Résumé. Sur base des sujets principaux représentant des bateaux, des figurines anthropomorphes et des animaux, l'art rupestre de la vallée du Nil est dans la plupart des cas d'âge préhistorique tardif (période prédynastique) ou d'époque archaïque (vers 4400-2650 av. J.-C.). Bien que diverses propositions aient été émises, peu d'arguments, à l'heure actuelle, ont été avancés pour soutenir l'origine paléolithique d'une partie des représentations rupestres. Les observations de terrain, effectuées sur le site d'El-Hosh en Haute-Égypte, suggèrent un âge paléolithique final pour certaines gravures curvilinéaires, fortement patinées, qui pourraient être interprétées comme des pièces à pêcher lithographiques.


Resumen. Sobre la base de su principal tema (botes, figurines antropomorfas y animales), la mayor parte del arte rupestre del valle en el Alto Nilo Egipto es manifestamente de edad Prehistórico Tardío (Predinástico) o Dinástico temprana (4400-2650 a.C.). Si bien varias sugerencias han sido hechas, pocos argumentos han sido expuestos para apoyar un posible origen Paleolítico de una parte de los dibujos rupestres. Sobre la base de observaciones de campo en el Alto sitio de El-Hosh, esta contribución sugiere un edad Paleolítica tardía para los diseños curvilineos, intensamente patinados, que tentativamente pueden ser identificados como trampas laberinticas para peces.

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EFFECT OF WATER ON LOWER PECOS RIVER ROCK PAINTINGS IN TEXAS

Elmo J. Mawk and Marvin W. Rowe

Abstract. We utilised scanning electron microscopy to investigate the physico-chemical changes that occur to rock painting surfaces following application of water. Dissolution effects are visible microscopically; gypsum is selectively removed, leaving the less soluble whewellite and possibly calcite relatively enriched on the remaining surface. It is not known how these changes affect long-term (>100 year) survivability of rock paintings during natural exposure, but anecdotal evidence indicates that subtle effects, not dramatic ones, are seen over a fifty-year time span.

Introduction

Natural mineral accretions slowly accumulate on rock surfaces and on top of rock paintings after they are painted. In the Lower Pecos River region of Texas, the mineralogy of this accretionary matter has been extensively studied (Zolensky 1982; Silver 1985; Russ et al. 1994; Hyman et al. 1996). Lower Pecos River area accretions are comprised primarily of whewellite (calcium oxalate, CaC$_2$O$_4$$\cdot$H$_2$O), with calcite (calcium carbonate, CaCO$_3$) and gypsum (hydrated calcium sulphate, CaSO$_4$$\cdot$2H$_2$O) to a lesser degree. Treating rock paintings with water, both to enhance photographic images and as a restoration practice through the application of water to absorbent paper placed over rock paintings (poultices), has been practiced in the past and may continue to the present. Stigma is now associated with the use of water to aid photography. We examined physical and chemical effects that occur with the wetting process.

Lower Pecos River region, Texas. The study area is in Seminole Canyon in the Lower Pecos River region of Texas (see Figure 1 in Hyman et al. 1996). Pre-Historic people have occupied the region beginning approximately 10,500 years ago, as shown by the archaeological occupational record (Hester 1988: 54-5; Turpin 1991), and were still living in the area at the time of European contact, as evidenced by the appearance of European influences in the rock art: e.g. churches, horses, European style dress (Jackson 1938: 227-8; Kirkland and Newcomb 1967: 104-5). However, no extant group has claimed this region as its homeland. The surface geology is dominated by Cretaceous limestone that has been eroded into numerous deep, narrow drainage canyons. The down-cutting is the result of drainage of three rivers, the Pecos, Devils and Rio Grande, and their tributary systems. Because of the variable density and solubility of the limestone walls of these canyons, countless solution cavities, overhangs and rockshelters were formed.

Rock art. These rockshelters provided protection for some of the most extensive rock art in North America (Jackson 1938; Kirkland and Newcomb 1967; Turpin 1982, 1984, 1986a, 1986b; Zintgraff and Turpin 1991). The Lower Pecos River area rock art seems to have been created in near isolation from other Pre-Historic cultures elsewhere in the Northern Hemisphere of the New World during any given time period. One genre of rock paintings from the Lower Pecos River region of Texas, 'Red Monochrome', is characterised by large, roughly life-sized, mostly red coloured anthropomorphous and zoomorphic figures. Dissimilarity between this genre and the older Pecos River genre led archaeologists to suggest that the Red Monochrome painters were newcomers into the region, unrelated to its former inhabitants (Kirkland and Newcomb 1968; Turpin 1986a). One Red Monochrome composite image with lizard-like features was dated by Ilger et al. (1996) at 1125 ± 85 radiocarbon years before present (BP); it showed some similarity with figures in the Four Corners region of Arizona, Colorado, New Mexico and Utah made during the Pueblo I period (A.D. 700-900; Schaufmacher 1980; Cole 1990), supporting the earlier contention of movement of the 'Red Monochrome people' from another area into the Lower Pecos River region. One sample of another rock painting genre, 'Red Linear', primarily tiny dark-red stick figures, usually <10 cm high, was dated by Ilger et al. (1996) at very nearly the same age, 1280 ± 135 years BP. The polychrome (shades of red, black, orange, yellow and white) Pecos River genre is the oldest in the region, having been dated at about 2750 to
4200 years BP (Hyman and Rowe 1997, and references therein from our laboratory). We chose a sample of the Pecos River genre for this study. Figure 1 shows a characteristic Pecos River genre rock painting, a composite anthropomorphic/zoomorphic figure between two panthers.

Shelter 41VV75 was chosen for sample collection because severe natural exfoliation has already occurred to the extent that less than half of most rock paintings at the site still remain on the wall. Because of the deterioration at that site, Turpin (1982) suggested that it as an ideal one for sampling for research studies. The shelter is situated in the Seminole Canyon State Historic Park about 50 km north-west of Del Rio, Texas, near the confluences of the Pecos, Devils and Rio Grande rivers. The area is the home of more than 250 rock art sites, almost exclusively rock paintings, some of larger-than-life-sized composite and abstract figures.

**Experimental procedure**

To examine the physico-chemical effect brought about by contact of water with the surface of a rock painting, we immersed half of a 5 mm-sized rock painting sample in distilled water for 30 minutes under ultrasonication. The half immediately adjacent to the water-soaked one was left dry to serve as a control. We have sometimes seen rock painting samples brightened considerably by such rinsing in water as a preliminary treatment before subjecting the sample to plasma-chemical treatment prior to accelerator mass spectrometric radiocarbon dating. In the sample studied here, however, we could ascertain no macroscopic visual difference between the water-treated and the dry halves due to rinsing in water. But we also examined the changes that occurred using scanning electron microscopy (SEM). The instrument used, under management of the Texas A&M University Electron Microscopy Center, is a JEOL JSM-6400 scanning electron microscope that is equipped with the capability of energy dispersive x-ray spectroscopy (EDS). A selected microscopic region of the sample can be analysed for major and minor element composition, and from that, mineral constituents often ascertained.

For visually observing the surfaces of rock paintings, SEM has considerable advantage over light microscopy in that: (1) the depth of field is much greater in SEM than in light microscopy and; (2) qualitative chemical analyses are possible using SEM-EDS. The former is important because of the roughness of a typical rock painting surface in the Lower Pecos River region, an example of which is shown in Figure 2.

**Results and discussion**

The formation of a botryoidal accretionary surface makes the surfaces rough as shown in the scanning electron micrographs of Figure 2. The effect of applying water to such a sample is not striking at the multiplication shown in the SEM photograph in Figure
2. However, a distinct change in appearance of the water-treated surface is seen at higher magnification. For example, the SEM photographic montage shown in Figure 3A-F demonstrates that effect. After the rock painting was immersed in water, the surfaces are much more highly crystalline (Figure 3A-D) than the unmoistened control sample (Figure 3E-F), as photomicrographs of the control sample at similar magnification show. Clearly, there is a substantial change in the physico-chemical nature of the rock painting surfaces after water treatment.

The change that would be predicted when a rock painting surface in the Lower Pecos River region is drenched with water is that gypsum, CaSO₄·2H₂O, present in the accretion layer, would dissolve selectively over the whewellite and calcite constituents. Calcium sulphate is roughly 100 times more soluble in pure water than calcium oxalate or calcium carbonate. Thus, we would expect to see considerably more gypsum in the untreated sample of the rock painting compared to the sample that was soaked in water. That was confirmed by SEM-EDS analysis, where the dry control sample showed significant peaks due to calcium and sulphur, indicative of the presence of gypsum. However, after water treatment, no x-ray peaks were seen for sulphur, indicating selective removal of gypsum. Isolated microcrystals of gypsum were still present on the water-treated sample, but were so rare that they had negligible effect on the overall elemental analysis.

Although physico-chemical change was apparent, the effect of that change on the stability of rock painting surfaces is not so adverse processes such as the freeze-thaw cycle that results in spallation, is more difficult to fathom. There is little evidence from which to infer what the effect of the selective dissolution of the gypsum will be over the long term. Three effects of water treatment, two acting in opposition to the third, can be surmised.

(1) Dust may be removed from the rock painting surface resulting in a brighter painted surface. That is one of the purposes of water poultice treatment in restoration attempts.

(2) A rock painting may be more clearly visible after water treatment due to removal of the translucent gypsum. However, the whewellite and calcite will remain largely unaffected, so the overall effect may not always be discernible — as it was not in the sample studied here. We have found that the visual aspect varies among individual samples; some are noticeably improved, some are not.

(3) Furthermore, whewellite accumulation may be enhanced in the long term by the treatment.

If whewellite accumulation is controlled by bacterial growth, it is conceivable that enhanced whewellite deposition may occur if latent bacteria flourish due to the increased moisture. Since water will evaporate normally in a matter of minutes from a natural rock surface in the arid Lower Pecos River region, we expect that effect will not be important. There are fifty years or more of anecdotal evidence in SW Texas that suggests negligible short-term effect on the rock paintings that were once sprayed with water for photographic enhancement. Many rock paintings moistened for photography are still visually indistinguishable from their photographs taken many years ago. Certainly possible deleterious effects of wetting rock paintings must therefore be subtle, rather than drastic; otherwise dramatic effects would have been noticed from the past practice of wetting for photographic purposes. We support the policy of not wetting rock paintings for photographic purposes, but further research is necessary to determine with certainty whether the changes associated with water treatment, whether from natural precipitation or by human application, are detrimental or beneficial to the long-term conservation of the visual artefacts.

We realise that the experiment reported here is not an accurate representation of what occurs when water is sprayed on a rock painting for enhanced photography,
Figure 3. SEM photographs of four areas on the water-treated rock painting sample (the top four panels of this figure) and the two from the unmoistened control rock painting (the bottom two panels). Notice that the water-treated sample is much more highly crystalline than the dry control.

or when water is applied to an absorbent sheet of paper for restoration, or even during a typical rainfall. In the first case, even if gypsum were initially dissolved preferentially, it would redeposit upon drying. How this recrystallisation would affect the paintings can only be hypothesised. Our experimental situation is closer to the paper/water poultice application. There it may be expected that when gypsum preferentially dissolves, it will then be absorbed onto the paper and thus removed. Rainfall would be similar to our experiment only for the case of heavy direct rains, where the dissolved gypsum would be washed away. Furthermore, these results cannot be extrapolated from one region to another. The effect of the water is dependent on the micro-geochemistry of the rock painting surface. The Lower Pecos River region is an arid limestone region with paintings on walls of open shelters and exposed canyon walls. Similar geochemical areas will likely yield results like those reported here; but different areas (e.g. sandstone formations) will not.
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Résumé. Nous avons utilisé l’ultramicroscopie pour examiner les changements physico-chimiques qui ont lieu sur la surface des peintures rupestres après l’application d’eau. Les effets de la dissolution sont visibles au microscope; le gypse est extrait sélectivement pour laisser sur la surface qui reste un dépôt relativement enrichi de wheewellite moins soluble et peut-être de calcite. Nous ne savons pas la manière dont ces changements affectent la survivance à long terme (>100 ans) des peintures rupestres durant une exposition naturelle, cependant l’évidence anecdotique indique que des effets stratégiques, plutôt que dramatiques, sont observés sur une période de cinquante années.

Zusammenfassung. Ein Elektronenmikroskop wurde verwendet, die physikalisch-chemischen Veränderungen zu untersuchen, die stattfinden, wenn Wasser auf die Oberflächen von Felsmalerien aufgetragen wird. Auflösungswirkungen sind mikroskopisch sichtbar; Gips wird selektiv gelöst, was den weniger löslichen Wheewellite und möglicherweise Kalzit relativ angereichert an der verbleibenden Oberfläche zurücklässt. Es ist nicht bekannt, wie diese Veränderungen die langfristigen (>100 Jahre) Überlebensfähigkeit der Felsmalerien unter natürlicher Aussetzung beeinflussen, doch anekdotische Evidenz deutet an, daß schwer merkbare eher als auffällende Effekte über einen Zeitraum von fünfzig Jahren zu sehen sind.

Resumen. Hemos utilizado el escudriñamiento de electrones por microscopía para investigar los cambios fisico-químicos que se producen en las superficies con pinturas rupestres después de la aplicación de agua. Efectos de disolución son visibles al microscopio; el yeso es selectivamente removido dejando el menos soluble oxalato de calcio (Wheewellite) y probablemente calcita relativamente enriquecida en la superficie que queda. No se sabe cómo estos cambios afectan la supervivencia a largo plazo (>100 años) de las pinturas rupestres durante la exposición natural, pero evidencia anecdótica indica que efectos sutiles, no dramáticos, son observados en lapsos mayores a los cincuenta años.

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