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*Progress in Physical Geography* 1982 6: 317  
DOI: 10.1177/030913338200600301

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# Rock varnish

by Ronald I. Dorn and Theodore M. Oberlander

Because of its wide distribution, the dark stain known as desert varnish, which covers rock surfaces in arid regions, has intriguing potential as a research tool in diverse fields of investigation. Dark coatings on rock surfaces can be seen in nearly all environments, but are most conspicuous in arid regions where coarse rock debris and solid rock outcrops dominate the landscape. The mode of origin of the coating and the enormous enhancement of manganese in it as compared with ambient levels have been topics of controversy for more than 100 years. More recently, there has been concern regarding the influence of desert varnish on the remote sensing of arid lands (e.g. Warner and El-Baz, 1978; Perry, 1979; Elvidge and Collet, 1981).

Desert varnish is the arid phase of a wider phenomenon that we have termed 'rock varnish' (Dorn and Oberlander, 1980; Dorn, 1980). Rock varnish is usually 10 to 30 microns thick, but we have observed varnish depths ranging from under two to over 500 microns. The constituents of all rock varnishes are derived from sources external to the underlying rock. Varnish is composed of clay minerals, oxides and hydroxides of manganese and/or iron, detrital particles such as  $\text{SiO}_2$  and  $\text{CaCO}_3$ , and trace elements, among which Mg, Ca, K, Na, Ti, and Cu are most notable. The classic rock varnish, frequently described in the literature on arid landscapes, is a manganese-rich black coating on rocks, but orange to dusky-brown varnishes are also widespread. Iron and manganese are the distinctive elements of rock varnish. Weathering rinds and encrustations of calcium carbonate, sulphate, and other salts are regarded as distinct from the phenomenon of rock varnish.

The degree of development of rock varnish has long been used by archaeologists to estimate the relative ages of stone artifacts and prehistoric rock inscriptions. Similarly, the relative development of varnish in arid regions has been used by geomorphologists to differentiate and correlate surface deposits of alluvium, talus, and eolian sand, as well as erosional features such as cliff faces and relict lake shorelines of varying ages. It has long been hoped that some characteristic of varnish might be used to establish absolute chronologies that could be used in both geomorphological and archaeological research. Wide variations in its chemical composition suggest that rock varnish could also be used as a geochemical prospecting tool. Finally, changes in chemical composition and micromorphology through the

depth of a varnish layer may be an index of the history of environmental fluctuations at a location. This paper discusses the intriguing potential of rock varnish both as an indicator of environmental changes through time, and as a chronological tool. However, an understanding of the origin of varnish films is a prerequisite for using them as a paleoenvironmental research tool.

## I Early research on rock varnish

The initial theories concerning the origin of iron-manganese films that cover rocks in various environments were evolved before the end of the last century. These ideas range from such long-discarded hypotheses as that explaining the films as iron and manganese salts desposited in a receding shallow (Loew, 1876), to the theories that have continued to attract adherents, including arrival on the surface of airborne dust containing iron and manganese, and derivation from the underlying 'heartrock' by internal decomposition and capillary rise of solutes to the rock surface where they are precipitated by evaporation (Walther, 1891). Early work often stressed the supposed effect of high desert temperatures in 'sweating' solutions from the interior of the rock, and drying of these solutions to form a resistant lacquer (e.g. Linck, 1900). Certain early investigators objected that varnished rocks did not contain adequate manganese to supply varnish by outward migration (White, 1924), but their arguments were — and continue to be — ignored by many commentators. Suggestions of an organic origin for varnish films came early, but until very recently have never been developed in detail. Francis (1921) attributed 'desert varnish' found along stream channels to algal activity, implying an external supply of iron and manganese. Recognizing the lack of a manganese source in many varnished rocks, Hume (1925) argued for a groundwater origin, with the varnish constituents brought to the surface by capillary action; and White (1924) proposed that airborne organic debris, especially pollen, may contain the constituents of desert varnish. Various early investigators noted iron-manganese coatings in such dissimilar locales as rainforests in Australia, South America, and Africa; the deserts of North America, North Africa, and Australia; and exposed rocks in various rivers. Even with limited analytical tools, these workers were able to establish the essential elements of varnish films.

Engel and Sharp (1958) were the first to quantify the enormous enrichment of manganese and to a lesser extent iron in varnish as compared to the 'heartrock', which many observers continue to cite as a probable source of varnish constituents (Peel, 1960; Opdyke, 1961; Marshall, 1962; Tricart and Cailleaux, 1964; Wilhelmy, 1964; Holmes, 1965; Wyckoff, 1966; Birot, 1968; Smith, 1968). Subsequently, Hooke *et al.* (1969) analysed varnish with an electron microprobe, revealing layering within varnish and defining the relative quantities of elements at various depths within varnish films. This study brought varnish research to a temporary plateau, from which renewed advances have occurred only in the past few years. Recent progress in varnish investigation has resulted from application of new instrumentation and the persistence of several questions left unanswered by the work of Engel and Sharp and Hooke *et al.*

*a The varnish substrate:* The simplest point of confusion concerns the nature of the substrate on which varnish forms. The origin of varnish by leaching from the heartrock has continued to be accepted by many observers (e.g. Glennie, 1970; Ugolini, 1970; Evenari *et al.*, 1971; Abu Al-Izz, 1971; Garner, 1974; Goudie and Wilkinson, 1977; Shlemon, 1978; Grant, 1978; Meyer, 1978; Besler, 1979; Krumbein and Jens, 1981). Some have insisted that varnish cannot develop on any rock not containing iron (Scheffer *et al.*, 1963). Carbonate rocks have often been excluded as a varnish substrate for this reason, as well as due to their solubility (Blackwelder, 1948; Hunt, 1954; Engel and Sharp, 1958; Hooke *et al.*, 1969; Cooke and Warren, 1973). However, we have observed varnish on all stable substrates, including limestone and smooth, colourless chalcedony and quartzite. Desert varnish in its classic lustrous form is not commonly found on weathered granite, marly sandstone, and unsilicified limestone, because the time usually required for desert varnish formation often exceeds that over which the surfaces of these materials remain stable.

*b Varnish sheen:* A conspicuous characteristic of much black desert varnish is its sheen. This has been attributed to dust polishing (Hunt, 1954; Grant *et al.*, 1968; Garner, 1974; Goudie and Wilkinson, 1977), to sand blasting (Blake, 1858; Begole, 1973), to a thin coating of goethite (Kelly, 1956), to the metabolic products of cyanobacteria (Scheffer *et al.*, 1963), and to a lamellate varnish micro-morphology (Krumbein, 1969, 353). Thus even one of the simplest and most obvious qualities of varnish seems to have eluded explanation.

*c Uniqueness of desert varnish:* The uniqueness of the varnish developed in deserts has been a point of disagreement. Some observers have held that desert varnish is distinct from other iron-manganese films (Blackwelder, 1954; Peel, 1960; Daveau, 1966; Allen, 1978), while others have observed that rock varnishing occurs in many environments but is best developed in deserts and deserves the name 'desert varnish' (Hunt, 1954; Engel and Sharp, 1958; Hunt, 1972). Nevertheless, 'desert varnish' has been noted by multiple observers in alpine, arctic and antarctic, riverine, littoral, lacustrine, and other humid environments. An extremely extensive literature on manganese-iron coatings on rock surfaces in non-arid environments exists (e.g. proglacial sediments — Koljonen *et al.*, 1976; streams — Carpenter and Hayes, 1978; caves — Moore, 1981; bog ores — Carlson *et al.*, 1978; soils — Ha-mung, 1968; fracture zones — Weaver, 1978; ores — Ostwald, 1981; fossil deposits — Crerar *et al.*, 1980; lacustrine environments — Dubinina, 1980; springs — Mustoe, 1981; and dendrites — Billy and Cailleaux, 1968).

*d Climatic requirement for varnish:* The climatic requirements for varnish formation are clearly associated with the foregoing question. The optimum conditions for varnish development have been asserted to be less than 4 inches (10 cm) of precipitation and some specific temperature following surface wetting (Engel and Sharp,

1958); dust storms followed by rainfall and high subsequent temperature (Grant *et al.*, 1968) and alkaline surface conditions (Elvidge, 1979); frequent moistening in a desert context, thus pluvial conditions (Passarge, 1955; Hunt and Mabey, 1966; Tricart and Cailleaux, 1964; Capot-Rey, 1965); and altithermal climates for manganese-rich black varnishes (Glennie, 1970, 19; Hayden, 1976; Allen, 1978; Elvidge, 1979). Varnish has been asserted to be forming at present on the Egyptian pyramids (Iskander, 1952), and in most of the world's deserts (Mojave: Hooke *et al.*, 1969; Colorado Plateau: Hunt, 1954; Negev: Krumbein, 1969; Sahara: Scheffer *et al.*, 1963; Daveau, 1966; Glennie, 1970; Harberland, 1975; Smith, 1978; Australian and Atacama: McGinnies *et al.*, 1968). Varnish is also thought to be forming on river boulders exposed at low stages (Hunt, 1954), in the arctic and antarctic (Washburn, 1969; Hooke *et al.*, 1969; Ugolini, 1970; Markov *et al.*, 1970, 273; Glazovskaya, 1971), on the Massachusetts coast (Hooke *et al.*, 1969, 287), in various alpine environments (Hollerman, 1963; Hooke *et al.*, 1969, 287), in the Sahel (Tricart and Cailleaux, 1964), and in cold desert uplands (Parfenova and Yarilova, 1965; Glazovskaya, 1968, 1971). Many authors stress that water is required to transport dissolved metals (e.g., Hunt and Mabey, 1966; Butzer and Hansen, 1968, 205; Glennie, 1970, 19; Hunt, 1972).

The chemical environment in which varnish forms has continued to be argued. Hooke *et al.*, (1969) have stated that varnish manganese and iron are in equilibrium with environmental physicochemical conditions for the deposition of the oxides of these elements. However, Hunt and Mabey (1966, A92), Krumbein (1969), and Rahm (1974, 106) expressed the opinion that physicochemical conditions at varnish surfaces do not permit manganese and iron concentration without the assistance of some biological process. The tremendous enrichment in manganese relative to iron in varnish was hypothesized by Engel and Sharp as proceeding from four causes: 1) arid weathering solutions may be enriched in manganese, which is more mobile than iron; 2) iron deposition may occur before the solution reaches the varnish site; 3) iron may be leached after the varnish is deposited; 4) the presence of manganese dioxide may have a catalytic effect on further manganese deposition. Hooke *et al.* (1969) stressed the importance of fractionation as a manganese-concentrating process, in which the greater mobility of manganese over iron favours the initial deposition of iron from a solution. The fact that an iron-rich and manganese-poor reddish varnish generally covers the undersides of rocks resting on desert soils and often also seems to underlie black manganese-rich surface varnishes was noted and explained by the fractionation process. Elvidge (1979), Elvidge and Moore (1979), and Elvidge and Collet (1981) have asserted that varnish development is accelerated by extreme alkalinity associated with arid conditions. They attribute varnish formation in Arizona to the mobilization of ambient manganese by wetting associated with summer thunderstorms, while immobilized iron blows away with the dust after the moisture evaporates. Where varnish is not in equilibrium with the alkalinity of the environment, Elvidge and Collet feel it is eroding.

*e Rates of formation:* Rates of varnish formation remain conjectural, with some confusion contributed by assertions by Engel (1957) and Engel and Sharp (1958)

of desert varnish formation in 25 years on an abandoned road in the Mojave Desert. This particular identification is erroneous in our view: the varnished cobbles in the road have unvarnished scratches generated by road construction 50 years ago; rocks that have been upthrust into the road by pavement forming processes have orange bottom varnishes now exposed on dorsal surfaces, and these orange bottom varnishes have not been invaded by manganese-rich black varnish. Our recently developed chemical age determination technique for varnish (Dorn and Oberlander, 1981b) shows no statistically significant age difference between the stones in a nearby natural pavement and the varnished stones in the road, indicating that the varnished stones in the road are remnants of the former pavement. Elvidge (in press) also concluded that this site does not reflect revarnishing of disturbed rocks.

Nevertheless, Engel and Sharp's conclusion that varnish can form in 25 years has been extensively cited without criticism (e.g. Hem, 1964, B10; Fairbridge, 1968, 280; Goudie and Wilkinson, 1977, 18) and occasionally with a critical eye (Mabbutt, 1977, 130). Others have noted that this single example was contrary to hundreds of observations of slow varnish formation in the western United States (Carter, 1964; Hunt and Mabey, 1966). Nevertheless, Scheffer *et al.*, (1963, 114) noted desert varnish on rocks disturbed by military manoeuvres in the 1940s in the Sahara, and Krumbein and Jens (1981) observed partial revarnishing of Negev Desert chipped rocks within 14 years. Most observers feel that arid rock varnish formation is extremely slow, being barely perceptible after a few thousand years (e.g. Blackwelder, 1948, 1954; Denny, 1965; Hooke *et al.*, 1969, 288; Hunt, 1972; Rahm, 1974; Hildreth, 1976; Elvidge and Moore, 1980, 108), becoming complete after 10 000 years or more (Blackwelder, 1948; Hayden, 1976; Carter, 1980). Our own observations and the observations of others (e.g. Butzer and Hansen, 1968, 74) all point towards a very slow rate of formation for arid varnish, with many thousands of years required to develop a complete coat of the manganese-rich type.

The possibility of employing varnish as an age determination tool is associated with the question of the rate of varnish formation. Mabbutt (1977) warned that the possibility of disparate growth rates in varnish might invalidate the use of varnish in the age determination of desert surfaces in different regions. However, geomorphologists have often used varnish as a relative age determination tool at a single locality (e.g. Hooke, 1967; Butzer and Hansen, 1968, 262; Hunt, 1972, 158–59; Oberlander, 1977).

Over the past 80 years, a large volume of literature indicates a continuing debate concerning the use of rock varnish to estimate the antiquity of cultural objects. The archaeological literature on varnish is difficult to evaluate due to the absence of a standardized terminology for various types of rock surface alterations. The term 'patination' is widely used in reference to typical orange to black rock varnish, but may also connote hydration rinds, silica glazes, percussion marks, milky-white coatings, fire darkening, ventification, thin limonite coatings, and unspecified weathering rinds. Many authors have been guilty of employing the term 'patination' without definition as if it were a precise concept.

Advocates of the use of rock varnish in relative age determinations in archaeology

have included Flammand (1921), Howard (1935), Renaud (1936), Amsden (1937), Wulsin (1941), Cooper (1947), Rhotert (1952), Grant (1967), Grant *et al.*, (1968), Cooke (1970), Evenari *et al.*, (1971), Hayden (1976), Bard (1979) and Schaafsma (1980). Scepticism has been expressed by Viereck (1964), Moen (1969) and Glenan (1974), among others, and many archaeologists have advised caution in the use of varnish for relative age determination. The findings of Heizer and Baumhoff (1963), von Werlhof (1965), Rusco (1970), and Nissen (1975) indicate that four different styles of petroglyphs in the Great Basin region form a progression through time (Stillwater Facetted, Pit-and-Groove, Great Basin Curvilinear, Great Basin Representational or Rectilinear) based on the relative degree of visible patination on each style. However, inconsistencies in the revarnishing of petroglyphs have been noted by many observers, creating doubt as to the utility of varnish colour or thickness as age determination tools. Thus the emphasis in archaeology has shifted to detailed analysis of varnish chemistry as a possible chronological indicator (e.g. Bard, 1979).

Geomorphologists have occasionally emphasized the role of desert varnish as an indurating agent (e.g. Butzer and Hansen, 1968; Tricart, 1972; Oberlander, 1977). We have observed desert varnish protecting the underlying heartrock from erosion in two situations: where varnish develops in a crack on friable rocks and is later exposed to subaerial processes, and where varnish forms on an indurated rock that later undergoes salt weathering under a varnish that is less susceptible to mechanical disintegration.

## II Recent advances in varnish research

Varnish research has proliferated in the last few years due to the application of new techniques. The work of Haberland (1975), Bauman (1976), and Potter and Rossman (1977) ushered in a period of advances characterized by several concerns: varnish microstructures, accretion from external sources, the possible role of organisms, mineralogy and trace element composition, and the chemical environment of varnish formation.

Using X-ray diffraction, Haberland (1975) identified varnish clay minerals including kaolinite, illite, and montmorillonite. Bauman (1976) reviewed similarities between marine iron-manganese nodules and desert varnish, including elemental enrichment, deposition of iron preceding manganese, similarities in manganese mineral phases, colloidal scavenging of trace element cations, external sources of cations, and the possible role of biological agencies, all of which suggested congeneric phenomena. Bauman also offered both chemical and physical explanations for the apparent preference of varnish for certain substrates.

Potter (1979) and Potter and Rossman (1977, 1978, 1979a, b, c), using infrared spectroscopy, x-ray diffraction, electron microscopy, and chemical analysis, contributed key facts relating to varnish by revealing that clay minerals constitute the bulk of varnish (up to 70 per cent of black manganese-rich varnish, and up to

90 per cent in bottom orange varnish). They demonstrated that varnish constituents, including clays, must have been transported to the rock surface from external sources, and stressed that varnish is a morphological entity distinct from the underlying substrate. Their infrared work indicated the presence of the manganese oxide birnessite in black varnish and hematite as an iron oxide in varnish. Birnessite is structurally similar to the manganese oxide vernadite, and Giovanoli (1980) believes that the latter differs only in having a disordered layer stacking. However, Chukhrov and Gorshkov (1981) feel that vernadite is distinct from birnessite and is the principal biogenic manganese oxide in many terrestrial weathering deposits.

Perry and Adams (1978) meanwhile used ultra-thin sections and electron microprobe analysis to find alternating black manganese-rich and red manganese-poor (iron-rich) laminations in desert varnish from several different locations. Perry (1979) also noted that varnish micromorphology varies from botryoidal to smooth and suggested that the smooth (therefore 'shiny') type is produced by aeolian abrasion of botryoidal varnish, which is taken to be the standard growth form. Like most other recent researchers, Perry and Adams (1978) stress that the major source of varnish constituents is airborne dust, not the underlying rock, as evidenced by superimposed microlaminations. They proposed that the manganese mineralogy of varnish may be a single silicate (unidentified) phase, rather than birnessite.

In an exploratory attempt to devise a method of varnish age determination for archaeological research, Bard (1979) and Bard *et al.* (1976; 1978) used neutron activation analysis and x-ray fluorescence to provide extremely precise elemental analyses of varnishes from Great Basin petroglyph sites. This work, which stresses the many difficulties encountered in dating varnish, produced relative chronologies at two petroglyph sites but did not attempt calibration experiments; thus absolute age determinations were not achieved. Furthermore, Bard's trace element age determination method seems to rely on the assumption, untenable in light of current research, that varnish is derived from the underlying heartrock.

Allen (1978) analysed varnish from Arizona with optical and electron microprobe techniques, verifying an external origin. Extensive electron microprobe work showed the lack of a concentration gradient from the heartrock into the varnish in all samples studied for manganese and iron. Allen attributed varnish formation to arid Altithermal conditions, with humid varnish formation outside the Sonoran desert possibly having a different mineralogy, structure, and rate of formation than 'desert' varnish.

In an attempt at radiometric dating, Knauss and Ku (1980) proposed that varnish absorbs uranium from the environment, producing a closed system suggesting that  $^{235}\text{Th}/^{234}\text{U}$  and  $^{231}\text{Pa}/^{235}\text{U}$  might be used for absolute age determination of varnish. Application of their technique to a varnish specimen from Utah produced an average age of over 300 000 years for the full thickness of the varnish. The assumption of a closed system seems to be inconsistent with the hypothesis that varnish forms by accretion of ambient clay minerals, as sorbed thorium could be worked directly into varnish by subaerial accretion.

Elvidge (1979), Elvidge and Moore (1979), and Elvidge and Collet (1981) presented a physicochemical model for varnish formation under dry (alkaline) althermal conditions by deposition of mostly airborne ambient material, suggesting that a span of 3000 to 5000 years is required to produce discernible varnish and much longer to form a solid coat. Elvidge (1979) stressed airborne dust as the source of desert varnish constituents on the basis of lack of manganese in many substrates, the presence of varnish on water partings that produce but do not receive runoff, and the lack of a rind depleted in manganese and iron in the heartrock beneath varnish layers. Minor Eh and pH fluctuations in dust covering rock surfaces are proposed as causing solution and reprecipitation of manganese, cementing ambient clay to rock surfaces, and extreme alkalinity is regarded as accelerating varnish development. This hypothesis was supported by the creation of 'artificial desert varnish' by purely physicochemical means (Elvidge and Moore, 1980). Our own findings agree with an external source of varnish constituents, but are in strong opposition to the preceding view of the role of alkalinity in varnish formation (This important divergence will be discussed in detail in later pages.)

Krumbein and Jens (1981) have reported the results of a long-term study of microorganisms on and within rocks in the Negev Desert, Israel. The initial results of this study were presented by Krumbein (1969, 1971). Krumbein and Jens concluded that a large variety of microflora, including cyanobacteria, fungi, and bacteria 'produce' manganese-rich and iron-rich rock varnish. Our study verified that Mn-oxidizing and Fe-oxidizing organisms are present on the varnish surface. However, we disagree with Krumbein and Jens on the mechanics of varnish formation and the relative importance of different types of microorganisms that perform the crucial role of manganese oxidation at rock surfaces.

The varnish research of Krumbein and Jens is part of a larger geomicrobiology study on the role of microorganisms on the weathering of partly silicified limestones in the Negev. Here epilithic and endolithic microorganisms form a 'microbial weathering front' that destroys the unsilicified limestone underneath it. When the 'solution front community' reaches increasingly more resistant (silicic) rocks, Krumbein and Jens propose that a protective 'artificial biogenic roof' of rock varnish is developed to protect the community from harsh desert environmental conditions. At this time, the microbial solution front community cannot penetrate deeper into the rock and reaches a stable condition. In some cases penetration is thought to resume after a long hiatus (Krumbein, 1969; Evenari *et al.*, 1971). To support their model, Krumbein and Jens presented field and laboratory evidence including the isolation of 17 strains of Mn- and Fe-precipitating fungi and 28 strains of bacteria (including *Metallogenium*-like organisms), as well as varnish generated biologically under laboratory conditions. Krumbein and Jens stress the role of often lichenized epilithic and endolithic cyanobacteria and fungi, rather than bacteria, in the production of varnish, and are dubious of the importance of physicochemical processes in the formation of varnish.

The earlier work of Krumbein (1969, 1971) has not been cited by most varnish researchers, and the mechanism of manganese enhancement has remained unclear,

although there has been constant speculation that a biological enhancement mechanism could be involved (Francis, 1921; White, 1924; Laudermilk, 1931; Blackwelder, 1954; Scheffer *et al.*, 1963; Hollerman, 1963; Jaeger, 1965, 153; Parfenova and Yarilova, 1965; Hunt and Mabey, 1966, A92; Glazovskaya, 1968, 303; Markov *et al.*, 1970, 273; Evenari *et al.*, 1971, 57; Hunt, 1972, 160; Rahm, 1974; Haberland, 1975, 49; Bauman, 1976; Mabbutt, 1977, 130; Perry and Adams, 1978; Borns *et al.*, 1980).

### III Initial results of the present study

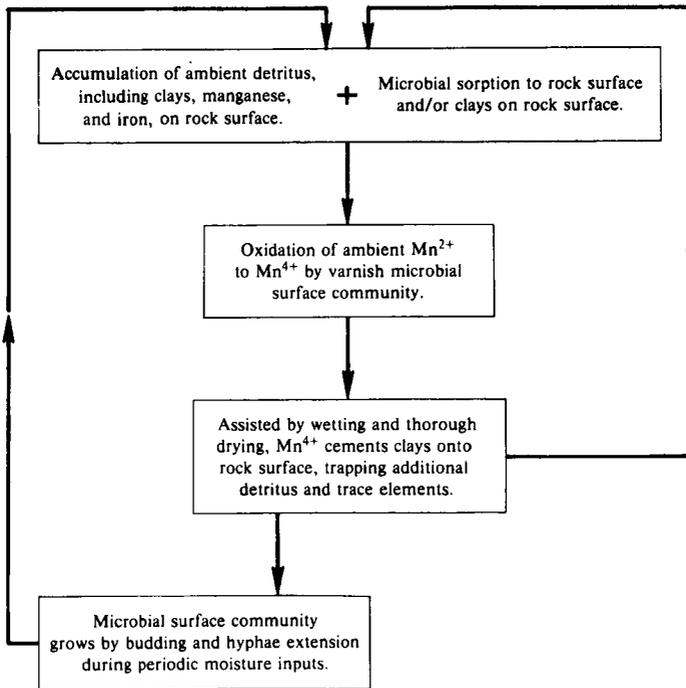
Our own field and laboratory work over the past five years has contradicted certain assumptions concerning varnish formation and characteristics and has shown that the phenomenon is considerably more widespread and more complex than the existing literature, including recent contributions, suggests. This work has been based on analyses of varnish sampled at over 100 widely scattered locations on six continents, including desert, alpine, coastal, riverine, spring, and subsurface environments. We have used a diversity of methodologies to analyse and characterize varnish films and soil and airborne dust, including scanning electron microscopy (SEM), biological culturing, electron microprobe analysis, energy dispersive analysis of X-rays (EDAX), organic carbon determination, ion particle acceleration, wet chemical analysis, and various physical tests and simulations of environmental processes.

#### 1 Biogeochemical model of rock varnish formation

A principal finding of our study is that classic manganese-rich black varnish is a biogenic chemical coating, with the manganese enhancement in varnish a product of mixotrophic manganese-oxidizing microorganisms. These organisms, which may be able to utilize both organic and/or inorganic sources of nutrition, are present in most rock surface environments, but find optimum conditions in arid to semi-arid regions and in certain humid microenvironments that are hostile to competing heterotrophic organisms. Once ambient manganese is emplaced and subsequently oxidized by bacteria, it cements environmental clay micelles to rock surfaces. These clay minerals may in turn help to shield the manganese-oxidizing microbes against harsh environmental conditions (Dorn and Oberlander, 1981b). In this way a positive feedback relationship develops, causing slow accretion of clays cemented by microbially-oxidized manganese to form rock varnish (Figure 1). This simple model excludes many facets of varnish development to be explored more fully later in this paper, but it can serve as a basis for further general discussion of the varnish problem.

We have verified the biogeochemical model by laboratory replication experiments. Manganese-oxidizing microorganisms were cultured and generated manganese micronodules and manganese-rich varnishes on freshly-broken rock fragments in nutrient-poor media with near-neutral pH values (Dorn, 1980; Dorn and

## SIMPLE MODEL OF ARID ROCK VARNISH FORMATION



**Figure 1** Simplified biogeochemical model of rock varnish formation.

Oberlander, 1980; 1981a; 1981b). These biogenic laboratory varnishes have a range of micromorphologies similar to natural varnishes. Comparisons between cultured and natural semi-botryoidal and lamellate varnishes have been presented (Dorn and Oberlander, 1981a, 1981b). Figure 2A and 2B compare intermediate natural and laboratory varnishes. Figure 2C juxtaposes the EDAX analysis of a laboratory varnish (about 80 per cent bentonite clays and 20 per cent Mn and Fe hydroxides) with a spot EDAX analysis of a *Pedomicrobium*-like organism that was oxidizing and concentrating manganese and to a lesser extent iron. Figure 2C is similar to the EDAX comparisons of natural varnishes and microbial oxide enhancements in Figure 3 and in Dorn and Oberlander (1981a; 1981b). Krumbein and Jens (1981) also reported the formation of laboratory 'varnishes', but did not specify the pH conditions, the micromorphology of these varnishes, the chemical composition of the coatings, or the presence or absence of microchemical laminations.

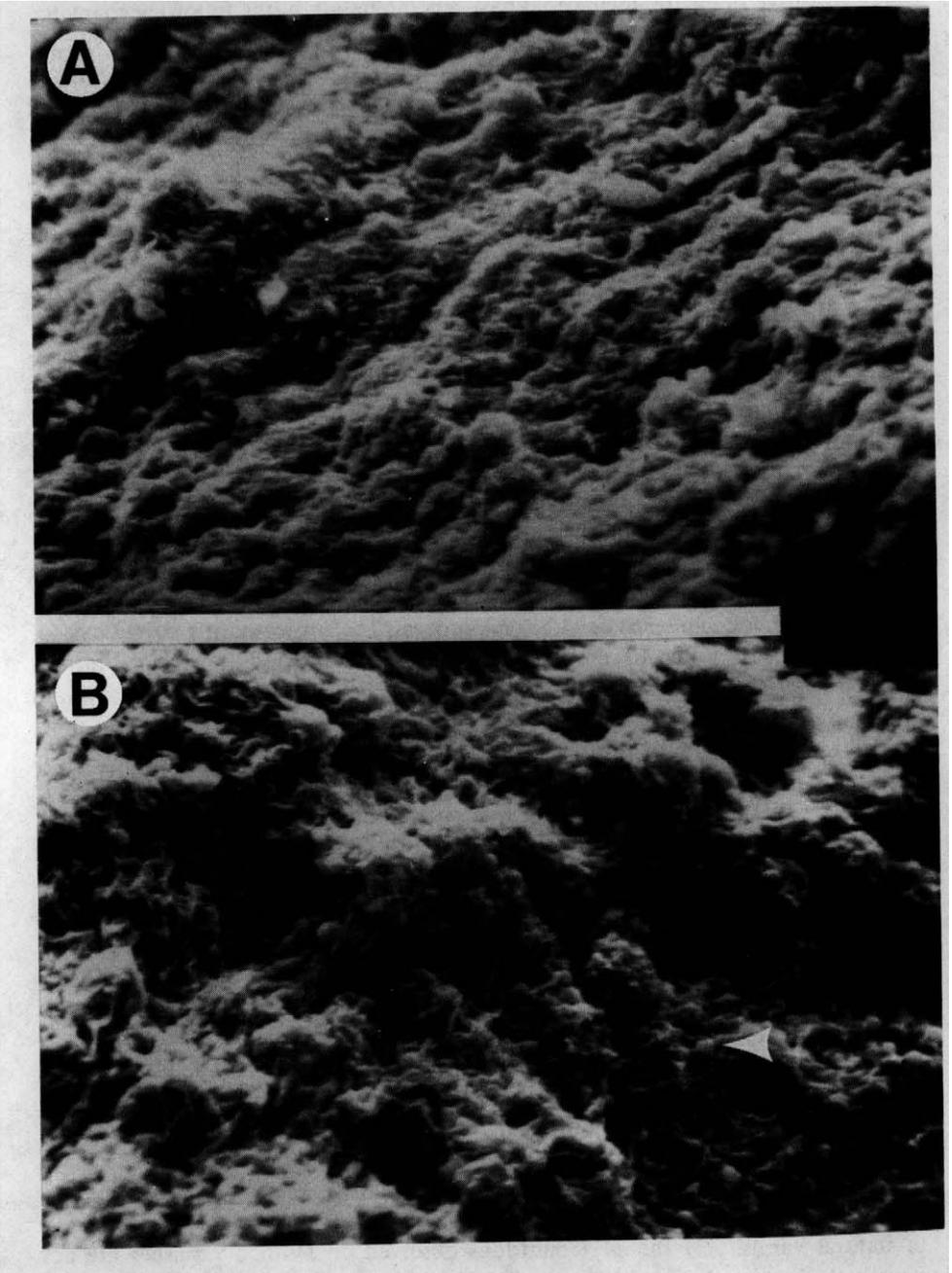
The essential type of manganese-oxidizing microorganisms on desert varnish appear to be mixotrophic bacteria that fill an environmental niche unsuited to faster growing organic-nutrient-loving heterotrophic organisms (Dorn and

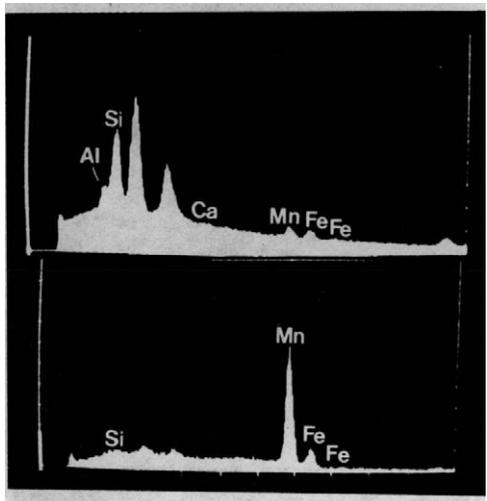
Oberlander, 1981a). Manganese enhancing bacteria on arid rock varnish (Figure 3) seem to thrive in environments that have a combination of the following characteristics: a minimum of organic matter, surfaces of near neutral pH, microenvironments that temporarily retain moisture and then dry thoroughly, trace amounts of copper, and an input of montmorillonite-type clays. These conditions are similar to the general environmental conditions described by Schweisfurth *et al.* (1980, 279) for the oxidation of manganese by microorganisms.

We stress the role of mixotrophic bacteria in varnish formation, because SEM/EDAX observations of rock varnishes from over 100 worldwide locations show only occasional manganese enhancement by other microorganisms, such as those associated with varnish by Krumbein and Jens (1981). We have cultured fungi from desert varnish capable of oxidizing manganese on a medium poor in organic nutrients (Dorn and Oberlander, 1981a). However, Stotsky and Rem (1967) demonstrated that fungal respiration may be inhibited by the montmorillonite clays present in varnish. This is consistent with our SEM/EDAX examination of varnished surfaces, where we find isolated examples of fungi that enhance manganese above adjacent varnish manganese concentrations (Figure 4) and very rarely cyanobacteria. As Krumbein and Jens note, the manganese oxidation they associate with fungi may be from budding bacteria and/or *Metallogenium* bacteria in intimate association with fungal hyphae.

There continues to be controversy over whether manganese enhancement in varnish is a physicochemical or biological process. The advocates of a purely physicochemical process point to the dominance of desert varnish in alkaline regions (Elvidge, 1979; Elvidge and Collet, 1981), proposing a fractionation mechanism in which slight Eh/pH fluctuations mobilize manganese from ambient dust, while most of the iron remains with the dust, eventually to blow away (Hooke *et al.*, 1969; Elvidge and Moore, 1979; Elvidge and Collet, 1981). This view is associated with 1) disbelief in the possibility that fragile microorganisms exist in harsh deserts on such a scale as to produce ubiquitous desert varnish (Lucas, 1905; Engel, 1957); 2) acceptance of claims for 'eroding' varnish in regions that are not alkaline enough to preserve it (Elvidge, 1979; Elvidge and Collet, 1981); and 3) the production of 'artificial desert varnish' by purely chemical means (Elvidge and Moore, 1980).

These ideas are internally consistent, and Krumbein and Jens (1981, 34–35) present several reasons why previous workers may not have realized the importance of biological agencies. However, we feel there is overwhelming evidence that the dominant mechanism of manganese-enhancement in varnish is biological. Several general ecological factors argue for a microbial origin for desert varnish (Dorn and Oberlander, 1981a; 1981b): 1) the clay mineralogy of varnish is inconsistent with the physicochemical mechanism required to produce juxtaposed orange and black varnishes; 2) 'artificial desert varnish' has a crystalline micromorphological appearance that is completely unlike natural varnish, and likewise lacks the abundant clay in natural varnish; 3) the pH conditions observed on Mn-rich varnishes are not usually high enough physicochemically to oxidize manganese; 4) rock surfaces adjacent to lichens have Eh/pH changes required to mobilize manganese from





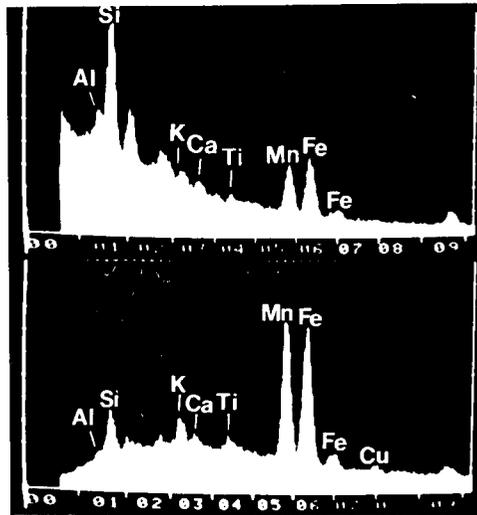
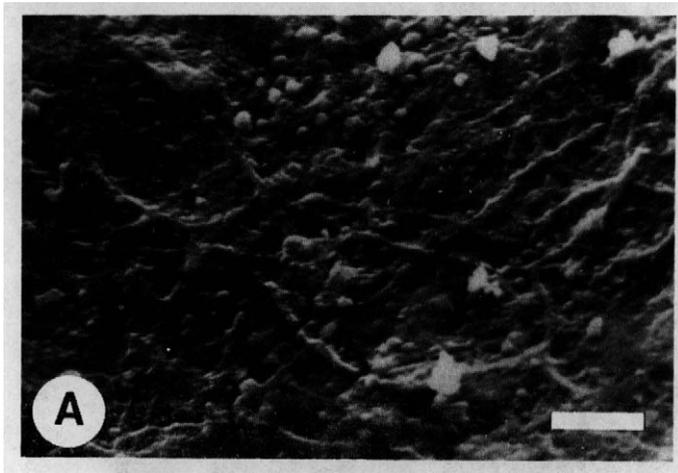
**Figure 2** Comparison of surface micromorphologies of laboratory-nodule and natural varnishes. SEM image of:

**A** Natural intermediate micromorphology from dull subsurface black varnish, Rainbow Basin, near Barstow, Mojave Desert. The ragged edges of varnish clays and oxides indicate a lack of wind action. Shiny black varnishes from this same location have smooth micromorphologies. 20  $\mu\text{m}$  scale bar.

**B** *Pedomicrobium*-like bacteria-generated Mn-Fe nodule with an intermediate micromorphology. The edges of the clays and hydroxides are preserved in this laboratory agglomeration because of lack of abrasion. The micron-size forms (arrows) are cocci of the *Pedomicrobium* that oxidize Mn (II) to Mn (IV). The medium used for culturing the nodule-producing microorganisms is the 'p' medium specified in Dorn and Oberlander (1981a). 20  $\mu\text{m}$  scale bar.

**C** Comparison of energy dispersive X-ray analyses (EDAX) of the overall nodule chemistry (upper panel) with the immediate vicinity of a bacterium (lower panel). This illustrates the large enhancement of Mn by microorganisms cultured from rock varnish. Peaks not identified in EDAX analyses are coating emissions and trace elements.

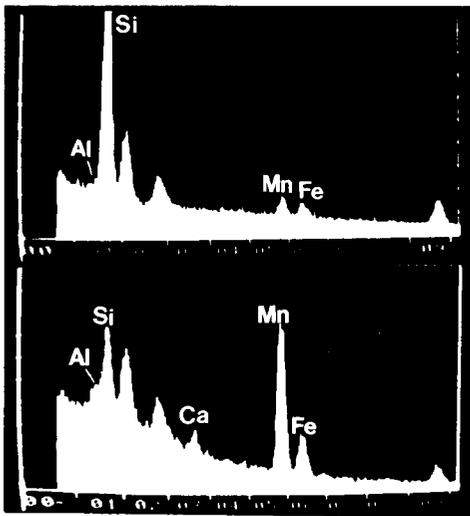
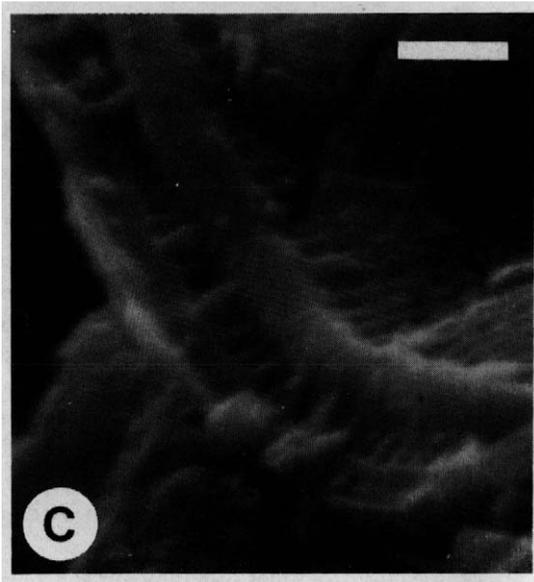
ambient material and subsequently fix it, but varnish is generally absent close to lichens on desert rocks; 5) unassisted clay fixation of metals is insufficient to produce the high concentrations of ambient heavy elements present in varnishes, and 6) manganese-rich varnishes are common in humid, non-alkaline environments (Dorn and Oberlander, 1980). Other evidence supporting a microbial origin includes the presence of organic material in varnish (Laudermilk, 1931; Dorn and Oberlander, 1981b; Krumbein and Jens, 1981), the non-uniform onset and irregular



**Figure 3** Manganese concentrating bacteria on desert varnish.

A SEM image of a colony of *Metallogenium*-like bacteria growing on and being incorporated into black surface varnish, on silicified limestone collected in the Negev Desert, Israel, about 50 km north of Eilat. Budding cells are visible in the upper centre of the image, extending out of partially buried hyphae. Reproduction by budding may be an adaptation to an environment with continually accreting material. 10  $\mu\text{m}$  scale bar.

B EDAX comparison of the overall varnish (upper panel) with a spot analysis of a hyphae (lower panel), demonstrating bacterial enhancement of both manganese and iron.



**Figure 3** continued

**C** Adsorption of *Metallogenium*-like hyphae onto Mn-rich black riverine varnish, on quartzite from a point bar deposit of Crooked Creek, near Scuffletown, Kentucky. The perpendicular filamentous material, possible slime, appears to be used by the bacteria to adsorb onto the varnish surface. 1  $\mu$  scale bar.

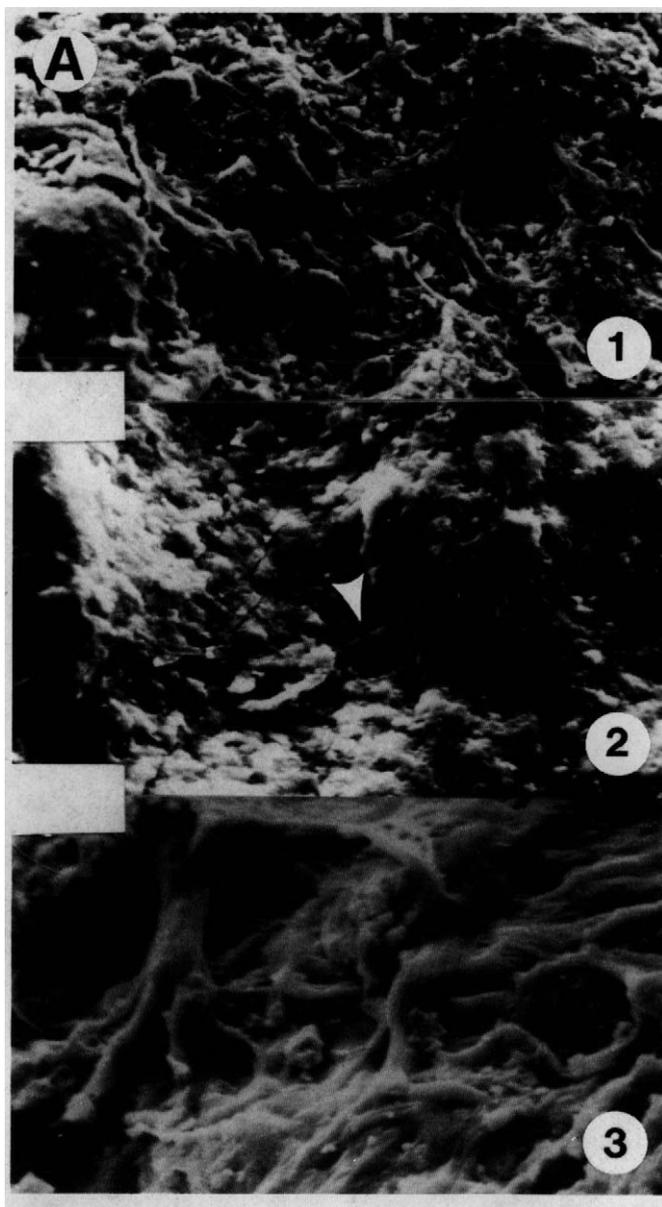
**D** EDAX analyses showing Mn and Fe enhancement around the hyphae (lower panel), as compared to an analysis of the adjacent clay-rich varnish (upper panel).

distribution of varnishing locally and on individual rocks in deserts, the absence of any documented mechanism for the formation of varnish with high Mn:Fe ratios by physicochemical means, and still other factors to be discussed subsequently. We do not completely exclude the possibility of fractionation playing a role in manganese enhancement, but the available evidence suggests that role must be a very minimal one.

The role of microorganisms in varnish formation is not limited to manganese enhancement. There is evidence for enhancement of iron by microorganisms on manganese-poor orange varnishes (Figure 5) and on manganese-rich black varnishes (e.g. Figures 3 and 4, where iron peaks in EDAX analyses are enhanced above adjacent varnish levels). This topic has been slighted by varnish researchers, because manganese in varnish is enhanced above ambient levels in far greater amounts than iron. More importantly, purely microbial oxidation of ferrous iron in desert regions is not required for varnish formation, as desert conditions are appropriate for physicochemical oxidation of iron without biological assistance. This can be seen in the uniform onset and degree of development of iron oxide discolouration of desert rocks and outcrops.

Our model differs significantly from that of Krumbein and Jens (1981). Whereas the latter stress the role of cyanobacteria and fungi, our view is that mixotrophic bacteria are the primary agents of manganese oxidation. A greater difference is conceptual. We feel the biogeochemical processes adduced by Krumbein and Jens as being involved in the microbial weathering of limestones and dolomites (e.g. Krumbein and Jens, 1981; Danin *et al.*, 1982) are not directly related to the formation of typical black desert varnish. We have observed lichen and lichenized epilithic cyanobacteria, involved in carbonate dissolution, that are also involved in the chemical dissolution of desert varnish. The Krumbein and Jens study of 'solution front' communities on and in limestone of varying degrees of silicification in the Negev may not be applicable to microbial communities on rock varnish on other substrates. We also question whether arid rock varnish is an evolutionary adaptation of a solution front community to protect itself from harsh desert conditions. Instead, we see varnish as a metabolic product of manganese-oxidizing microorganisms (with concomitant clay fixation), some of which are also associated with solution front communities.

It appears that arid rock varnish, on non-carbonate and carbonate rocks, is composed of allochthonous materials with a surface microbial community oxidizing ambient manganese during periods of temporary moisture abundance and near-neutral pH conditions. Mixotrophic budding bacteria are particularly suited to an environment involving burial by clays and oxides, because hyphae extension allows them to 'escape' burial (e.g. Figure 3a). How these bacteria survive harsh desert conditions and high levels of oxides probably has to do with their interaction with varnish clay minerals (Dorn and Oberlander, 1981a), with their autecology (Schweisfurth *et al.*, 1980) and with temporary periods of moisture abundance setting off 'microbial blooms'. During the relatively dormant low moisture periods, microbial oxidation of manganese does occur, but probably at much slower rates.



**Figure 4** Fungi on rock varnish.

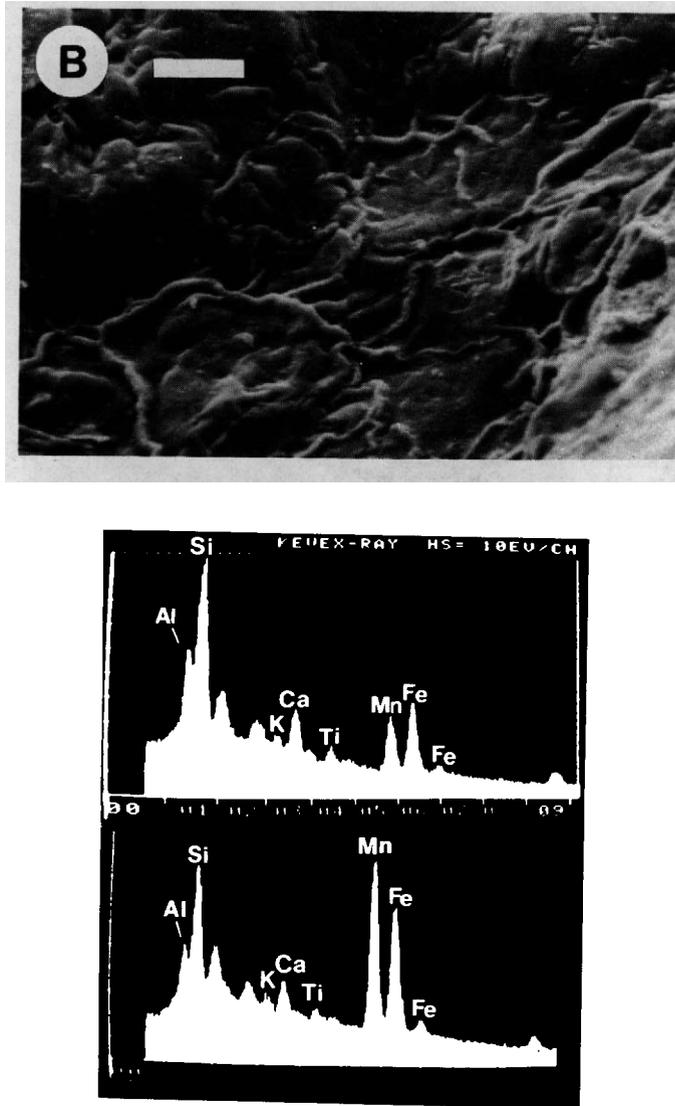
A SEM of fungal-like structures not concentrating manganese.

1) Fungal mat on black varnish on moraines in British Columbia, Canada.

2) Fungal hyphae (arrow) on black varnish collected in the Wallowa Mountains, northeastern Oregon.

3) Hyphae on dusky-brown varnish on an uplifted terrace on the east coast of the Sinai Peninsula, Israel.

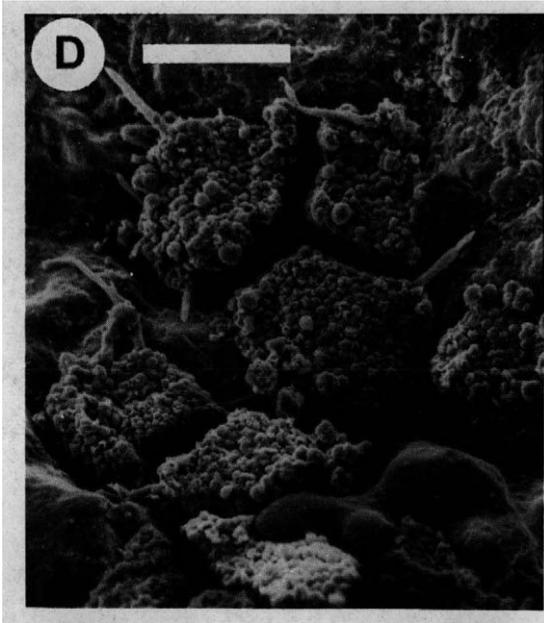
Scale bars: 20  $\mu\text{m}$  2) 10  $\mu\text{m}$  3) 10  $\mu\text{m}$



**Figure 4** *continued*

**B** Partially buried Mn-concentrating fungal structures in a micro-pit on black surface varnish on basalt of Pisgah Crater, Mojave Desert, California. 40  $\mu\text{m}$  scale bar.

**C** EDAX comparison of the Pisgah varnish (upper panel) with varnish-encrusted fungal hyphae (lower panel) showing concentration of both Mn and Fe.



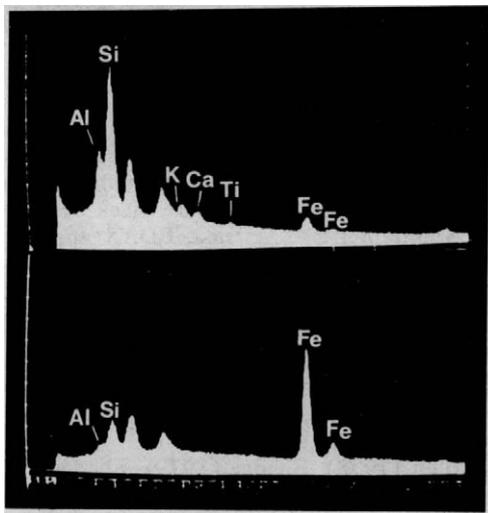
**Figure 4** *continued*

**D** Fungal 'botryoidal plateaus' with spike-like hyphae extending out of the botryoidal structures, growing adjacent to lamellate black desert varnish, collected by C. Elvidge at South Mountain Park, Arizona. EDAX analyses indicate that some botryoidal plateaus, which are associated with rock surface fungi, have chemistries similar to rock varnishes. Mn-rich varnish botryoids should not be confused with purely fungal structures sometimes seen on arid rock surfaces. 50  $\mu\text{m}$  scale bar.

## 2 *Source of varnish constituents*

Evidence presented by Potter and Rossman (1977; 1979a; 1979b; 1979c), Perry and Adams (1978), Allen (1978), Elvidge (1979), Elvidge and Collet (1981), and Dorn and Oberlander (1981b) demonstrates that the constituents of desert varnish are not derived from the underlying heartrock, but come from sources external to the underlying substrate. Figure 6 presents visual substantiation of this point. We have collected many specimens of thick black varnish superimposed on heartrocks virtually devoid of detectable manganese (to 0.01 oxide weight per cent).

The source of varnish constituents must, therefore, be the external environment: principally dust and runoff from surfaces above varnished rocks. We concur with Perry and Adams (1978) and Elvidge (1979) that atmospheric dust is the most common manganese source. However, desert pavement soil solutions have relatively high concentrations of divalent manganese (Vinayak *et al.*, 1964), and the occurrence of ground-line bands on rocks in desert pavements suggest that these soil solutions supply some varnish manganese. Conspicuous streaks of black (manganese-



**Figure 5** Orange bottom varnish bacteria.

**A** Bacteria on orange bottom varnish collected from a Pleistocene shoreline of Lake Lahontan, north of Schurz, Nevada. 4  $\mu\text{m}$  scale bar.

**B** EDAX comparison showing iron enhancement by the microorganism in 5A (lower panel), relative to the overall orange bottom varnish chemistry (upper panel).

rich) varnish where water occasionally streams over rocks or cliffs suggest that manganese is mobilized in and accreted from runoff.

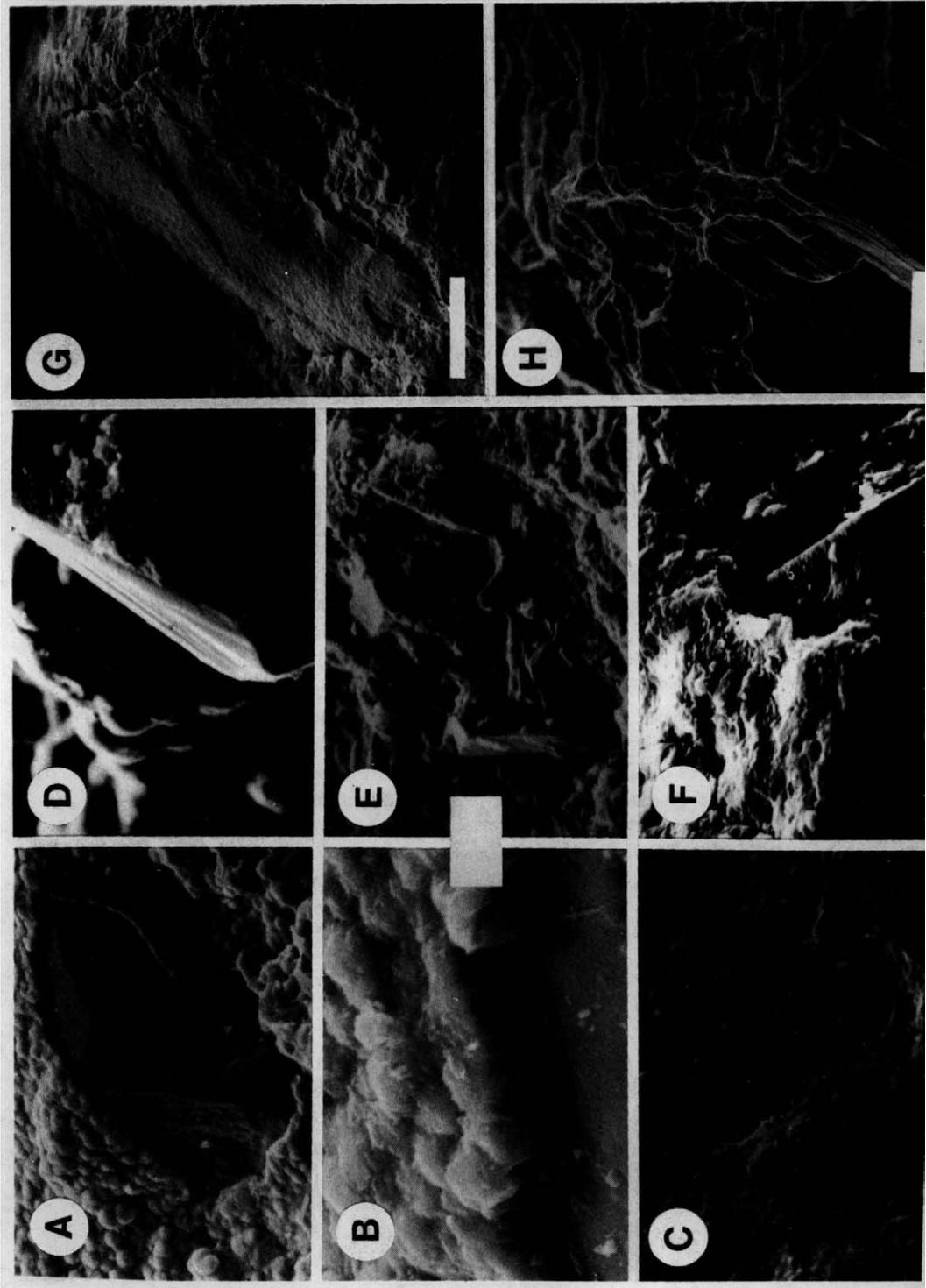
There remains the question of the ultimate source of the manganese in atmospheric dust. Sampling of airborne fallout suggests that the dominant source of atmospheric manganese in arid inland locations is the soil surface. A comparison of the Fe:Mn ratios of soils to that of airborne material collected at sampling stations in the southwestern Mojave Desert; in Death Valley, and near Schurz, Nevada, produces a Pearson correlation coefficient of + 0.96. Airborne aerosol data gathered in the desert of the western US (e.g. Cahill *et al.*, 1979; Barone *et al.*, 1979) reveal Fe:Mn ratios similar to the desert soil chemistry data generated by Boerngen and Shacklette (1981). Both data sets have typical Fe:Mn ratios in the range of 40:1 to 70:1. The similarity of soil and airborne Fe:Mn ratios suggest that the source of the sampled airborne material is surface soil, ultimately derived from rock weathering.

Other sources of atmospheric manganese exist. Bowen (1966) notes that the average ratio of Mn:Fe in land vegetation is approximately 4.5:1. White (1924) and Krumbein and Jens (1981) note that pollen may supply manganese to rock surfaces. An occasional pollen rain or forest fire in a relatively nearby coniferous forest could supply a large amount of divalent manganese for microorganisms to oxidize. Volcanic dust and gas inject manganese into the atmosphere, and Nadiradze (1980) presented evidence to support significant periodic cosmogenic inputs of manganese. However, a cosmogenic source seems inadequate in light of the widespread and extensive accumulation of manganese deposits in present-day basins (see Roy, 1981). There has been some discussion of an oceanic sea salt source for continental atmospheric manganese, but such a source seems inconsistent with the known sea surface chemistry (e.g. Callender and Bowser, 1980), and the chemistries of snow (Warburton *et al.*, 1980), the atmosphere (e.g. Chester and Stoner, 1974; Asman and Slanina, 1980), and marine sediments (Chester *et al.*, 1979).

Regardless of the origin of manganese and other varnish constituents, they appear to be 'sieved' out of ambient environmental clay and debris by bacterial oxidation of manganese (and to a lesser extent iron), and subsequently cemented by manganese, with trace elements incorporated in debris trapped during the cementation process (Figure 7).

### 3 Varnish characterization

*a Macrochemical variations:* The typical elemental composition of black desert varnish can be divided into the major elements (O, H, Si, Fe, Al, Mn, and sometimes, Ca), the minor elements (Ca, K, Mg, Na, Ti, Rb, Sr, and sometimes Ba and Cu), and more than 30 identified trace elements. However, the colour of rock varnish depends principally on the relative abundances of iron and manganese and the degree of hydration of the iron oxides. Iron-rich (manganese-poor) coatings tend to be orange in colour (Munsell 10R4/8, 2.5YR4/6 to 5/6, 5YR7/6 to 7/8). Manganese-rich varnishes are black, occasionally with a blue to purple tinge. Chemically



intermediate varnishes are a dusky-brown colour (Munsell 10R3/3 to 4/4, to 2.5YR3/2).

Orange desert varnishes are commonly found adjacent to alkaline material: on the undersides of rocks in desert pavements; in closed cracks in desert rocks, and on the surfaces of rocks in alkaline environments. Bulk ion particle acceleration (Cahill, 1975) and energy-dispersive X-ray analyses of varnishes we have collected in the Atacama and Sinai deserts show that the common varnishes in such hyper-arid regions are rich in iron and orange to dusky-brown in colour (Oberlander, 1982; Dorn, 1982). In these hyper-arid environments black varnishes are limited to microenvironments that are more moist and are flushed of alkaline particles (Figure 8).

Other researchers have noted the association between iron-rich (manganese-poor) varnishes and extremely arid and/or alkaline environments. Glazovskaya (1971, 236) observed 'brownish-red' desert varnish on granite on the edges of alkaline basins in Antarctica, with only occasional patches of black desert varnish. Walker (1979) and El-Baz and Prestal (1980) analysed orange to red coatings of 'desert varnish' on sand grains in intensely arid regions of northern Africa that were composed of clays and iron oxides and hydroxides.

In the somewhat less arid deserts of the western US black varnishes are frequently found covering exposed rock surfaces, the sides of rock cracks that have not been in recent contact with alkaline dust, and as a band at the ground line on rocks in well developed desert pavements.

The association of hyper-arid/alkaline macro and microenvironments with orange varnish on one hand, and moderately arid/near-neutral macro and microenvironments with black varnish on the other hand, is decisive evidence arguing against a physicochemical model associating classic black varnish with alkaline surface conditions and accentuated aridity.

**Figure 6** SEM images illustrating the morphological distinctness of varnish, as compared to the underlying heartrock. The central scale bar applies to images A through F. The scale bars for G and H are located on the respective images.

**A** Botryoidal black varnish growing on an albite crystal, collected on talus, near Obsidian Spring, Three Sisters Wilderness, Oregon Cascades. 20  $\mu\text{m}$  scale bar.

**B** Close up of the varnish/heartrock interface in 6A. 4  $\mu\text{m}$  scale bar.

**C** Semi-botryoidal varnish on the exposed underlying mica schist (centre of image), collected on a recent moraine of the Khumbu Glacier, Everest region, Nepal. 10  $\mu\text{m}$  scale bar.

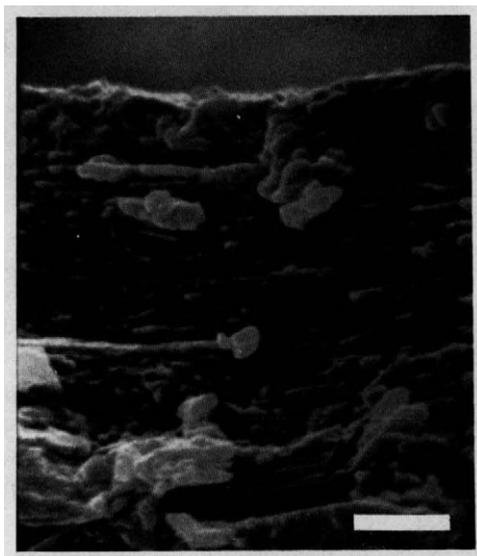
**D** Varnish growing on crystal. Site specified in 6A. 4  $\mu\text{m}$  scale bar.

**E** Black subsurface varnish from the Rainbow Basin, near Barstow, Mojave Desert, growing on Quartz crystals. 40  $\mu\text{m}$  scale bar.

**F** Black crack varnish on granite from Joshua Tree National Monument, California, growing laterally onto a heartrock crystal. 20  $\mu\text{m}$  scale bar.

**G** Patch of black Mn-rich lamellate varnish on a gneissic substrate from a young flow of a talus cone, just south of Copper Creek alluvial fan, Death Valley National Monument. 50  $\mu\text{m}$  scale bar.

**H** Broken edge of black Mn-rich semi-botryoidal to lamellate varnish on biotite from the oldest flow of the talus cone, described in Figure 6G. 25  $\mu\text{m}$  scale bar.



**Figure 7** Edge micromorphology of a thin lamellate black surface varnish on a microridge on a Capote Creek desert pavement fragment (contributed by Julian Hayden, 1981), north of Candelario, Texas, east of the Rio Grande. Buried lamellate layers and detritus are visible. The detritus is incorporated into varnish with the accumulating clays and is cemented by varnish oxides. The heartrock (arrow) is visible in the bottom of the image. 1  $\mu\text{m}$  scale bar.

*b Microchemical variations:* Microchemical variations occur laterally on varnish surfaces, vertically in transects normal to varnish surfaces, and with the aging of varnish. Spot energy dispersive X-ray analyses have shown that characteristic surface chemistries are more variable from point to point on arid varnishes than on more humid varnishes (Figure 8).

Perry and Adams (1978) were the first to identify microchemical laminations of Mn-rich and Mn-poor layers with depth in desert varnish. Our electron microprobe work at four arid sites in the western US verifies the presence of these laminations in lamellate as well as the botryoidal varnish surfaces discussed by Perry and Adams (Figure 9 A–D). However, it should be noted that these laminations tend to be discontinuous (perhaps a reflection of point to point surface microchemical variation) and do not exist in some varnishes found in more humid regions (e.g. Figure 9E). In addition to these microlaminations, sometimes larger scale superposition of Mn-rich and Mn-poor layers occurs; these are visible in Figure 10.

Perry and Adams (1978) proposed that chemical laminations in varnish are primary depositional features, and Elvidge (1979) concurs. We also feel that these laminations represent periodic manganese deposition, separated by periods in which manganese accretion declines and iron accumulation is dominant. It is conceivable that laminations could represent periodic growth of manganese-rich varnish with intervals of chemical erosion of manganese from the top layer, leaving a residual

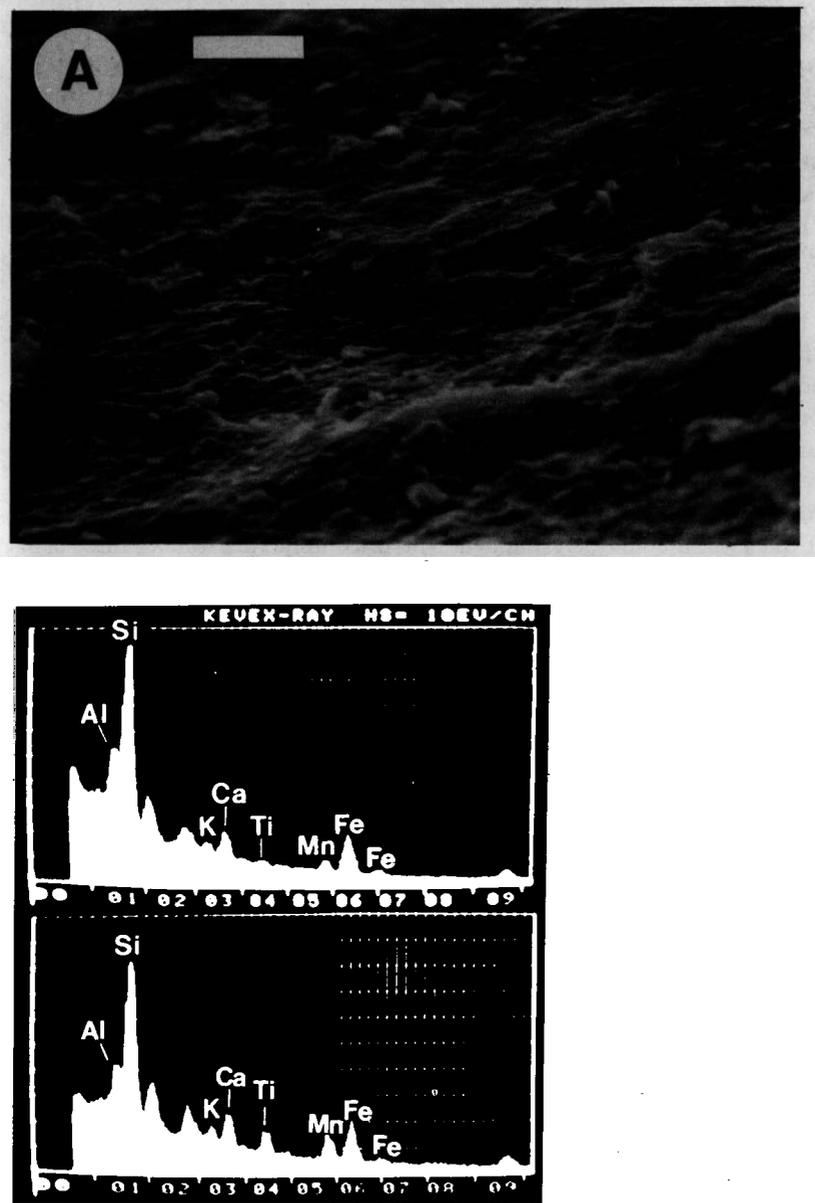
iron-rich lag. Resumed accretion of manganese would encase the iron-rich (manganese-poor) layer between manganese-rich layers. This alternative seems unlikely for several reasons. Manganese-deficient varnishes that are orange and dusky brown in colour are the dominant surface types in hyper-arid/alkaline environments. Except for microbially precipitated iron stains in acid waters, orange varnishes are common only in alkaline microenvironments. For instance, orange varnishes are common in rock cracks that accumulate alkaline dust and on the undersides of desert cobbles in contact with alkaline soil.

Chemical laminations are discontinuous over short distances. If a sustained period of manganese erosion (e.g. a glacio-pluvial period) were recorded in varnish microchemistry, the resulting iron-rich residual layer should be continuous and widespread. It seems much more likely that the chemical laminations in varnish represent oscillations in microenvironments alternating between conditions favourable and unfavourable to manganese-concentrating microorganisms.

If increased alkalinity is responsible for manganese-poor layers, varnish laminations might be used as an indicator of palaeoenvironmental changes, assuming the age of the varnish could be estimated. The discontinuous nature of these laminations complicates such a hypothesis. However, discontinuities in varnish laminations may arise from variations in the rate of varnish formation, and, hence variable sensitivities to microenvironmental changes through time. Varnishes in micropits are deeper, develop more rapidly, and are less subject to aeolian abrasion than are adjacent varnishes on more exposed microsurfaces. It seems that chemical laminations may be useful in palaeoenvironmental research if the sampling points are restricted to sites favouring continuous deposition and if extensive work is done on local and regional correlations of the laminations.

Some variations in varnish microchemistry appear to be a function of time. While Fe:Mn ratios in bulk analyses of varnish are unsystematic, we have found that changes in trace element cation ratios in bulk analyses provide a new age determination technique. We have found that the mobile cations incorporated into varnish are depleted systematically with time relative to less mobile ions, such as titanium. Thus the simple ratio Ca+K:Ti correlates remarkably well with surfaces of known relative age, and may be a means of establishing varnish chronologies (Dorn and Oberlander, 1981b; Dorn, in preparation).

We have also observed that copper (and to a lesser extent nickel and zinc) concentrations are significantly higher in varnishes that, according to their locations, are fairly old. For example, varnishes in desert pavements in the Poverty Hills, Owens Valley, California and in thick patches on sandstone in Snow Canyon, Utah, have copper concentrations of approximately 11 per cent and 13 per cent, respectively. Buried varnishes from the Neville formation and Indian Springs Basin, Davis Mountains, Texas (specimens contributed by Julian Hayden, 1981), have copper levels, sometimes exceeding 20 per cent, compared to contemporary surface varnishes in the same area, in which copper concentrations are under 2 per cent (Figure 11). That copper and nickel accumulate with time in older manganese-rich varnishes is consistent with the widely noted phenomenon of cation scavenging



**Figure 8** Varnish from hyper-arid regions.

**A** Lamellate dusky-brown surface varnish on a terrace on the eastern edge of the Sinai Peninsula, Israel. Note the incorporation of some clay platelets into the varnish. 10 μm scale bar.

**B** EDAX comparison of the normal dusky-brown surface varnish (upper panel) in 8A with occasional black varnish in micropits (lower panel). This illustrates point to point variability in the surface microchemistries of some arid varnishes.

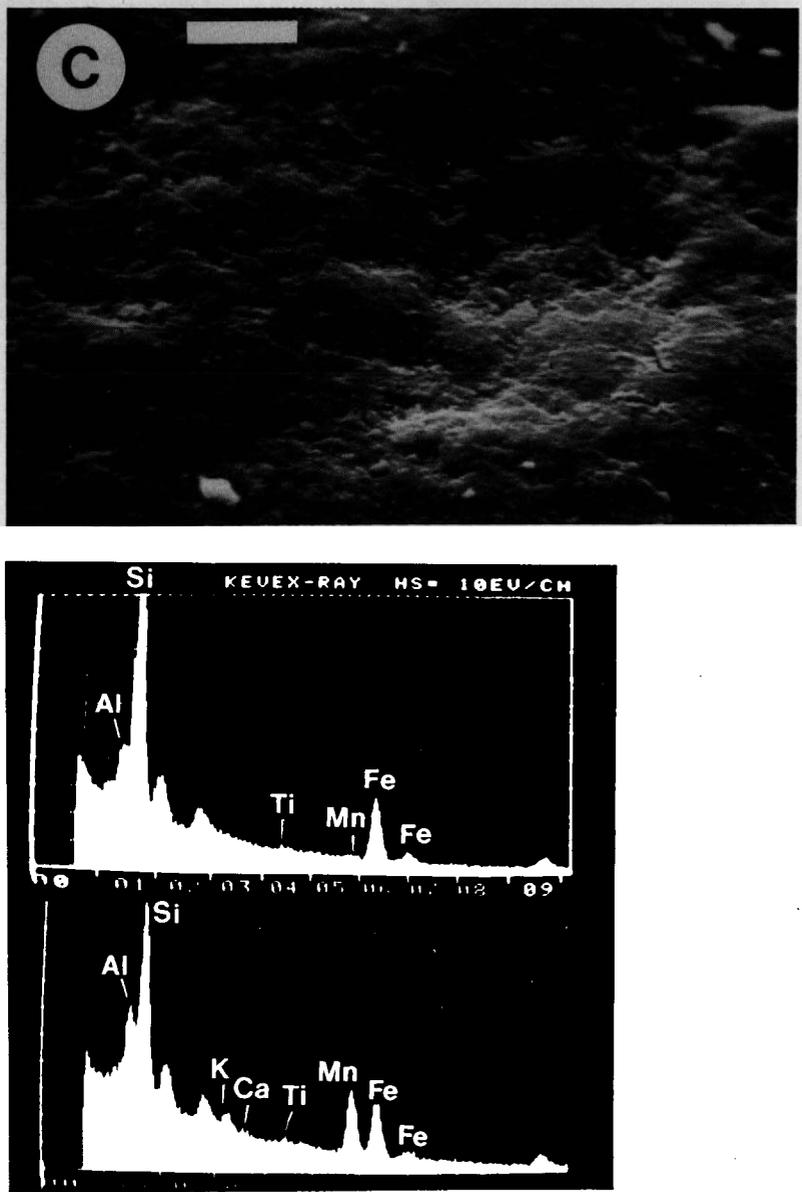
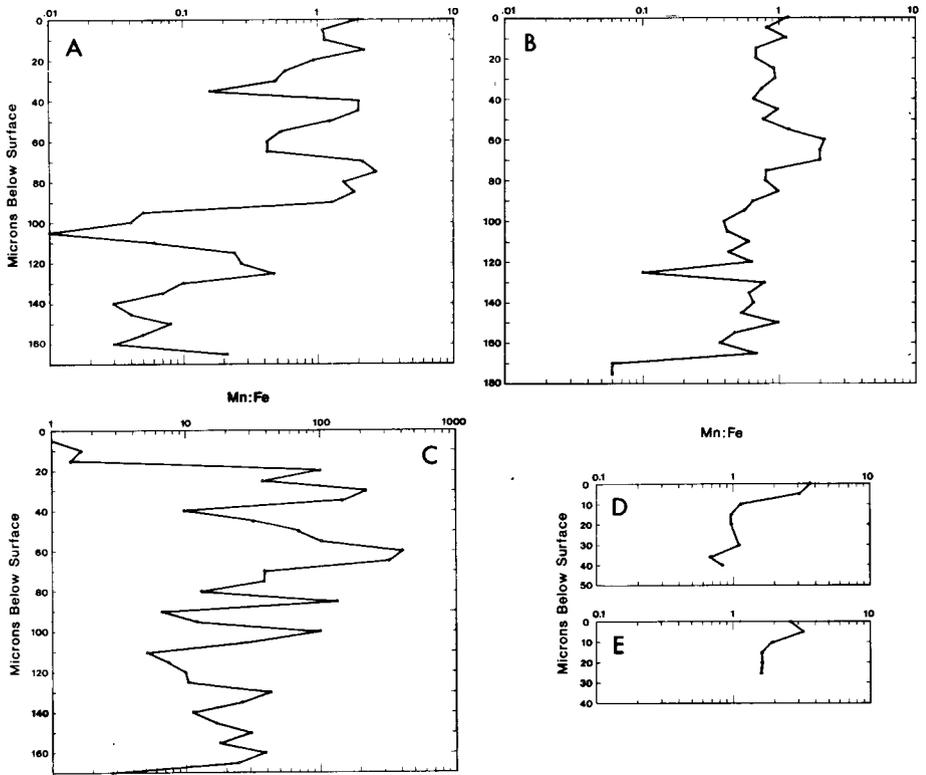


Figure 8 continued

C Orange surface lamellate varnish from Quillagua, Antofagasta Province, Chile. 10  $\mu$ m scale bar.

D EDAX comparison of orange surface varnish (upper panel) in 8C with Mn-rich black varnish in some micropits (lower panel). This also demonstrates microchemical point to point variability in arid varnishes, as well as superior microenvironmental conditions in rock surface depressions for Mn-enhancing microorganisms.



**Figure 9** Microchemical laminations in varnish. Electron microprobe data showing Mn:Fe ratios in transects normal to the varnish surface. Both Mn-rich and Mn-poor laminations are visible in the arid varnishes (A-D); however, only Mn-rich laminations are noted in the semi-arid to humid varnish (E). All transects were taken in micropits.

**A** Salt Springs, Mojave Desert, California on quartzite.

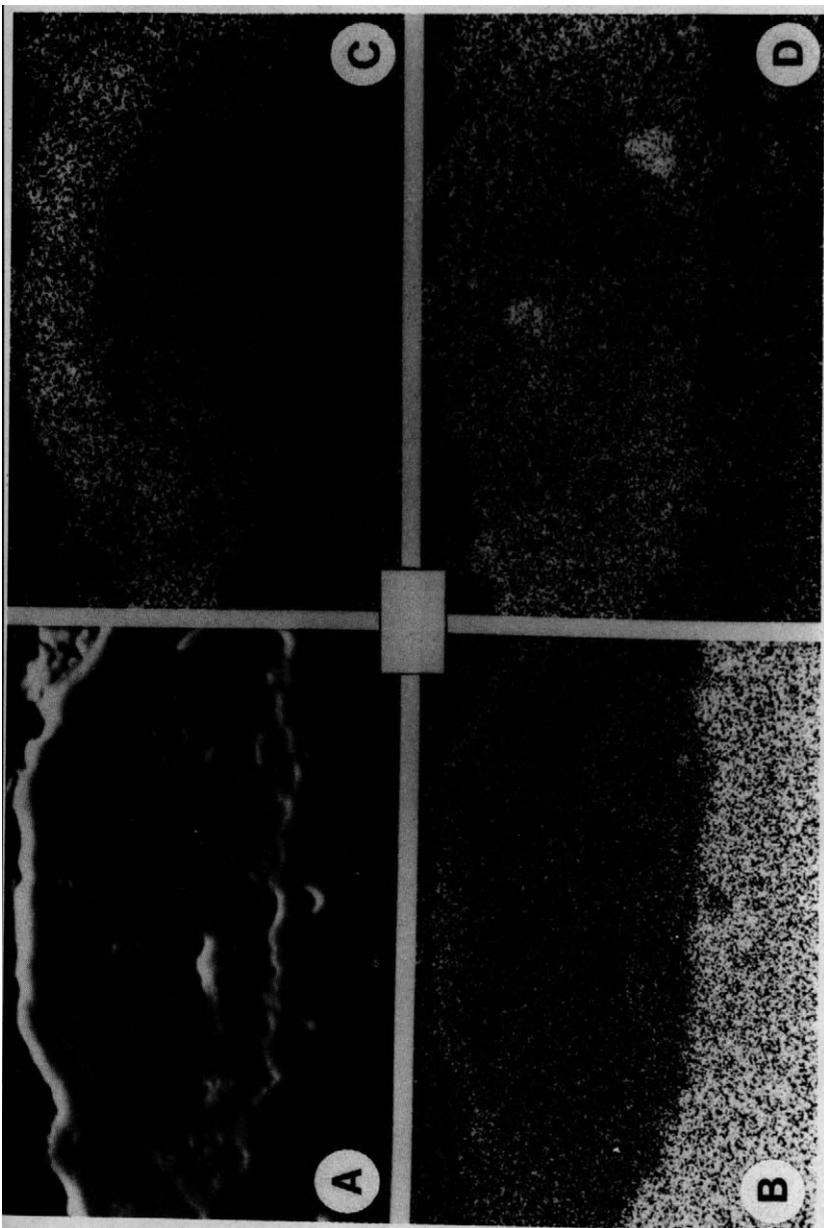
**B** Grimes Point Petroglyph Site, near Fallon, Nevada on andesite.

**C** Snow Canyon, Utah on sandstone.

**D** Tule Elk Viewpoint, Owens Valley, California on granite.

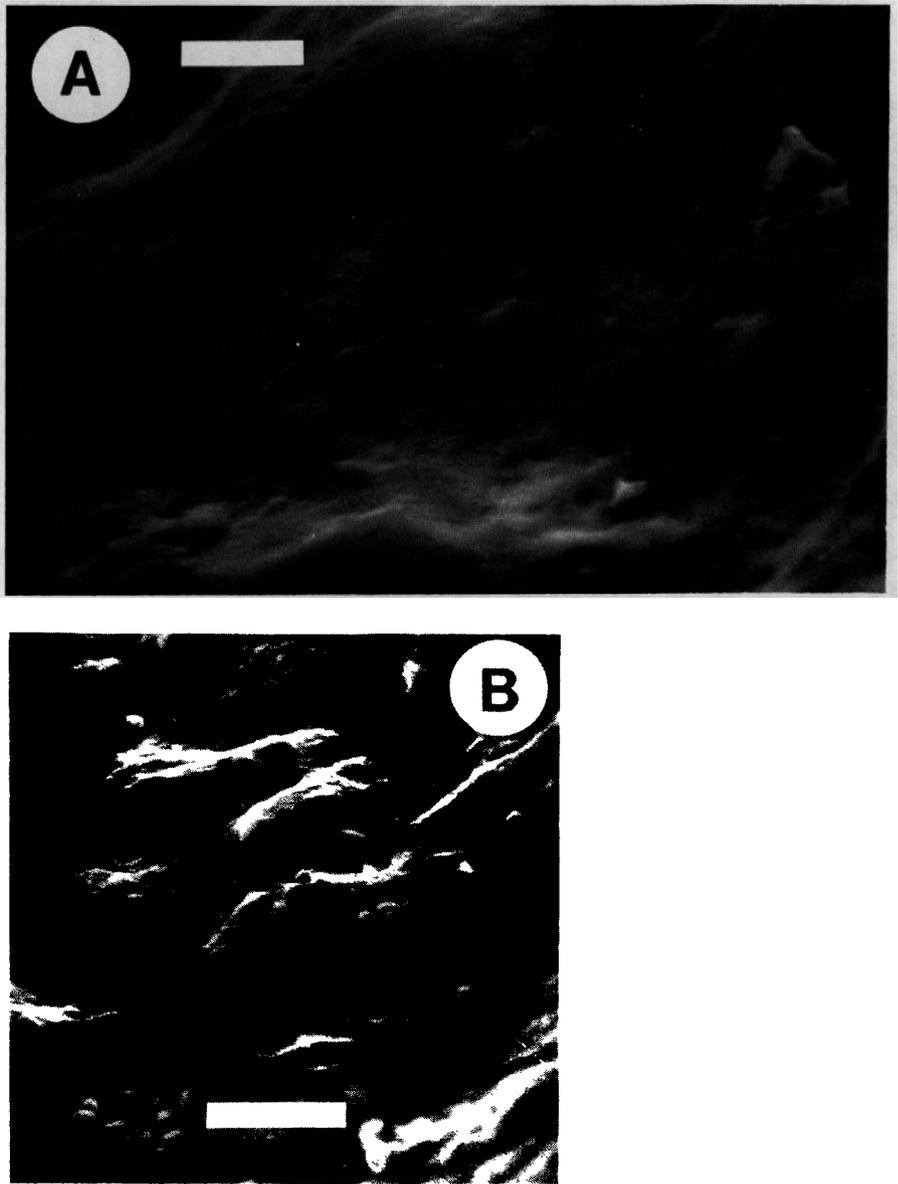
**E** Schulman Bristlecone Pine Grove, White Mountains, California on silicified dolomite.

In the case of E, there have been no periods of sufficient alkalinity to produce Mn-poor laminations since the inception of varnishing.



**Figure 10** Macrochemical laminations in varnish. X-ray maps of manganese, iron, and silica of varnish on quartzite from Salt Springs, Mojave Desert, show laminations that are less detailed than those in Figure 9A. 20  $\mu\text{m}$  scale bar for all images. Background levels are in the upper left and right corners of the X-ray maps.

A SEM of varnish on the heartrock. B Silica map showing a fairly even concentration throughout the varnish. C Manganese map showing an outer layer with manganese enrichment over an inner layer relatively poor in manganese. In the corresponding SEM image (Figure 10A) the Mn-rich layer appears better cemented than the subjacent portion of the varnish. D Iron map showing a fairly even distribution, with the exception of nodes of concentration, possibly reflecting trapped detritus.



**Figure 11** Copper accumulation in a buried varnish.

A SEM of lamellate black varnish on a cultural flake (contributed by Julian Hayden, 1981) from an 11 foot depth in alluvium of the Neville formation, near Limpia Creek, Davis Mountains, Texas. 20  $\mu\text{m}$  scale bar.

B Black varnish on an artifact from Hayden's (1976) Malpais period (contributed by Julian Hayden, 1981), collected on the surface above the pit where 11A was collected. 10  $\mu\text{m}$  scale bar.

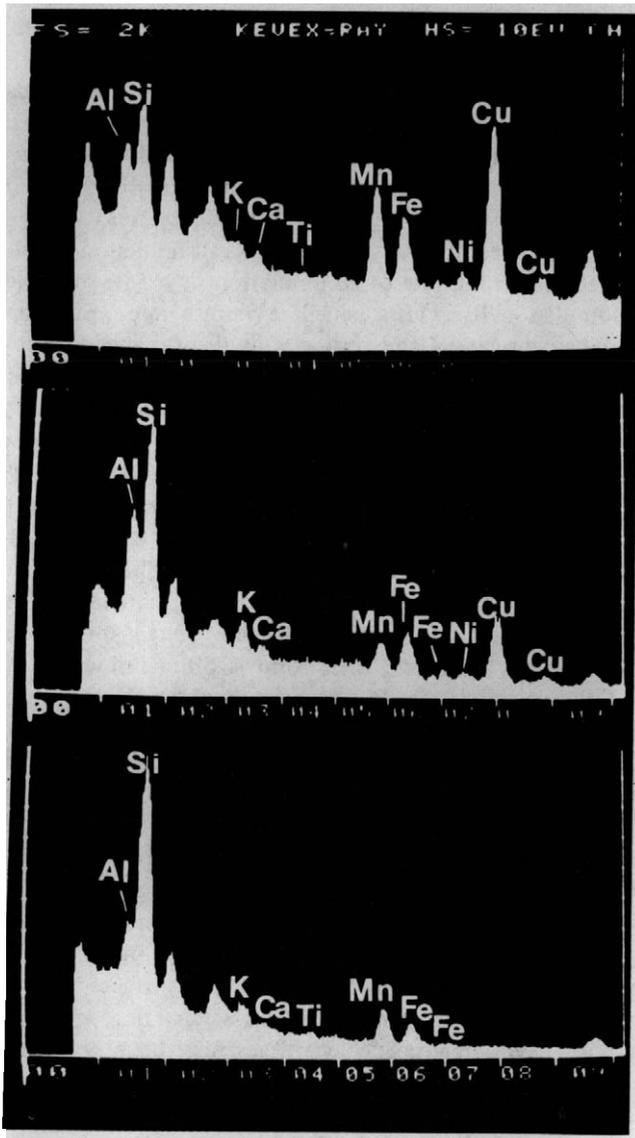


Figure 11 continued

C EDAX comparison of different areas on the copper-rich buried varnish (upper two panels) with the surface varnish (lowest panel). The middle panel is the usual chemistry of the buried varnish, but micropits rich in Mn are often very rich in Cu (top panel).

by manganese oxides and hydroxides (e.g. Jenne, 1968; Robinson, 1981).

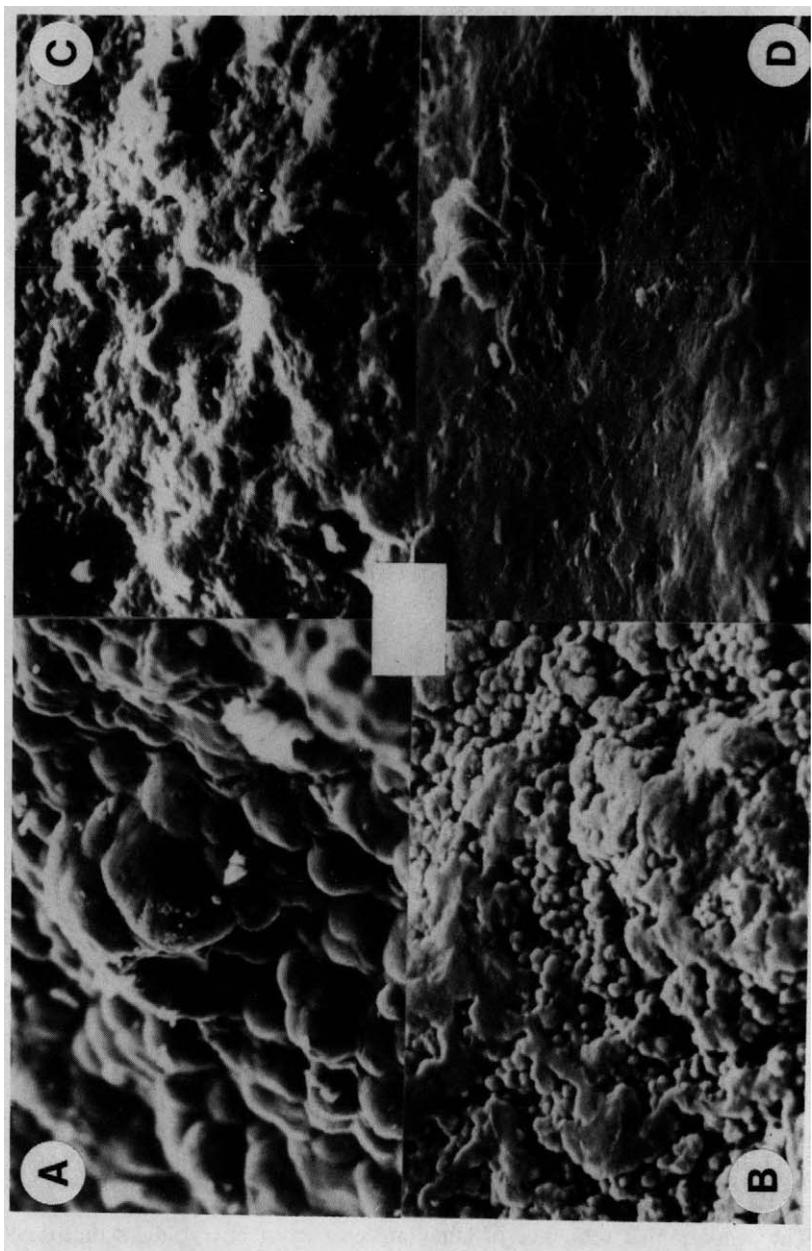
*c Micromorphology:* The surface micromorphology of rock varnish is variable and complex. However, after scanning electron microscope (SEM) examination of hundreds of varnish specimens from a wide range of environments, we have established some facts that suggest the possibility of using rock varnish micromorphology on the micron scale as a paleoenvironmental research tool.

Two factors seem to be dominant controls of varnish micromorphology: the rate of clay accumulation and the rate of accumulation of oxides at nucleation points. When clay accumulation is rapid, a lamellate varnish micromorphology develops (Figure 12D). When the lateral and vertical growth of manganese and iron oxides and hydroxides at biogenic nucleation points is significantly more rapid than clay accumulation, a botryoidal varnish develops (Figure 12A). Semi-botryoidal micromorphologies form when clay incorporation and oxide accretion operate with approximately equal potency (Figure 12B). Therefore, the basic varnish micromorphologies form a continuum from lamellate (clay-rich) to semi-botryoidal to botryoidal (clay-poor). More than half of the varnish surfaces we have examined with scanning electron microscopes can be fitted into this continuum. However, a significant number of surfaces have rough textures than cannot be classified as lamellate, semi-botryoidal, or botryoidal. These rough intermediate varnishes (Figure 12C) are usually thin, and their form is often influenced by the micromorphology of the underlying rock, and sometimes by abundant detrital organic and inorganic material on the varnish surface.

Botryoidal, semi-botryoidal, intermediate, and lamellate micromorphologies compose the vast majority of varnish surfaces, but highly unusual types do exist and are examined in greater detail elsewhere (Dorn, in preparation). It should also be noted that the tendency of varnish to begin accreting at scattered small nucleation points (Figure 13A) is consistent with a microbial origin.

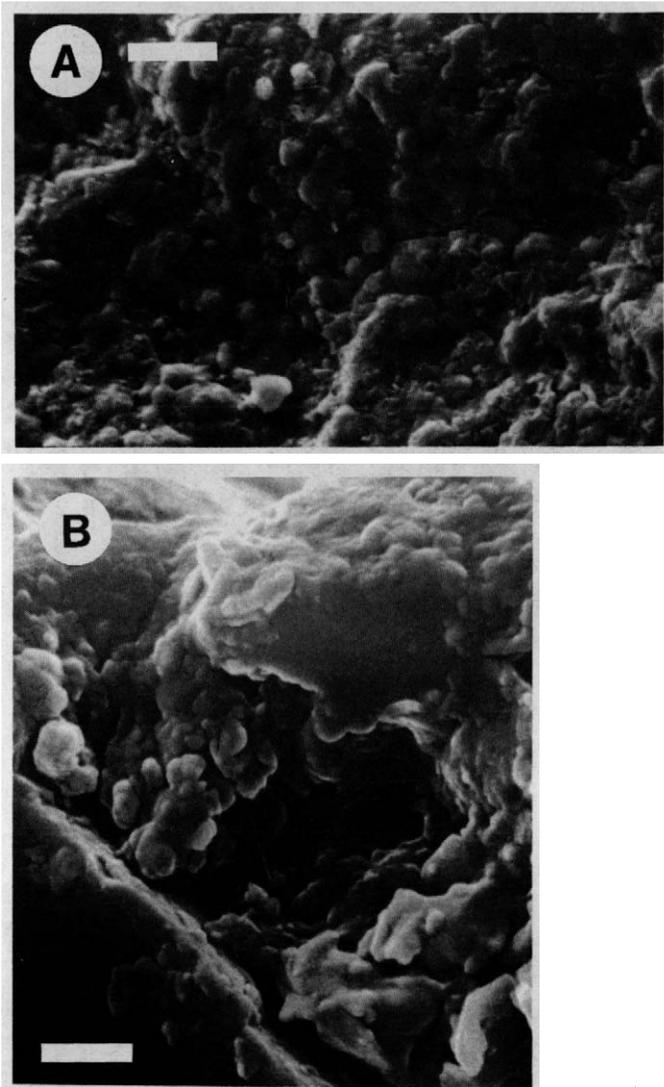
Energy dispersive analysis of X-ray (EDAX) in conjunction with SEM observations reveal that botryoidal varnishes are typically rich in oxides and hydroxides and relatively poor in clay. They are common on rock surfaces in alpine locales and in semi-arid regions, but do occur in arid regions where microenvironmental factors create a clay-poor environment. Such varnishes may be very black, but are not highly reflective. Botryoidal layers are found in the varnish of arid regions, and probably reflect periods with low levels of atmospheric dust, presumably intervals of greater moisture availability.

Lamellate varnish micromorphologies are characteristic of two settings: areas of extreme aridity where dust is frequently mobilized, and stream channels, where turbid flows supply abundant micelles to be adsorbed onto river rocks. The varnishes of the Sinai and Atacama Desert are lamellate (Dorn, 1982; Oberlander, 1982), as is much Death Valley varnish. Lamellate varnish may be either manganese-rich, and highly reflective, or iron-rich and non-reflective (unless glazed with silica). Nichol and Phillips (1965) have commented on the high reflectivity of manganese oxides in other types of occurrences. It may be that the varnish oxides (e.g.



**Figure 12** Micromorphological continuum of varnish.

**A** Botryoidal varnish from Tule Elk Viewpoint, Owens Valley, California. 20  $\mu\text{m}$  scale bar. **B** Intermediate (semi-botryoidal) varnish from a microplit on varnish collected in Darwin Canyon, California. 10  $\mu\text{m}$  scale bar. **C** Intermediate (rough) thin varnish on greywacke collected in Olympic National Park, Washington. 10  $\mu\text{m}$  scale bar. **D** Lamellate varnish from shorelines of Lake Lahontan, south of Fallon, Nevada. 10  $\mu\text{m}$  scale bar.



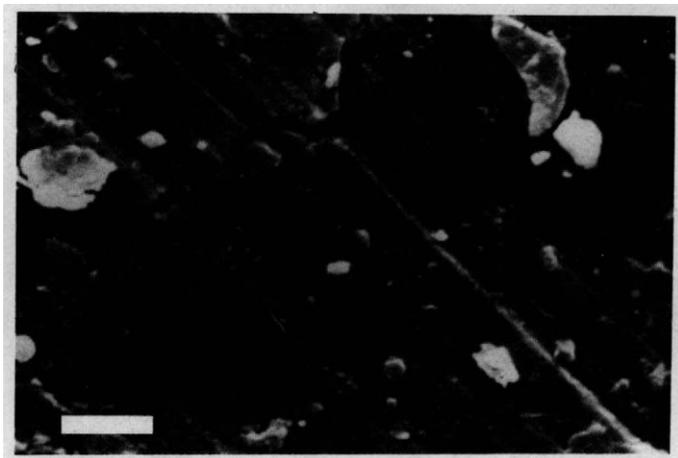
**Figure 13** Semi-botryoidal surface and buried micromorphology.

**A** Intermediate (semi-botryoidal) dusky-brown varnish from the summit of the Old Man Range, central South Island, New Zealand (collected by Barry Fahey). The tiny bumps are Mn-rich nucleation sites in a depression on a predominantly iron-rich varnish. 10  $\mu\text{m}$  scale bar.

**B** Edge micromorphology of varnish in a micropit, same site as Figure 7. The top section is the lamellate surface, folded over during breakage to obscure the buried lamellate structures revealed in Figure 7. The lower structures are botryoidal in tendency. The stratigraphic sequence of lamellate on top of botryoidal structures probably indicates a change in the aeolian environment from one that is clay-poor (dust limited, presumably more moist) to a relatively clay-rich (dusty) environment. 2  $\mu\text{m}$  scale bar.

birnessite) are highly reflective when deposited with a roughly parallel orientation. Sequences of alternating lamellate and botryoidal layers within varnish seem to imply changes in local abundance of ambient clay, with Mn-rich botryoidal layers forming during more humid, less clay-rich phases, and lamellate layers indicating accentuated aridity. Such sequences are not uncommon in varnish from the southwestern United States (e.g. Figure 13B).

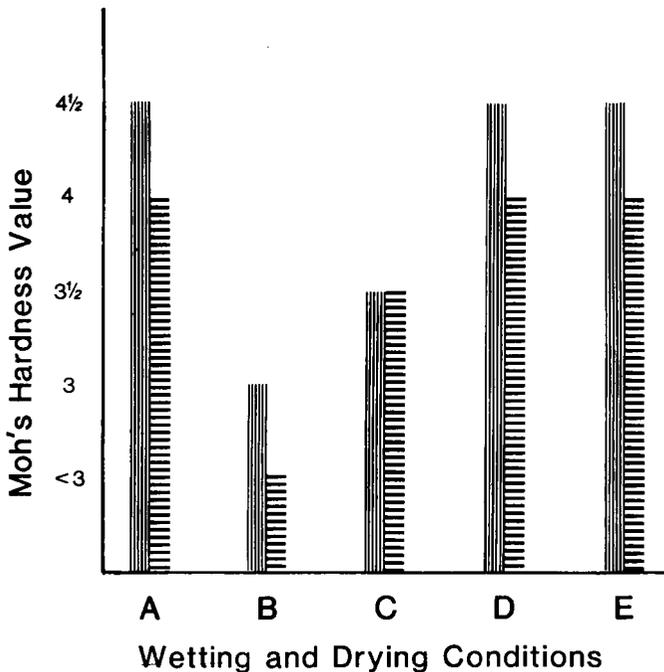
We find that no major varnish characteristics, including micromorphology and sheen, are related to aeolian abrasion, as has been proposed by several authors. We have observed shiny varnishes in subsurface environments exposed in excavations. Our laboratory experiments in dust blasting natural lamellate varnishes produce an artificial surface that has no resemblance to natural varnishes (Figure 14). Where aeolian activity is dominant, rock varnish cannot form, or if formed previously under different conditions, is removed (e.g. Rahm, 1974, 117). We should stress that the sometimes shiny appearance of varnish occurs when the varnish is both lamellate (smooth) in its primary form and rich in manganese (e.g. Figure 12D). In the absence of either of these two requirements, varnishes have a dull lustre (e.g. Figures 12A and 12C).



**Figure 14** SEM observation of a laboratory dust-blasting experiment illustrating the lack of similarity between natural glossy varnishes (see Figure 12D) and this experimentally dust-blasted surface from the same site as 12D. 10 $\mu$ m scale bar.

Dust and wind activity do have an effect on the appearance of varnish surfaces on the micron scale. Wind related abrasion tends to remove delicate asperities on varnish surfaces. Ragged clay edges and other delicate features of submicron scale rarely appear, except at locations where micelles are newly accumulating and on subsurface and laboratory varnishes that are protected from aeolian activity (Figures 2A and 2B). Wind action puts a final light touch on a surface micromorphology that is dominantly controlled by other factors.

*d Hardness:* The abrasion resistances of 16 arid and 17 non-arid black surface varnishes were tested using the scratch hardness test under 30x to 45x magnification (Figure 15). The hardness of rock varnishes collected in the field ranges from under 3 to 6 1/2 on Moh's scale of hardness, more variable than previously reported (Laudermilk, 1931, 55; Engel and Sharp, 1958, 489). Arid varnishes resist abrasion better than those from more humid environments. Laboratory wetting decreases the durability of varnish (Figure 15) by increasing the thickness of the adsorbed water layer on varnish clay, which in turn reduces the resistance to shear stresses (Martin, 1962). The adsorbed water responsible for the reduction in varnish shear strength is probably bulk water, described by Martini (1981) as Region C. Subsequent drying recovers the original hardness. Higher temperatures during laboratory drying produced greater resistance more quickly (Figure 15). Therefore, in addition to the degree of cementation of clays by manganese and (to a lesser extent) iron, the abrasion resistance of varnish is affected by prolonged wetting. That varnish durability is lessened with wetting partially explains why rock varnish is so dominant in deserts.



**Figure 15** Abrasion resistance of manganese-rich rock varnish from 16 arid and 17 non-arid locations. The abrasion resistances were determined using the scratch hardness method. Moh's hardness values were derived for arid (vertical lines) and non-arid (horizontal lines) varnishes for the following conditions: A) as collected in the field; B) after 24 hours of soaking in tap water; C) after 24 hours of air drying following 24 hours of wetting; D) after one month of air drying following 24 hours of wetting; and E) after 24 hours of oven drying at 105°C following 24 hours of wetting.

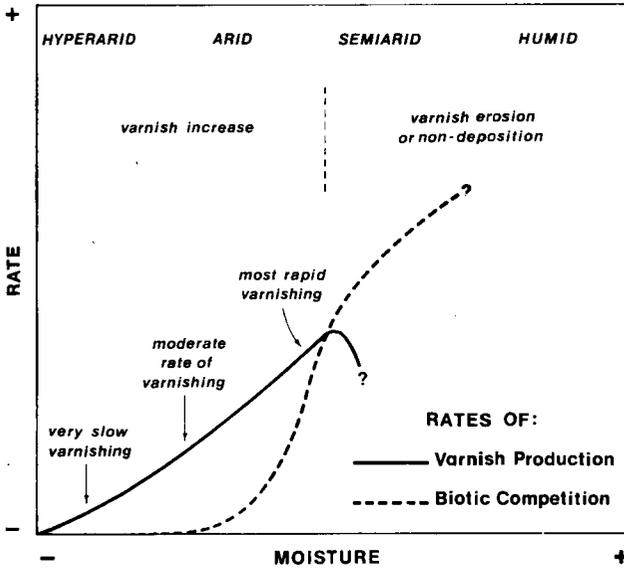
*e Rate of formation:* As noted earlier, in arid regions rock varnish forms very slowly. However, manganese-rich rock varnish has been observed to form a complete coat within a century in riverine environments (Carpenter and Hayes, 1978; Butzer *et al.*, 1980, 1208), and within 40 years in periglacial, arctic, and antarctic environments (Klute and Krasser, 1940; Budel, 1960, 46; Holleman, 1963; Washburn, 1969; Figure 6C). In our laboratory replication experiments, where varnish limiting factors were absent or controlled, biogenic varnishes formed within six months (Dorn and Oberlander, 1981a).

A biogeochemical model explains the apparent contradiction between widely disparate growth rates in some humid and arid environments. One of the most important limiting factors in the development of black rock varnish is the rate of manganese oxidation and accretion by microorganisms. In the desert environment the deficiency of water slows the rate of varnish formation, and the paucity of organic matter encourages some mixotrophic microorganisms to oxidize manganese more rapidly (e.g. Bolotina, 1976; Nealson and Ford, 1980; Schweisfurth *et al.*, 1980) and to grow with less competition from faster growing heterotrophic microorganisms that require relatively abundant levels of organic nutrients. In our culturing experiments we found that slow-growing manganese-oxidizing bacteria on desert varnish require a small amount of organic material. True chemolithotrophic and heterotrophic bacteria do not compete for organic nutrients (Fredrickson and Stephanopoulos, 1981). However, in a transition zone between environments relatively rich and poor in organic nutrients, competition for such nutrients from faster growing heterotrophs may play a significant role in limiting the development of manganese concentrating mixotrophic microorganisms.

Where varnish develops rapidly in humid regions, as on barren rock surfaces, the microenvironment tends to be low in organic matter, but has abundant moisture and sometimes a copious supply of ambient manganese. This allows manganese oxidizing microorganisms to produce varnish at a rapid rate, without competition from competitors that require organic nutrients.

This simplified relationship between moisture, competition, and the rate of varnish formation is modelled in Figure 16. While the factors shown may be the major influences on growth rates, biogeochemical factors such as Eh, pH, concentration of clays and copper, physical nature of the substrate, and other micro-environmental factors also affect the rate of varnish formation. For instance, high pH levels would slow or halt the rate of manganese enhancement by microorganisms (e.g. Uren and Leeper, 1978; Schweisfurth *et al.*, 1980), thus allowing the development of a ferric rather than manganic varnish, relying on less effective iron cementation of clays, rather than manganese fixation. Mulder (1972) put the effective range of manganese oxidizing bacteria between pH 5 and 8. Our culturing experiments indicated the upper limit to be between 7.5 and 8, which is consistent with the results of Schweisfurth *et al.*, (1980, 179).

Microorganisms other than mixotrophic manganese-oxidizers in low-nutrient environments are known to play a role in producing manganese films in non-arid environments that are rich in organic nutrients (e.g. Ljunggren, 1953). We stress



**Figure 16** Hypothetical model of the rate of varnish production, based solely on moisture input and biotic competition.

the role of microbes that favour environments poor in organic nutrients, because these are the organisms that seem to be dominant in the production of 'desert' varnish (Dorn and Oberlander, 1981a).

#### 4 *Geographic distribution*

A biogeochemical model of rock varnish formation explains the observed geographic distribution of rock varnish – both its characteristic occurrence in arid regions and occasional occurrence in more humid environments.

*a Arid rock varnish:* There is no single reason why rock varnish is so widespread in deserts. The paucity of organic matter encourages the oxidation of manganese by mixotrophic microorganisms, and at the same time reduces competition from heterotrophic microorganisms. Increased stability of rock surfaces allows time for varnish development. Brief wetting and very thorough drying promotes the diffusion and fixation of manganese, bacterial adhesion, and increased abrasion resistance of varnish films (Figure 15).

However ubiquitous the occurrence of rock varnish in deserts, it is far from a continuous coating. Even in deserts Mn-rich rock varnish is patchy from mountain range to mountain range, from outcrop to outcrop, from stone to stone, and often from point to point on a single rock fragment. The appearance of tiny black dots precedes the formation of a complete varnish coating. This spotty distribution on several scales is characteristic of biogeochemical coatings. In contrast orange

varnishes, which appear to form almost entirely by physicochemical processes, coat surfaces much more uniformly, merely altering in hue and intensifying in value with the passage of time. When the physicochemical conditions are suitable for the formation of orange varnish, a uniform stain begins to appear. When the biogeochemical conditions are appropriate for the formation of black varnish, it forms in the manner of separate nucleation points, growing in size, and eventually merging.

While the locations of limestone solution front communities are influenced by macrorelief and aspect (Krumbein and Jens, 1981, 31), rock varnish seems to be unsystematic with regard to these two variables. An important and generally neglected factor affecting the micro-distribution of arid rock varnish is the periodic exposure of a well developed crack varnish. Black varnishes initiated in widened rock crevices are often darker than varnish on exposed surfaces, where the environmental stresses may be greater or more persistent. The first author observed dusky-brown surface varnishes that appear to be 'eroding' in an environment as dry and alkaline as the Sinai Peninsula. This 'eroding' appearance seems to be largely a function of weathering of the underlying heartrock. Another influence on varnish distribution on rock surfaces is the location of periodic streams of water, which can result in particularly thick and lustrous varnish films.

As Elvidge (1979) and Elvidge and Collet (1981) stressed, widespread occurrences of desert varnish are associated with drier, more alkaline regions. However, the alkalinity of deserts is important not for the genesis of varnish but for varnish preservation. The lack of acidity allows the varnish manganese, oxidized by microorganisms and fixed by wetting and drying (Reddy, 1973), to be preserved. Thus the formation of desert varnish causes deserts in general to be an important biogeochemical sink for manganese. We have presented the concept of rock varnish as manganese sink and concluded that once manganese is oxidized and fixed in rock varnish, only extreme pH/Eh shifts to a more acidic environment would cause chemical erosion of the manganese in desert varnish (Dorn and Oberlander, 1981c). The stability of rock varnish is supported by the observations of Hem (1964, B10), Glazovskaya (1971, 236), and Allen (1978, 751), who feel that 'desert varnish' is eroded only by sandblasting and mechanical weathering of the underlying heartrock.

A slight increase in moisture availability should increase the rate of manganese-rich varnish formation in very arid regions. When such an increase in moisture is sufficient to generate more organic nutrients and to trigger competition, the rate of varnish formation should drop off. We have noted in the Mojave, Great Basin, and Atacama deserts that the development of lichens and other acid-secreting organisms is inimical to arid rock varnish. Acid rain should also erode varnish. However, according to our model, additional neutral-pH rainfall should not by itself cause varnish deterioration. Thus, when a semi-arid environment alters to a semi-humid environment, the increases in microbial competition, organic acids, rainfall to leach the reduced manganese, and weathering of the underlying rock should all act together to erode varnish. In isolation near-neutral rainfall would actually cause varnish enhancement. We mention this in reply to previous interpretations of

of varnish deterioration when specimens are transferred to humid climates (e.g. D. Martin cited by Grant, 1967).

We have undertaken experiments to assess the effect of increased moisture on varnish stability as theoretical Mn-stability predictions based solely on Eh-pH stability field diagrams are known to be inadequate in some natural systems (e.g. Feagley, 1979; Sholkovitz and Copland, 1981). The expected colour changes in varnish subjected to manganese leaching would be from black to light chocolate to dusky brown and eventually to dull orange.

In one ongoing experiment, chips of desert varnish from Death Valley were exposed to the moist Berkeley environment on a cement surface for two years. There was no visible change in the samples, and optical and SEM/EDAX examination revealed no chemical or micromorphological change in the exposed pieces (Figure 17). Half of the exposed pieces were then put under a fern that produces acidic leaf litter. These chips have noticeably deteriorated in two years. After four years of exposure to the humid Berkeley environment, the remaining pieces appear unchanged.

In another experiment, varnish chips from humid and arid environments have been exposed to running tap water in an open system for over six months with no change observable by optical or SEM/EDAX examination, except for the inception of one to 10 micron diameter manganese nucleation sites on one varnish chip from the Mojave Desert.

Grant (1967, 44) cited an experiment by D. Martin, in which varnished rocks from China Lake, California, were taken to Santa Rosa, California. After being left outdoors for two years, the rocks reportedly lost their varnish. The specific type of varnish and the environment in which the rocks were placed was not mentioned. If the varnished rocks were situated near vegetation in an organic-rich environment, varnish erosion would be expected. This point is significant, as Martin's experiment has been used by recent researchers (e.g. Bard, 1979; Elvidge, 1979) to support the hypothesis that varnish developed in a dry altithermal period, even though the specific environmental factors were not reported. Hunt and Mabey (1966) and Hunt (1972) expressed the opposite view, that the formation of desert varnish requires an increase in the moisture supply, with varnish developing in pluvial periods or where water seepage currently occurs in deserts.

Our interpretation of the evidence is that the rate of Mn-rich varnish growth is dependent on a number of variables, only one of them being the moisture regime. How environmental oscillations affect varnish growth depends mainly on how the change of environment affects factors limiting bacterial oxidation of manganese. The limiting factors appear to be organic acid formation, abundant organic matter on rock surfaces, low levels of ambient clay, microbial competition, and high pH levels. However, if the combined varnish-limiting factors are not adequate to inhibit microbial oxidation of manganese, an increase in moisture should accelerate the rate of formation of manganese-rich varnish.

The hyper-arid environments we sampled have a dominance of dusky-brown or orange varnish. Black varnish is present only as coatings in small pits, or as

microscopic flecks or spots. Semi-arid to sub-humid environments generally have too many varnish-limiting factors operating to permit the formation and persistence of a good cover of rock varnish, consequently most subaerial black varnish is in microenvironments poor in organic nutrients, such as talus and alpine moraines that are composed of coarse debris. Arid to semi-arid environments, having a small but measurable annual moisture supply but less than the critical value to develop varnish-limiting factors, appear to maintain the best developed black desert varnish.

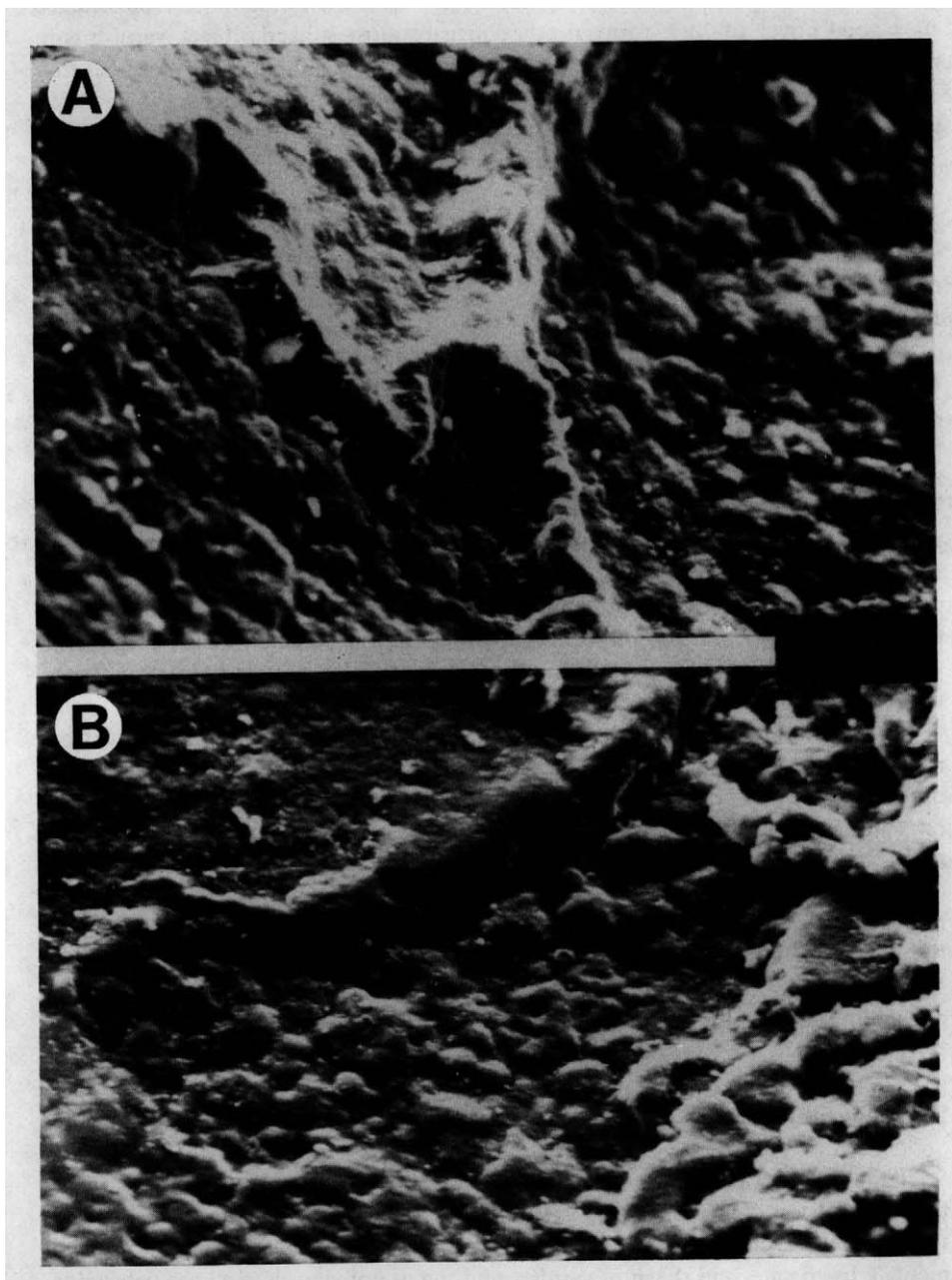
*b Non-arid rock varnish:* Factors involved in the distribution of non-arid rock varnish are much more complex, because the ecological requirements of the organisms that oxidize manganese in non-arid environments are much more varied than in deserts.

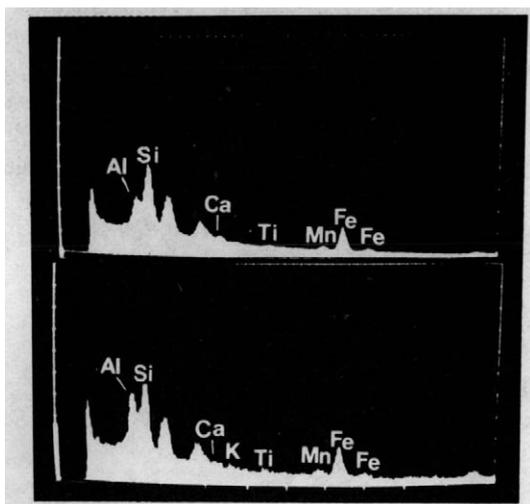
Certain mixotrophic manganese-oxidizing organisms produce varnishes in locations of low organic matter and low light. We have noted extensive deposits of sub-surface varnish developed in fractures and along partings in regolith in many exposures in mesic California and other more humid areas. Similar observations of subsurface oxide films have been recorded by Hunt (1972) and Weaver (1978). The low levels of organic nutrients in rock fractures reduces heterotrophic competition. Percolating meteoric waters supply basic cations and metallic ions as well as moisture. The lack of sunlight removes competition from photoautotrophs, common on humid rock surfaces. Riverine varnish, varnish on subsurface soil peds and rocks within the soil, some morainal and high alpine varnishes, subglacial and proglacial varnishes, as well as other rock varnishes are examples of coatings that fall into this mixotrophic category.

Nevertheless it seems likely that some manganese-rich coatings on rock surfaces may be deposited by non-mixotrophic organisms such as algae (e.g. Francis, 1921), bryophytes (e.g. Ljunggren, 1953), and lichens. Using an electron microscope we have analysed manganese-rich coatings adjacent to and interfingering with *Staurothele umbrenes* lichen streaks at Tamarack Creek, Yosemite National Park. The chemistry of this rock varnish is almost identical to some iron-poor desert varnishes in the Mojave Desert. In oxide weight per cent, normalized to 100 per cent, the analysis of this lichen-associated varnish is: SiO<sub>2</sub> 38.65, MnO 36.69, Al<sub>2</sub>O<sub>3</sub> 16.49, CaO 6.60, FeO and Fe<sub>2</sub>O<sub>3</sub> 0.52, BaO 0.91, and Na<sub>2</sub>O 0.14. The factors controlling the distributions of such deposits requires investigation.

#### IV Conclusion

Over the last 150 years desert varnish research has been concerned mainly with the problems of the constituents and origin of varnish; the source of varnish elements; the uniqueness of varnish in deserts; the climatic requirement, chemical environment, growth rate, and sheen of varnish; and the use of varnish as an age determination technique. Only recently, with the advent and use of new analytical tools, have some of these problems been partially solved.





**Figure 17** SEM/EDAX observations of the Death Valley to Berkeley deterioration experiment.

**A** Fresh semi-botryoidal varnish collected on the darkest surface of a talus cone, just south of Copper Creek Fan, Death Valley National Monument. The filamentous structures are fungal hyphae being covered with varnish. 20  $\mu\text{m}$  scale bar.

**B** Predominantly semi-botryoidal varnish after being exposed to the Berkeley environment for two years. 20  $\mu\text{m}$  scale bar.

**C** EDAX comparison of the fresh varnish (upper panel) in 17A with the exposed varnish (lower panel) in 17B.

Thus we conclude that there is little significant micromorphological or chemical difference between the original desert varnish and varnish weathered in a mesic environment, in the absence of abundant organic matter.

We have presented a biogeochemical model of varnish formation that treats 'desert varnish' as one of the many biogeochemical ferromanganese deposits on terrestrial rock surfaces, properly termed *rock varnish*. These coatings have in part a biological origin. Our biogeochemical model and the concept of desert varnish as a manganese sink provide the theory for the use of desert varnish in a wide variety of endeavours: age determination, palaeoenvironmental research, and geochemical prospecting.

If rock varnish is to be developed as a significant research tool, it is important that it be characterized by future investigators in standardized terms. Ideally, a complete description of varnish at a site should include as many as possible of the following: whether the varnish is a crack, bottom (ventral), or surface (dorsal)

type; a description of the environmental setting; Munsell colour characterization; bulk chemical and pH analysis of scraped varnish; scanning electron microscope image of microstructures on the surface and at the broken edges of varnish with corresponding energy dispersive X-ray analyses; pH and chemical analysis of dust in contact with varnish and of soils near the collection site; mineralogy of varnish constituents; scratch hardness data; organic matter determination; data on microchemical variations in a transect from the surface through the varnish layer to the underlying substrate; as well as any other characterization that the researcher finds appropriate. Varnish research is, in fact, a stratigraphic problem on the micron scale.

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### *Acknowledgement*

We thank Julian Hayden, Barry Fahey, and Chris Elvidge for contributing samples for analysis. This research was supported in part by National Science Foundation grant SES80-24555 and the University of California.

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