First paleoenvironmental interpretation of a pre-Quaternary rock-varnish site, Davidson Canyon, southern Arizona

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ABSTRACT

Dark, manganese-rich rock varnish of probable Miocene age is exhumed in a road cut in the drainage of Davidson Canyon, southern Arizona. Its structure and inorganic chemistry is similar to modern arid and semiarid rock varnishes. The δ^{13}C content of organic matter in the varnish is consistent with a C_4 photosynthetic pathway for adjacent plants. Organic and inorganic chemical analyses of paleovarnishes can be used to interpret past subaerial environments.

INTRODUCTION

Rock varnish is a dark coating found on rocks in virtually every terrestrial weathering environment, from deserts to the high alpine, to point bars in humid-continental climates, even to soil peds in the Olympic Peninsula of Washington (Dorn and Oberlander, 1982). It is most common in arid and semiarid lands, in part because both the rock surfaces and the varnishes are most stable in arid nonacidic conditions. Quaternary varnish has a variable composition, from about 40% to 70% clay minerals, 10% to 40% manganese and iron oxides, and more than 30 minor and trace elements (Potter and Rossman, 1977, 1979; Dorn and Oberlander, 1982; Duerden et al., 1986); the manganese, and possibly the iron, is concentrated by bacteria (Dorn and Oberlander, 1981, 1982; Krumbein and Jens, 1981; Palmer et al., 1985). This study presents the first quantitative microchemical analyses of pre-Quaternary paleovarnish. These analyses are used to infer paleoenvironmental conditions associated with a Miocene paleosurface.

Fossil varnishes have been observed in Cenozoic, Mesozoic, and Precambrian geologic deposits. Paleovarnish from beneath a mudflow in Death Valley, California, has been radiocarbon dated to be about 11,000 yr B.P. by accelerator mass spectrometry, and it has a chemistry similar to adjacent subaerial varnishes (Dorn, 1988). Manganese-iron varnish has been observed in Triassic desert deposits of the Budleigh Salterton Pebble Beds (Green, 1985). Manganese-iron crusts have been found associated with a 2200 Ma paleosol that could be analogous to modern rock varnish (Retallack, 1986a, 1986b); it is possible that the Early Proterozoic microfossil *Eoastrion* spp. could have been involved in its development, because *Eoastrion* is similar in morphology to contemporary manganese-oxidizing budding bacteria (Barghoorn, 1977; Schopf et al., 1984) that are involved in the formation of modern varnish (Dorn and Oberlander, 1982).

Fossil rock varnishes are relatively rare. Preservation requires both mechanical and biogeochemical stability. The abrasion hardness of rock varnish is ≤4½ on Mohs scale (Dorn and Oberlander, 1982), and virtually any sustained mechanical abrasion will remove varnish. Because the manganese and iron in varnish are reduced and mobilized under acidic conditions, sustained low pH in vadose water will dissolve varnish. Preservation requires a low-energy depositional process for the material burying the varnish and nonacidic conditions after deposition.

STUDY SITE

Fresh samples of paleovarnish preserved on clasts of Miocene rubbly colluvium were collected from a steep roadcut on the interfluve between Davidson and Barrel canyons about 50 km southeast of Tucson (Fig. 1). The varnished colluvial layer (Fig. 2) mantles a buried paleosurface formed during Miocene erosion of the mid-Tertiary Pantano Formation, which is a local red-bed sequence of alluvial-fan, braidplain, and associated lacustrine deposits (Balcer, 1984). Intercalated volcanics have yielded late Oligocene K-Ar ages (n = 6) of 25–30 Ma (Dickinson and Shafiqullah, 1989). Prior to mid-Miocene time, Pantano strata were broken into multiple tilt blocks with dips of 20°–40° by extensional deformation associated with tectonic denudation of the nearby Catalina core complex. The colluvium that is coated with black varnish is a thin lag derived from conglomeratic Pantano beds.

The varnished colluvial horizon is overlain depositionally by gently dipping and weakly consolidated sandy gravel deposits whose pale gray to buff color contrasts strongly with the dark brown to red conglomeratic strata of the underlying Pantano Formation. The younger fluvial gravels onlapped a paleoslope developed by prior erosion of the more strongly deformed Pantano Formation (Fig. 2). The overlying gravels are laterally contiguous with the Neogene basin fill of Sonoita Valley to the south, and they are exposed where modern headward

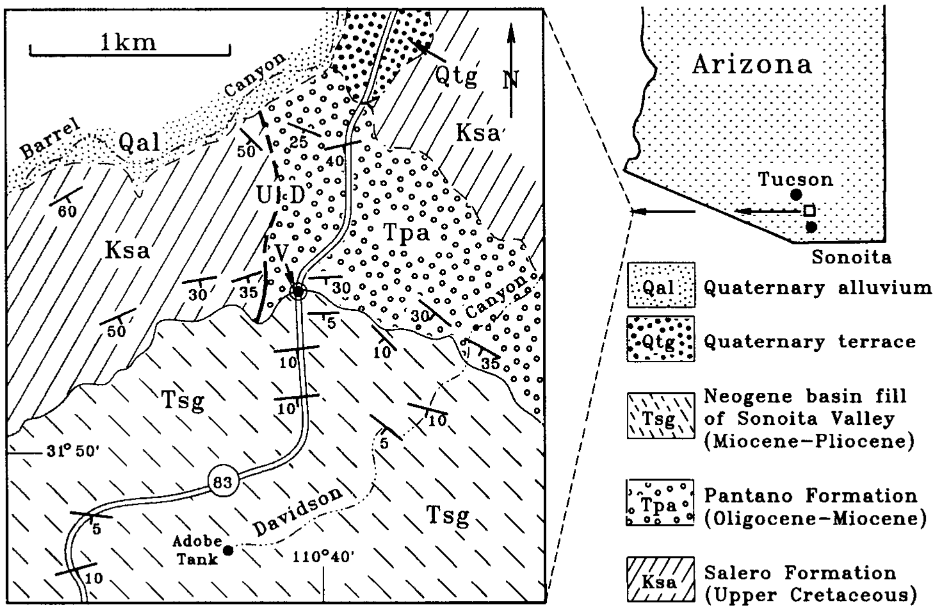

Figure 1. Geologic sketch map of area surrounding Miocene fossil varnish locality (V) along State Highway 83 in SE¼NW¼ sec. 27, T. 18 S., R. 16 E., Empire Ranch quadrangle, Pima County, Arizona. Modified after Finnell (1971). Alluvium shown only along wash floor of Barrel Canyon.

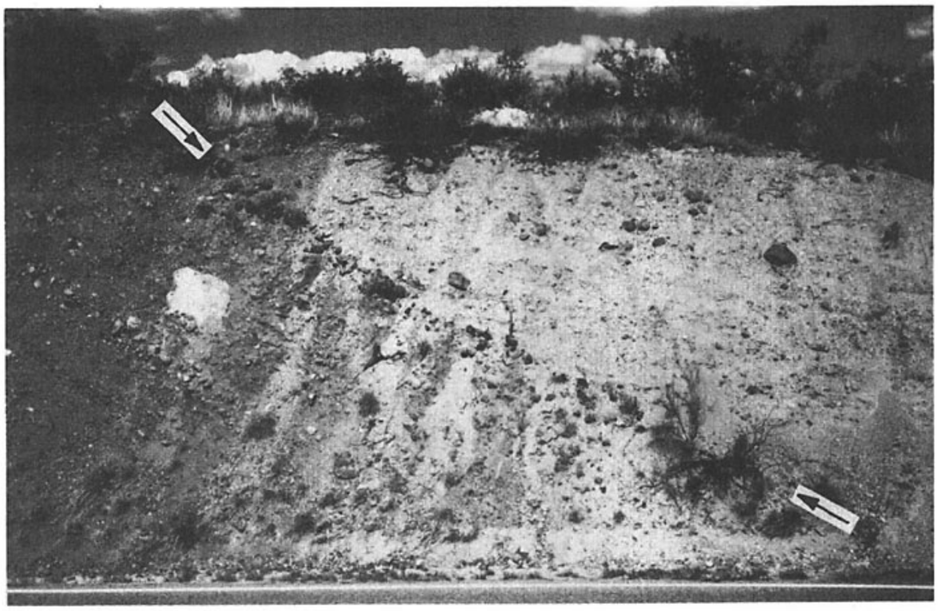

Figure 2. View east of roadcut outcrop at study locality (V in Fig. 1) showing Miocene paleovarnish horizon (arrows mark either end of horizon) mantling erosional paleosurface developed on tilted upper Oligocene to lower Miocene(?) alluvial strata of Pantano Formation (dark beds on left dipping 30° to right; note large pale clast); varnished clasts are overlain by upper Miocene(?) to Pliocene basin-fill gravel deposits of Sonoita Valley (pale beds on right dipping 5° to right). Head of rock hammer in center rests on paleovarnish horizon.

erosion of Davidson and Barrel canyons has truncated the northern edge of th basin fill. Magnetostratigraphic studies 12–15 km to the south indicate that the undeformed basin fill near Sonoita ranges from late Miocene to late Pliocene in age (Menges and McFadden, 1981). Thus, the paleovarnish we sampled is of approximately mid-Miocene age, but stratigraphic data do not allow a more precise age assignment.

PALEOVARNISH ANALYSIS

The structure and inorganic chemistry of the Davidson Canyon Miocene fossil varnish is similar to semiarid and arid rock varnishes observed elsewhere. Figure 3 illustrates that structures of the Davidson Canyon varnish are similar to structures found in contemporary rock varnishes. The bulk chemistry of the Davidson Canyon varnish is also similar to contemporary arid varnishes (Table 1).

Microchemical laminations of alternating Mn-rich and Mn-poor layers are found in contemporary varnishes (Perry and Adams, 1978; Dorn, 1984, 1989). When local environmental effects are avoided in sampling, these laminations reflect regional fluctuations between alkaline and less alkaline conditions (Dorn, 1989). The Davidson Canyon varnish also contains microchemical laminations. Figure 4 illustrates alternating dark and light bands of varnish on the rock; the dark bands are enriched in manganese, and the light bands are poor in manganese. Many of the Davidson Canyon varnishes observed in thin sections and by scanning electron microscopy had continuous and uneroded microchemical laminations. These fluctuations probably record changes in the alkalinity of the environment, reflecting alternating arid and less arid environments as the varnish was being deposited (cf. Dorn, 1989). However, the limited exposure of the paleovarnish at Davidson Canyon did not permit the normal tests of reproducibility from outcrop to outcrop that are required to assure that the microchemical laminations do not record primarily local environmental changes (cf. Dragovich, 1988; Dorn, 1989).

TABLE 1. CHEMISTRY OF SELECTED ROCK VARNISHES

Element	Alibates	Timna	Trail Canyon	Davidson Canyon
Mg	0.26	1.23	0.14	0.31
Al	27.91	20.93	23.74	25.14
Si	38.56	42.36	39.09	43.79
P	bld	0.26	0.49	0.11
S	bld	0.40	0.70	0.60
K	2.53	2.00	3.45	2.88
Ca	6.76	5.29	4.87	3.35
Ti	2.10	1.62	1.52	1.23
Mn	10.70	9.01	10.87	12.39
Fe	8.90	14.17	13.47	8.45
Ni	0.24	bld	0.13	bld
Cu	0.30	0.36	0.12	0.26
Zn	0.21	bld	0.27	bld
Rb	bld	0.22	bld	bld
Zr	bld	0.12	0.29	bld
Ba	1.53	1.40	0.85	0.29
Pb	bld	0.63	bld	1.20

Note: Davidson Canyon, Arizona, is paleovarnish site; Alibates National Monument (Texas), Timna (Negev Desert, Israel), and Trail Canyon (Death Valley California, alluvial fan) are desert sites. bld = below limit of detection.

* Analyses by PIXE (Cahill et al., 1984); results are normalized to 100% by weight.

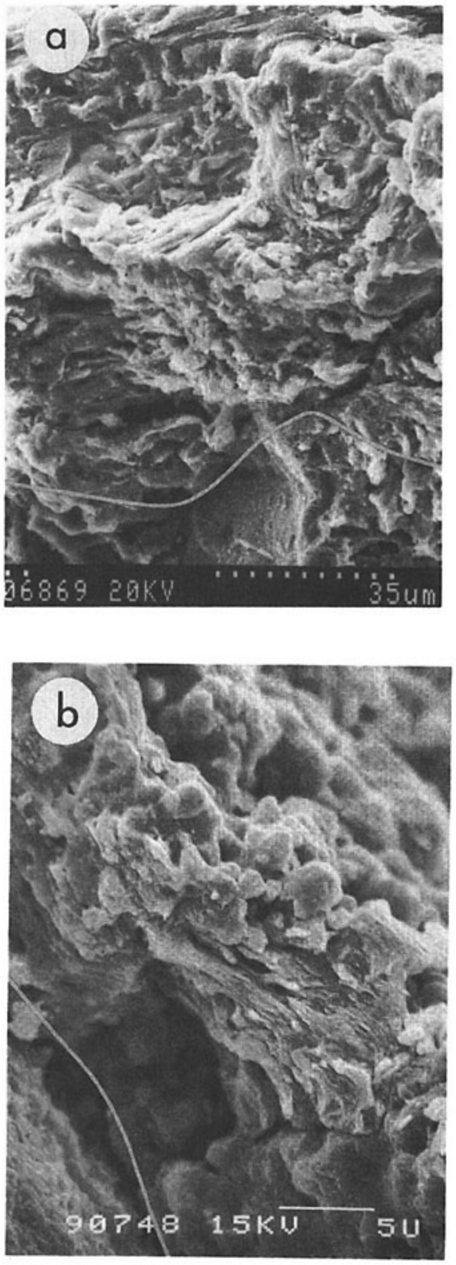

Figure 3. Representative cross section of Davidson Canyon paleovarnish (a) compared to cross section of contemporary varnish collected from base of Kitt Peak, Arizona (b). Both have lamellate subsurface structures of subparallel platelets of clay minerals and oxides, but Kitt Peak varnish (b) also has rounded botryoidal forms. Lines indicate varnish-rock contact. Length of scale dots in a is 35 μm, and line in b is 5 μm.

The stable carbon isotope composition of organic matter incorporated into Davidson Canyon varnish is consistent with a C_4 photosynthetic pathway for some of the surrounding plants during the Miocene. The varnish was treated chemically to concentrate stable organic matter, as described by Dorn and DeNiro (1985). Values of $\delta^{13}C$ from three different samples yielded similar results: $-16.5^0/_{00}$, $-17.4^0/_{00}$, and $-18.0^0/_{00}$. C_3 plants supply or-

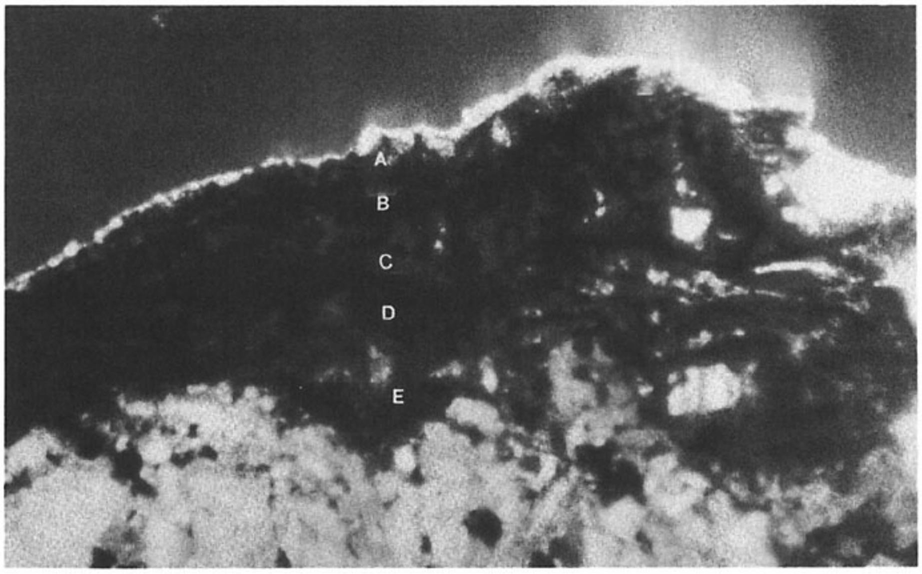

Figure 4. Ultrathin section of Davidson Canyon paleovarnish (darker) on underlying rock (lighter). Thickness of varnish ranges from 30 to 60 μm. Mn:Fe ratios (determined by electron microprobe) are 0.41 at A, 1.84 at B, 0.20 at C, 3.46 at D, and 0.77 at E.

ganic matter to Holocene varnishes with $\delta^{13}C$ values of about $-23^0/_{00}$, whereas C_4 plants have less negative values. The Davidson Canyon varnish measurements probably reflect the fallout of organic detritus from plants that have both C_3 and C_4 photosynthetic pathways (Dorn and DeNiro, 1985). Thomasson et al. (1986) reported a Miocene fossil grass with a Kranz leaf anatomy which indicates that C_4 photosynthesis did occur in the Miocene. The presence of Miocene plants at Davidson Canyon with a C_4 photosynthetic pathway is consistent with the microchemical laminations, indicating varnish deposition during arid and semiarid times.

It is unlikely that the organic matter analyzed was from exchangeable sources. Accelerator mass spectrometry radiocarbon dating of the same material analyzed for stable carbon isotopes yielded an age for the paleovarnish of >43,000 yr B.P. (Dorn et al., 1989). If the organic matter extracted was from exchangeable sites, even a small amount of contamination by younger organic matter would have produced a finite radiocarbon age.

DISCUSSION

These results are significant not only because they provide the first detailed analysis of pre-Quaternary rock varnish, but also because they illustrate that paleovarnish can be used as an indicator of past subaerial environments in sedimentary deposits. Paleoenvironmental data are essential in reconstructing the history of Earth. Stable carbon isotope measurements of varnish organic matter can yield insight into past depositional environments. Inorganic geochemical analyses can be used to indicate the presence of environmental fluctuations from arid to semiarid conditions. In Davidson Canyon, the Miocene environment fluctuated between semiarid and more arid conditions during the stabilization of the fossil slope and the development of the varnish.

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