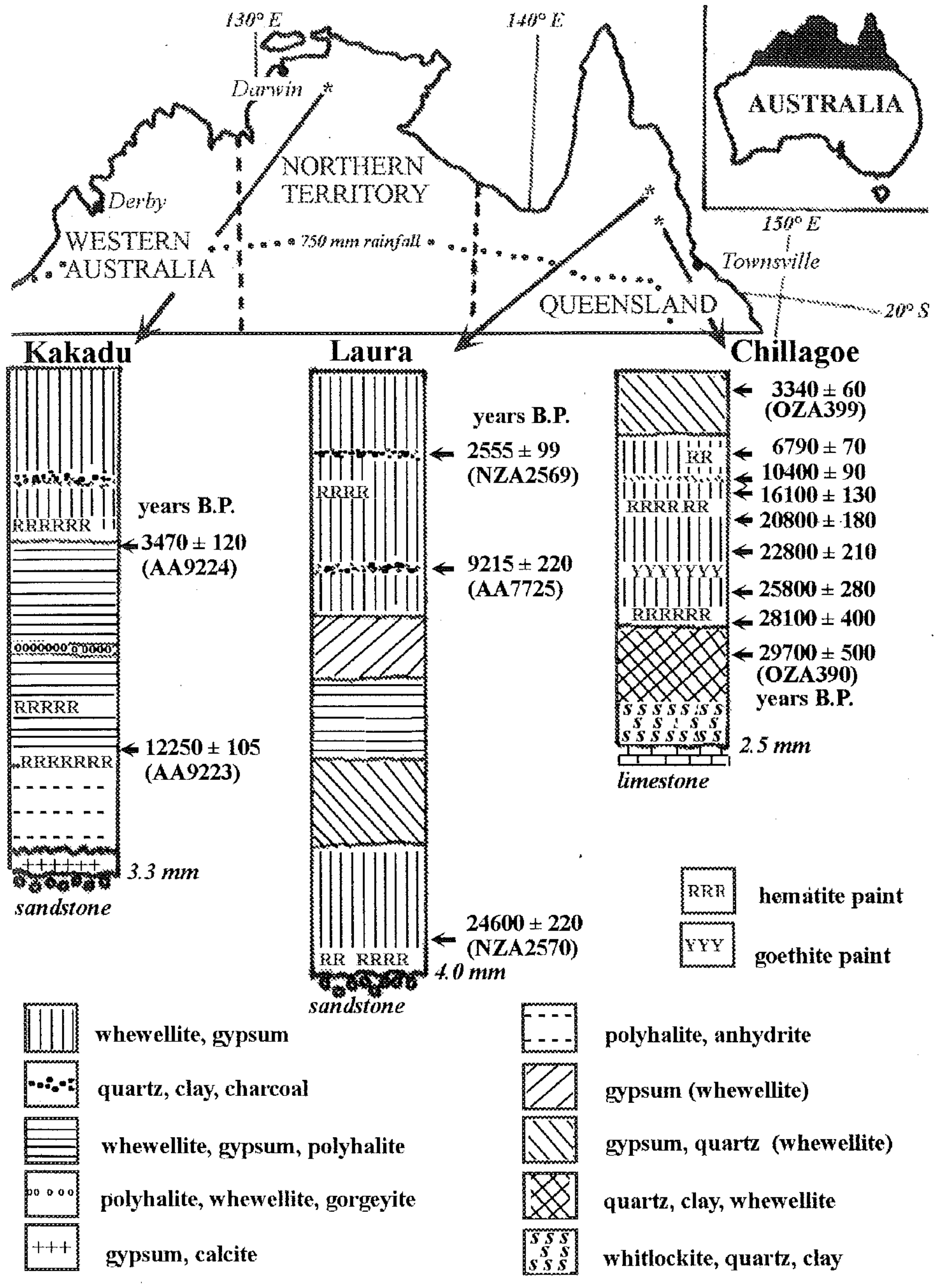

Figure 1 - Summary of the mineralogical sequences and AMS 14C determinations in Kakadu, Laura and Chillagoe crusts.

agencies (Gagudju Aboriginal Co-operative, Australian National Parks and Wildlife Service, Ang-Gnarra Aboriginal Corporation, Queensland Department of Environment and Heritage, Kuku Djangan and Chillagoe Station). Partly detached encrusted flakes were prised from each rock shelter's walls and sub-samples were broken, mounted in rapidly setting epoxy resin, ground flat and polished. Reflected light microscopy was used to observe and photograph sequences of grey, brown, orange, red, yellow and white laminae representing compositional changes in the crusts. Layer thicknesses, evidence of prehistoric painting and post-depositional structural disturbances were recorded before scanning electron microscopy and mineralogical analyses were made.

2.2 *X-ray diffraction (XRD)*

2.2.1
Gandolfi Debye-Scherrer XRD patterns were obtained using a Rigaku RU200-BVHF 12 kW rotating anode generator equipped with a Cobalt target (1.7889 Ka X-rays) and a normal focus filament (0.5 x 10 mm) operated a 45 kV and 160 mA. The CoKb component was eliminated with an iron filter mounted on the incoming beam collimator. Powdered samples, scraped from selected layers in the crusts, were mounted on low background glass plates, and where necessary, mounted on the end of glass fibres with silicone grease and exposed for 2.5 hours under vacuum in a 114.6 mm Gandolfi camera.

2.2.2
Interpretations of the resulting spectra revealed complex mixtures of several salt and mineral phases that varied stratigraphically throughout each crust. Whewellite, gypsum, polyhalite, quartz, kaolinite and whitlockite were the major identifiable phases. Minor phases of anhydrite ($CaSO_4$), gorgëyite ($K_2Ca_5(SO_4)_6.H_2O$), mohrite ($(NH_4)_2Fe(SO_4)_2.6H_2O$), and darapskite ($(Na,K)_3(NO_3)(SO_4).H_2O$) were also found.

2.3 *Fourier transform infrared spectroscopy (FTIR)*

2.3.1
FTIR spectra were obtained using a low pressure diamond micro-sample cell and a Bomen MB-120 spectrometer fitted with a microbeam compartment equivalent to a four times beam condenser and liquid nitrogen cooled wide band mercury-cadmium-telluride detector. A small portion of powder taken from layers using the tip of a scalpel was placed on one face of the diamond cell, and after positioning the second half of the cell on top, the sample was squeezed between the two diamond faces by adjusting the tension on three fastening screws. Transmittance spectra were collected in the 4 000 to 400 cm^{-1} range at a resolution of 4 cm^{-1}. Spectral data were collected by a NEC MultiSync 2A computer loaded with 'Bomem Easy' software, and plotted using a Hewlett-Packard colour plotter.

2.3.2
Spectra obtained were consistent with the findings of the XRD analyses. Absorptions at 1320 cm^{-1} and 1620 cm^{-1}, indicating oxalate, and peaks representing sulphate clearly revealed the presence of whewellite and gypsum. Quartz appeared in every spectrum.

2.4 *Scanning electron microscope energy dispersive X-ray analysis (SEM/EDXA)*

2.4.1
For SEM observations and analyses individual broken and polished sections, and specks of scraped particles from individual laminae were mounted on strips of double-sided sticking tape attached to a 25 mm diameter carbon disc. Au-Pd coated particles were analysed using a JEOL JSM-840A SEM equipped with a beryllium window and energy dispersive X-ray analytical system (Tracor Northern) capable of measuring elements heavier than carbon. Operating conditions were 15kV and 100 μA with uniform working distances of 15 mm.

2.4.2
Energy dispersive spectra obtained from these samples reflected the relative presence of cations and anions associated with the major mineral species in the crusts. The dominant elements included Ca, Si, O, C, S, and Al, with highly variable occurrences of K, Fe, P, Mg, Na and Cl. These results are consistent with the XRD and FTIR mineralogical identifications.

2.5 *Accelerator mass spectrometry radiocarbon dating (AMS ^{14}C)*

2.5.1
Whewellite is considered suitable for ^{14}C dating because once this oxalate salt has precipitated it is highly unlikely that its carbon isotopes are exchanged with atmospheric, diagenetic or geological carbon sources. We have assumed that carbon in oxalate was derived through a pathway involving the uptake of micro-organic carbon, principally from algal sources (ongoing research is examining this assumption).

2.5.2
Powdered samples, weighing about 60 mg and containing whewellite and charcoal, were obtained by progressively grinding successive laminae from about 2 cm^2 of each crust. The powders were combusted in evacuated, sealed glass tubes at 900°C and the resulting carbon dioxide was converted into graphite for accelerator ^{14}C analyses at Tucson, Arizona (AA-numbers), Lower Hutt, New Zealand (NZA-numbers) and Sydney (Australian Nuclear Science and Technology Organisation; OZA-numbers).

3. MICROSTRATIGRAPHIC SEQUENCES

3.1 *Kakadu (Anbangbang site)*

3.1.1
The crust formed on sandstone measures 3.3 mm thick and consists of a variable sequence of finely laminated bands whose compositions can be grouped according to the presence of two or more major characteristic mineral and salt components. These components were identified by combining information obtained using XRD, FTIR and SEM/EDXA analyses. A mineralogical sequence of gypsum-calcite, polyhalite-anhydrite, whewellite-gypsum-polyhalite, and whewellite-gypsum is observed from bottom to top (Figure 1). A thin layer of polyhalite-whewellite-gorgëyite and a narrow band of quartz-clay-charcoal lie between the three main mineralogical zones.

3.1.2
The shift from one set of major salts to another throughout the crust, for example from gypsum-calcite to polyhalite-anhydrite, is thought to represent changes in the composition and rate of evaporation of surface waters. Rock surface salt crystallization is affected by rain water chemistry and the amount of rain splash and spray that fall inside the natural dripline. The most likely source of oxalic acid, and therefore oxalate crystallisation, is considered to be the growth of algal colonies on the periodically damp surfaces [Watchman et al. 1995]. Dry fallout from terrestrial dust, local and regional fires and marine aerosols contribute soluble and insoluble inorganic components that may or may not react with rainwater to form the observed variety of salts [Watchman 1987, 39; Watchman 1991, 29].

3.1.3
Fine laminations in these mineralogical zones are currently interpreted as indicating fluctuations in supplies of salts and minerals, possibly reflecting cyclical climatic extremes that have taken place over centuries and millennia. Resolution of these inorganic variations using closely spaced electron microprobe spot analyses is planned so that geochemical interpretations can be proposed based on fine-scale, rather than general, compositional trends. The distinct band of quartz-clay-charcoal at about 2,500 years ago probably reflects a long period of extreme drought when dust storms and drying winds spread fine quartz, clay and particulate charcoal (from frequent fires) across the landscape.

3.2 *Laura (Sandy Creek 2 site)*

3.2.1
The mineralogical sequence illustrated in Figure 1 is a composite of information obtained from studying the micro-stratigraphy in three cross-sections of crusts formed on sandstone [Watchman 1993a]. Essentially the section comprises whewellite-gypsum near the base, followed sequentially by quartz-gypsum (minor whewellite), whewellite-gypsum (minor polyhalite), gypsum (minor whewellite), and then whewellite-gypsum near the top. Two quartz-clay-charcoal bands in the upper zone of whewellite-gypsum are interpreted as representing extremely dry periods.

3.2.2
Fine scale laminations are less obvious in the Laura cross-section compared with those observed in the Kakadu crust, possibly indicating that although minor fluctuations in site conditions have taken place the regional environmental circumstances have remained relatively constant over 25,000 years. Throughout this long period the regular dampness of the rock shelter has provided suitable conditions favouring whewellite crystallization. Oxalate formation therefore seems to have taken place in a uniformly slow continuous process in association with sulphate formation.

3.3 *Chillagoe (Walkunder Arch site)*

3.3.1
The crust about 2.5 mm thick has developed on a boulder just inside the dripline of this large limestone shelter. Initial deposition on the limestone surface consisted of whitlockite-quartz-clay. The origin of the phosphate mineral whitlockite, ($Ca_3(PO_4)_2$), is unknown, but its dominance in the lower part of the crust indicates a very high phosphate environment at the beginning of crust accretion. A sequence of quartz-clay-whewellite, whewellite-gypsum and gypsum-quartz (with minor whewellite) follows the basal phosphate accumulation. Thin white lenses and laminae consisting primarily of gypsum occur at different depths throughout the crust.

3.3.2
Transitions between these major mineralogical zones is gradual with occasional subtle banding, for example in a layer of quartz-clay-charcoal, near the top of the section. One sub-sample of crust reveals laminated sediments draped across hard basal layers, including red and yellow paint horizons (Plate 17A). The inference made from this break in the depositional record is that part of the crust exfoliated about 18,000 to 20,000 years ago (presumably during the very dry glacial maximum period), with subsequent sedimentation occurring over the angular crustal remnants.

3.3.3
A discernible, though diffuse, dark band consisting of quartz, clay and charcoal particles cemented by gypsum coincides with the Pleistocene-Holocene boundary. Whether this indicates a long period of drought, as interpreted for similar bands in other crusts, requires further study.

4. AGE OF THE ROCK PAINTINGS

4.1 *Kakadu (Anbangbang site)*

4.1.1
The basal layer of red hematite paint in this cross-section was applied to an encrusted rock face before 12,250 ± 105 years ago (AA9223, Figure 1). Two other layers of paint occur at about 10,000 and 3,000 years ago. Paintings observed today on the encrusted surfaces at this site were therefore painted in relatively recent times.

4.1.2
As the crustal components have accumulated at an average rate of 0.2 mm/millennium salts and dust particles began to settle on that stable surface at least 16,500 years ago (assuming that the present thickness represents continuous deposition without erosion or exfoliation).

4.2 *Laura (Sandy Creek 2 site)*

4.2.1
A basal layer of red hematite paint occurs at a stratigraphic position equivalent to the age of an oxalate-rich layer whose carbon was dated at 24,600 ± 220 years BP. (NZA2570). Another red layer, also representing a buried painting, occurs at about 4,000 years ago between two distinct quartz-charcoal-clay horizons dated to 9,215 ± 220 years (AA7725) and 2,555 ± 99 years ago (NZA2569).

4.2.2
Salt and dust particulate components in the crust have accumulated at an average rate of 0.16 mm/millennium. Crust formation therefore started at least 25,000 years ago.

4.3 *Chillagoe (Walkunder Arch site)*

4.3.1
A series of radiocarbon determinations was obtained from oxalate rich laminae, some of which also contained charcoal particles (especially above 0.75 mm depth). The measurements range from 29,700 ± 500 years (OZA390) to 3,340 ± 60 years BP. (OZA399).

4.3.2
Red hematite paint layers occur at 28,100 ± 400 (OZA391), at about 17,000 and 6,000 years ago, and yellow, goethite paint was applied approximately 24,000 years ago (Figure 1). These results are consistent with other rock surface and archaeological dates obtained at this site [Campbell 1982; Campbell and Mardaga-Campbell 1993; Watchman and Hatte in press].

4.3.3
Phosphate salt, quartz and clay began to accumulate as a crust on the sub-vertical faces at this site before 30,000 years ago. The average accumulation rate of crust components is approximately 0.07 mm/millennium.

5. ANALYTICAL AND DATING IMPLICATIONS

5.1 *Correlations between sequences*

5.1.1
Local variations in microclimatic conditions within a rock shelter affect the rate and nature of salt and dust accumulation. Particle settling velocities, extent and degree of surface wetting and rates of evaporation are determined by shelter geometry, orientation to principal rain direction and solar aspects, and to air dynamics. These factors affect the establishment and productivity of micro-organisms that use the periodically damp surfaces as habitats. Variables such as the rock surface moisture level, air and rock surface temperatures, relative humidity and wind currents affect the rates and nature of processes leading to salt formation near the dripline and inside moist rock shelters [Watchman et al. 1995]. Therefore correlations between compositional laminations observed in cross-sections of crusts on different parts of a shelter wall may be severely limited by these site specific factors, a matter which is currently under investigation at Walkunder Arch, Chillagoe.

5.1.2
Nevertheless, the three cross-sectional sequences briefly described here appear to contain laminae indicating micro-and macro compositional changes through time, and these are considered to be correlated with major regional environmental fluctuations, particularly in rainfall and temperature. For example, the quartz-clay-charcoal bands dated to about 2,500 years ago in the Kakadu and Laura sections may correlate with a very thin white gypsum lamination near the surface of the Chillagoe section, and represent deposition during an extremely dry period that affected the whole of northern Australia. Similarly, the polyhalite-whewellite-gorgëyite layer in the Kakadu crust may be equivalent to the quartz-clay-charcoal bands in Laura and Chillagoe crusts formed between 9,000 and 10,000 years ago.

5.1.3

Now that it is possible to measure the radiocarbon ages of carbon-bearing substances, especially oxalate minerals, in individual laminae [Watchman 1993b, Watchman et al. 1993] greater chronological control can be used to detect environmental changes indicated by salt and dust variations.

5.2

The archaeological significance of this work is enormous because carbon-bearing substances (oxalate salts and charcoal particles), associated with rock paintings and engravings can now be dated. The wealth of information about human expressions on rocks can be combined with other archaeological information from the same site, region and time period to greatly improve our understanding of the changes in cultural activities of the rock shelter inhabitants.

6. CONCLUSIONS

6.1

Mineralogical and chemical analyses of major laminations in crusts from different rock shelters indicate that local and regional environmental factors contribute to the observed variations in their inorganic contents. It may be possible to make general regional comparisons between laminae in rock surface crusts, but only after much more detailed work is done to refine observations about the small scale mineralogical fluctuations, and to identify diagnostic compositional traits that can be used for cross-correlations.

6.2

Sources of carbon occurring in oxalate salts and the organic components in the crusts are currently under investigation in a multi-disciplinary research project based at the James Cook University, Townsville.

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PRELIMINARY MONITORING ON PAINTED PLASTERS AND MARBLE SURFACES OF A MINERAL PROTECTIVE TREATMENT BASED ON ARTIFICIALLY FORMED CALCIUM OXALATE

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