FACTORS THAT INTERFERE WITH THE
AGE DETERMINATION OF ROCK VARNISH

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Abstract: Over the past few years the rock varnish literature has proliferated. More than a dozen research groups in at least six countries are now investigating the potential of rock varnish as a Quaternary dating technique for geomorphical and archaeological studies. New backscattered electron microscopy imagery of varnishes from southwestern North America illustrates the need for great caution in the selection of samples for all varnish dating methods. Nine general factors that may interfere with varnish dating are presented. For varnish dating to be successful, these factors must be evaluated by careful examination of samples in the field and by analyses of many cross-sections in the laboratory. [Key words: rock varnish, Quaternary dating methods, geomorphology, backscattered electron microscopy, geochronology.]

INTRODUCTION

Rock varnish, a dark thin (<1 to >500 microns) layer composed of clay minerals, manganese, and iron oxides, and a variety of minor and trace constituents, forms on rocks in the terrestrial weathering environment. In acid environments, varnish accretes over periods of thousands of years, where age has been established independently by historical, radiocarbon, and K-Ar dating (Blackwelder, 1948; Dorn and Oberlander, 1982; Whalley, 1983; Dorn, 1989). Rock varnish has been used for over a century in geomorphological (e.g., Merrill, 1898; White, 1924; Blackwelder, 1954; Hunt and Mabey, 1966; Bull, 1977) and archaeological studies (e.g., Basedow, 1914; Heizer and Baumhoff, 1962; Hayden, 1976) to assign relative ages to natural and human-manufactured surfaces in arid lands.

Significant advances have been made recently in the numerical and calibrated dating of rock varnishes. Paleomagnetism (Potter, 1979), uranium-series (Knauss and Ku, 1980), scavenging of heavy metals (Dorn and Oberlander, 1982), depth profiles of trace elements (Bard, 1979), layering of Mn-Fe laminations (Dorn, 1984, 1990), radiocarbon dating of carbonate rinds over varnishes (Dragovich, 1986), recognition of ash in varnish (Harrington, 1988), and K-Ar dating of varnish clays (Dorn, 1989) have been proposed. Most geomorphological and archaeological applications, however, have used cation-ratio (CR) dating (e.g., Dorn and Oberlander, 1981; Dorn, 1983, 1986, 1988, 1989; Dorn and Whitley, 1984; Dorn et al., 1986, 1987a,b, 1988a,b; Glazovskiy, 1985; Harrington, 1987, Harrington and Whitney, 1987; Whitney et al., 1988; Detheir et al., 1988; Pineda et al., 1988; Liu

and Zhang, 1990) and accelerator radiocarbon dating (Dorn et al., 1989) of rock varnish.

In the recent flurry of interest in varnish-dating methods, many have pointed out that rock varnish is incredibly complex: it is chemically, texturally and mineralogically heterogeneous on a scale of meters, millimeters, and microns (Dorn and Oberlander, 1982; Dorn, 1990; Dragovich, 1988a,b; Smith and Whalley, 1988; Krinsley and Manley, 1989; Krinsley and Anderson, 1989; Raymond et al., 1988a,b, 1989). The purpose of this paper is to add support to these concerns by urging caution to those trying to derive an age signal from rock varnish. We used backscattered electron microscopy (BSE) and several other techniques listed below to illustrate new and previously recognized factors that may interfere with the dating of rock varnish.

METHODS

Aspects of the analytical techniques and methods used to obtain the information in this paper are discussed below. Secondary electrons (SE) are conventionally used to form images in scanning electron microscopy (SEM), producing topography or relief with a simulated three dimensional view of the object. Generally, a rough object is coated with a heavy metal, observed on a cathode ray screen, and then photographed. Backscattered electron production (BSE) involves making a flat, well polished, uncovered thin section of a rock or other object. The section is then coated with carbon in a vacuum evaporator and observed, as above. In the BSE method, however, some of the electrons striking the section are reflected out of the specimen; the number of these electrons divided by the number of primary electrons that strike the target gives the backscattered coefficient which varies with the atomic number (Z) of the target.

Values of this coefficient range from about 5% for pure, light elements such as carbon (Z = 6), to about 50% for pure, heavy elements such as gold (Z = 79) (Robinson and George, 1978). When the target consists of a homogeneous mixture of several elements, as is the case with most minerals, an average atomic number applies. Thus, quartz and feldspar appear relatively darker than minerals containing heavy elements such as pyrite and ilmenite (Pye and Krinsley, 1984). Compositional contrast is seen most clearly on polished surfaces, because topographic contrast is suppressed. Robinson and Nickel (1979), for example, were able to distinguish between Fe_7S_8 and Fe_9S_{10}. The differences in contrast between individual minerals make it possible to observe very fine textural relations, with a spatial resolution of about 0.1 microns, and atomic number resolution of 0.1Z. Texture, combined with energy dispersive X-ray analysis (providing chemical information on individual minerals) and X-ray diffraction (bulk mineralogical data), permits the determination of individual minerals in section. The BSE technique produces approximately the same kind of information that one is able to obtain from a petrographic microscope, but with a resolution of more than ten times the 2000 Angstrom resolution of the light microscope.

The electron beam in both an SEM and an electron microprobe produces a wide range of radiation, including X-rays, which are characteristic of the elements

present, and their intensity is an approximate linear function of concentration. Energy dispersive X-ray (EDX) and wave length dispersive X-ray (WDX) analyses provide a means of determining the chemical composition of very small volumes on the surface of polished thin sections of rocks or mineral mounts. Units may be mounted on SEMs and electron microprobes so that chemical analyses and photographs of the areas analyzed can be accomplished almost simultaneously. In general, WDX is more accurate, can analyze more elements, but is slower than the EDX system (Long, 1967; Goldstein et al., 1981).

RESULTS AND DISCUSSION

What is the difference between a varnish sample that will yield a reliable and reproducible date and one that will not? Dorn et al. (1989) and Dorn (1989) defined certain empirical factors that can be assessed in the field or the laboratory that have caused a varnish-age signal to deviate from a control K-Ar or radiocarbon date. These nine factors are discussed and illustrated below; the first three (unstable surfaces, different types of varnish, and particular microenvironments) may be assessed in the field; the remaining six factors in the laboratory using electron microscopy.

Unstable Surfaces

When a rock surface spalls, flakes, or undergoes disintegration, a varnish age reflects only the time since weathering. Fluvial or aeolian abrasion can also restart the varnish clock, or can incompletely remove a varnish (Fig. A), yielding an uncertain age signal. For instance, silicic lava flows frequently tend to be highly vesicular, and thus unstable (Anderson and Krinsley, 1989). Weathering might therefore be very rapid, and until a porous vesicular layer has weathered down to a less porous layer, varnish would not be preserved. In addition, range fires can induce spalling of rock surfaces (Gillespie, 1987), and hence the varnish. Even in deserts as dry as southern Nevada this can be a problem, as Spaulding (1985) reports the occurrence of dwarf conifer woodlands from over 45 ka to ~ 10 ka where only desert scrub vegetation now grows. The varnish that is present on unstable surfaces is usually quite thin and would produce erroneously young ages. The key is to be aware in the field of what composes a constructional geomorphic surface, as compared to a weathered surface.

Different Types of Varnish

Thorough testing of age signals in varnish has been conducted at sites of known age only for black, manganese-rich varnishes (Mn:Fe ratio ≥ 0.3) formed in a subaerial environment from the deposition of airborne fallout. There are, however, many other types of Mn-rich and Mn-poor varnishes (Dorn and Oberlander, 1982) that have not been well tested. For example, orange varnishes formed on the undersides of cobbles in a desert pavement (Mn-poor, Mn:Fe ratio < 0.3) have potential for radiocarbon dating (Dorn et al., 1989). Figure B presents varnish
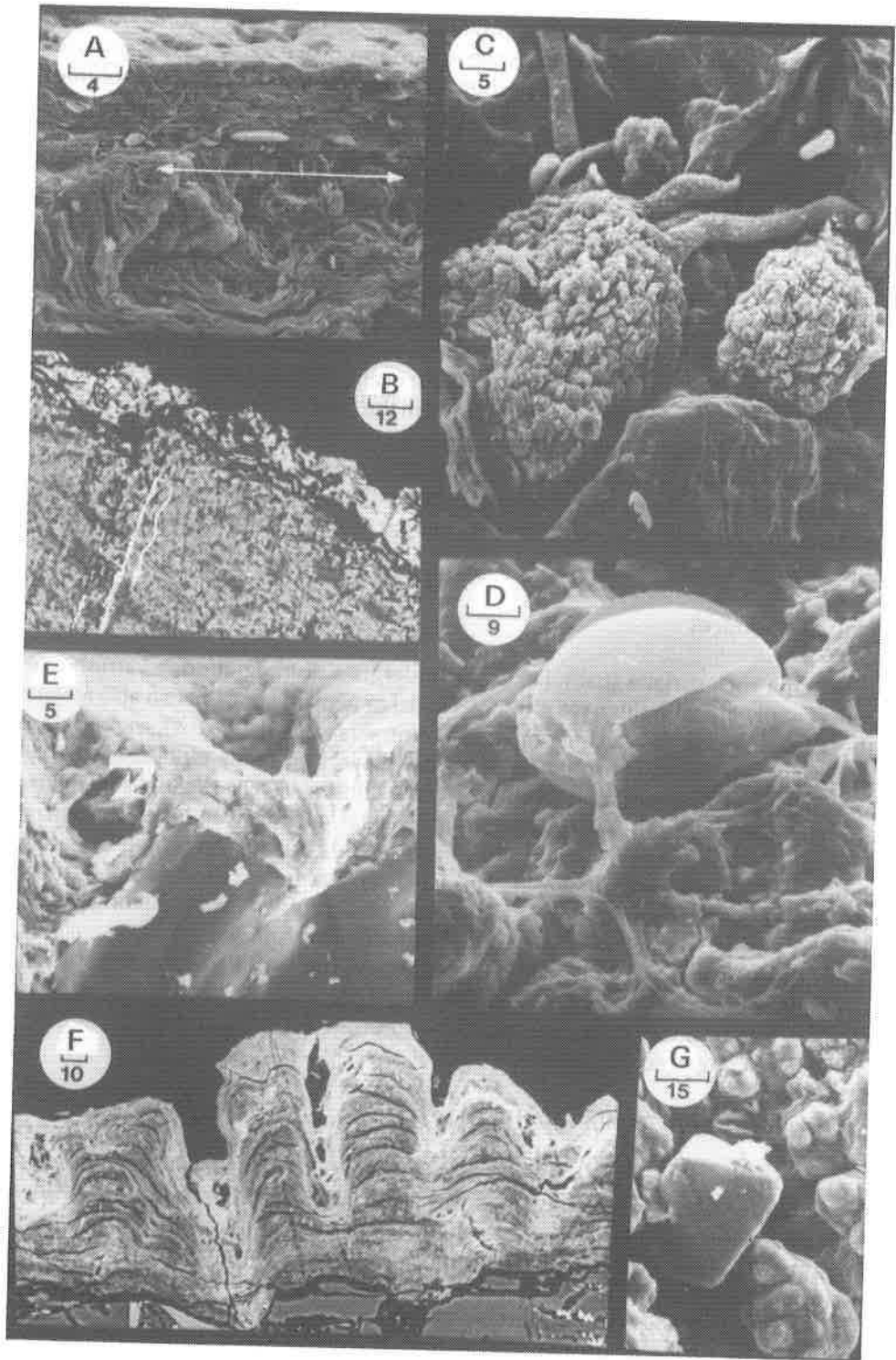
Plate 1.

Fig. A. SE (secondary electron) section illustrating a rare situation where aeolian abrasion has not completely eroded varnish; sample from a protected depression in a rock from the Cronese Basin, Mojave Desert, California. Three phases of varnish build-up and two (possibly three) phases of varnish erosion are recorded. First, the lower layer was deposited. Second, the area beneath the double arrow was eroded, most likely by the secretion of organic acids by fungi or lichens. Third, varnish filled in this depression. Fourth, aeolian abrasion truncated the varnish above the double arrow. Fifth, a newer layer of varnish has been deposited above the double arrow. Sixth, it is possible that some aeolian abrasion has occurred on top of the newest varnish layer.

Fig. B. BSE (backscatter) section of varnish from the west-central side of the Marble Mountains, SE Mojave Desert, California. The varnish is the lighter, thin ridge running roughly from upper left to lower right. The gray material is the supporting rock. A bright layer of varnish has penetrated from the surface into the rock through a crack (left of the wavy arrow). There is also another crack to the left, which contains considerably less varnish.

Fig C. SE image of microcolonial fungi (Staley et al., 1982; Taylor-George et al., 1983) from near Florence, Arizona. Depressions around fungi are probably due to the secretion of organic acids.

Fig. D. SE image of pollen grain resting on the surface of varnish, Hanaupah Canyon alluvial fan, Death Valley, California. Note the abundant filaments of fungi which may be obtaining organic matter from the pollen grain. As pollen and fungal filaments are buried by accreting varnish, organic matter is incorporated.

Fig. E. SE image of varnish on quartz, from Death Valley Canyon alluvial fan, Death Valley, California. One erosional hollow has been filled in by younger varnish (including the barium-rich crystal identified by the arrow), and would not be visible to a purely surface inspection. Another hollow is more recent, and would be visible during SE examination of the varnish surface.

Fig. F. BSE section of rock varnish from Death Valley Canyon alluvial fan, Death Valley, California. Note the roughly parallel layering near the rock/varnish contact, and the layering within the "stromatolite-like" structures. The very bright layers are generally high in Mn, while the black layers are open cracks. The depressions between the stromatolitic structures were probably formed by biological erosion of the varnish. After their formation, they have been subsequently filled in by younger/Mn-rich varnish. The depression on the far left side has been completely refilled. The other depressions are at various stages of refilling.

Fig G. SE view of the surface of varnish collected from the Bishop Tuff, on the Sherwin Grade, north of Bishop, California. Note the crystal of calcium carbonate that has dropped into the depression in the varnish. This particular varnish was a few centimeters away from an eroding vein of calcrete that had formed in an eroded outcrop of the Bishop Tuff.

Scale bar in microns.

formed in a rock fracture beneath a subaerial surface. 'Crack' varnishes have both Mn-rich and Mn-poor zones (Dorn and Oberlander, 1982; Dorn and Dragovich, 1990).

Crack varnishes pose a potential problem when the overlying rock spalls off, exposing varnish formed in a rock crevice. Crack varnishes can appear better developed to the naked eye than a varnish formed in an exposed subaerial environment, if the lithology is smooth like quartzite or chert. Dust and microbes are slow to adhere to these smooth rock types in an exposed subaerial environment. A rock crevice, however, is a more favorable environment for varnish adsorption. Alternatively, if the rock is weathered granite that readily sheds grus, or foliated metamorphic rock that salt-weathers rapidly, varnish formed in a crevice will typically be better developed than varnish developed on such easily weathered exposed surfaces. The danger in CR dating here rests in preferentially sampling these seemingly better varnished surfaces that originated in crevices. The crack environment is a totally different cation-leaching environment than the exposed surfaces. For example, cation ratios [(K+Ca)/Ti] of crack varnishes in the Coso Range were about 30% higher than subaerial varnishes from the same lava flow (Dorn, 1989).

Particular Microenvironments

Empirical data indicate that proximity to lichens, abundant detrital organic matter and cryptogamic soil lower varnish cation ratios, probably due to enhanced leaching from more abundant organic acids (Dorn, 1989). Underhangs, extremely rough lava flow surfaces, and proximity to desert soil surfaces, in contrast, increase cation ratios as compared to values for varnishes collected over a meter above soils. The reasons for this are uncertain, but they may involve different inputs of cations close to a soil and differential fluid movement over the surface of rock with a significantly different geometry (Dorn, 1989).

Organisms That Erode Varnish

Microcolonial fungi (Staley et al., 1982; Fig. C), cyanobacteria, and filamentous fungi (Fig. D) can lower cation ratios (Dorn, 1989) and make radiocarbon dates too young (Dorn et al., 1989). This is because younger varnish is deposited in the depressions created by the biogeochemical erosion (Figs. E,F,L). In addition, organic acids probably enhance the cation-leaching process (e.g., Truter, 1973; Talibudeen, 1981).

Anomalously High Concentration of Elements in Cation Ratios

All of the elements in the CR of (K+Ca)/Ti may occur in anomalous concentrations which vary tremendously from one place to another in the varnish (Dragovich, 1988a,b; Dorn, 1989). In many cases, concentrations of what appear to be different types of detrital minerals are observed at the micron-level. These anomalies are detectable by examining varnish scrapings and varnish cross-sections by electron microscopy (Figs. G,H,I,J,K). High levels of these cations are

produced by proximity to a source: for example, calcrete rubble for calcium (Fig. G). Varnishes influenced by these elemental anomalies should not be used for dating. It should also be noted that when these elements are studied in varnish cross-sections with the ion microprobe, they vary irregularly from top to bottom (O'Hara et al., 1989), just as they do in electron probe studies (Dragovich, 1988a,b; Dorn, 1990a).

A more difficult problem involves barium. Ba, sometimes contained in crystals of sulfate, is common in arid varnishes (Engel and Sharp, 1958; Lakin et al., 1963; Potter and Rossman, 1979; Bard, 1979; Duerden et al., 1986; Dragovich, 1988a,b; Dorn, 1990a). Typical values for bulk chemical measurements are <1% (Bard, 1979; Duerden, 1986; Dorn et al., 1990), but may reach over 4% on a micron-scale using a wavelength dispersive microprobe (Krinsley and Anderson, 1989; Krinsley, unpublished data). If an EDX unit attached to a scanning electron microscope is used to analyze varnish cation ratios (Harrington and Whitney, 1987), the Ti K-alpha and Ti K-beta peaks overlap the Ba L-alpha and Ba L-beta peaks, respectively (Harrington et al., 1989). When the concentration of Ti is considerably less than Ba, which can happen frequently in arid varnishes, the Ba and Ti peaks partially overlap, are difficult to separate, and may produce a false cation ratio. It is possible to deconvolute the overlapping lines, but resolution is considerably better if WDX is used. When the same varnish scrapings are analyzed by other methods, proton-induced X-ray emission, WDX, and inductively coupled plasma, virtually identical chemical analyses are obtained for varnish cation ratios (Dorn et al., 1990).

Surface Topographies That Trap Aeolian Detritus

Since rock varnishes collected for dating are from subaerial exposures, the material that accumulates is aeolian fallout, or from material that has weathered from rock surfaces that may be topographically above the sampled varnish. If surface topography is irregular, coarse angular aeolian fallout is more readily trapped (Figs. G,H,I,J). More than a third of surfaces we have examined fall into this category.

Many surface depressions are produced by erosion of varnish, typically by the secretion of acids by organisms such as microcolonial fungi (Figs. C,L). Material that fills in these depressions is younger than the surrounding varnish and much younger than what is of interest, the geomorphic or archaeological exposure of the underlying rock. The SEM method of CR dating only views varnish from the top (Harrington and Whitney, 1987). This source of contamination is, therefore, not assessed, since infilled depressions are often not visible by viewing the surface (Fig. E).

It is necessary to evaluate multiple varnish cross-sections to check for these infilled depressions before varnish material is chemically analyzed for dating. If infilled depressions are found, the sample should not be used. This is not just a theoretical concern. When samples that contained these infilled depressions were analyzed for CR dating or radiocarbon dating, the varnish ages were significantly younger than the control dates for the same site (Dorn et al., 1989; Dorn, 1989).
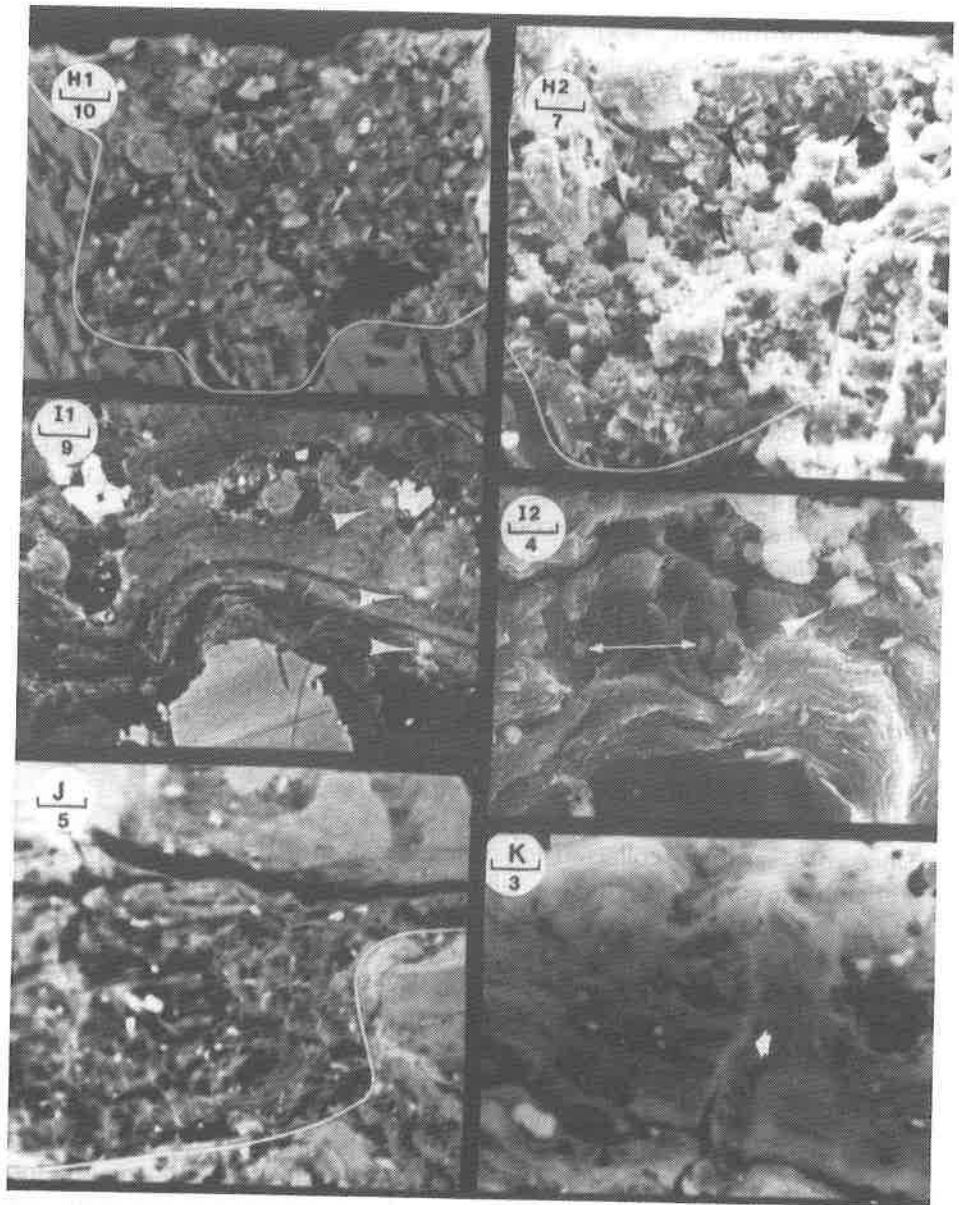
Plate 2.

Figs. H1 and H2. Deposits of relatively deep varnish in rock depressions, illustrated by both BSE (H1, from the Marble Mountains, Mojave Desert, California) and SE (H2, from Crater Flat in southern Nevada). Note that the texture is not layered, but a chaotic mix of typical varnish constituents (Mn-Fe oxides and clays) and a high concentration of aeolian detritus (for example the barium-sulfate crystals identified by the arrows in H2). This 'granular' texture may have been produced during rapid aeolian deposition in a rock depression, as opposed to slow rates of growth of the more layered varnishes. The rock/varnish boundary is indicated by the line. Immediately to the left and right of these pockets, the varnish is less than 5 microns thick.

Figs. I1 and I2. Layered structures of varnish at the rock/varnish boundary, illustrated by BSE (I1, from Coso basalt flow 28; see Dorn, 1989 for site) and SE (I2, also from Coso basalt flow 28). The arrows in I1 identify microprobe points; the uppermost arrow is adjacent to a bright (high Z contrast) grain that is barium sulfate. There is a change in the structure of the varnishes, that occurs about the position of the uppermost arrows in I1 and I2. Below is layered varnish; above is more porous varnish. There are a series of paleodepressions at this level that have been infilled by varnish and aeolian detritus. The arrows in I2 point to barium-rich detritus trapped in paleo-depressions. The bright detritus in I1, iron oxide and barium sulfate, appear to be trapped in paleodepressions. Because the layering appears to be truncated in I1, the depressions probably represent a paleoerosional episode.

Fig. J. BSE section from Death Valley, California. The line represents a textural change from layered varnish on the right to more porous, granular varnish on the left. There are three possibilities to explain the change. This may represent a former erosional depression, filled in by the porous varnish (hypothesis favored by Dorn). It could represent a diagenesis, whereby the porous-granular varnish is gradually plugged by the mobilization and reprecipitation of Mn-Fe oxides, and layering is produced (hypothesis favored by Krinsley and Anderson). Alternatively, it could represent two different styles of varnish deposition, occurring side by side. Dorn cites the difficulty in reorganizing the chaotic texture on the left into layers. Krinsley and Anderson observe that above the big crack (from right to left, three-quarters to the top of the image), porous layers merge into well-cemented and bright layers enriched in Mn-Fe oxides.

Fig. K. BSE section of varnish from Death Valley Canyon alluvial fan, Death Valley, California. Note the partially filled fracture in the middle of the image (highlighted by arrow). The crack, which is perpendicular to the layering, is partially filled with high Z material and vanishes into a layered, mound-like structure of high Z material. Krinsley and Anderson also feel that in places, the high Z material in the filled cracks appears to have moved parallel to the layering. Dorn feels the layering is depositional. Note that aeolian detritus has been trapped as these layers accrete. Most of this detritus is low Z material, probably quartz or feldspar, while a few are high Z material, perhaps barium or iron.

Scale bar in microns.

The type of varnish that yields ages similar to control dates is evenly layered, showing regular laminae which are not eroded (Figs. M,N,O,P).

Another implication of these surface irregularities for the dating of rock varnish concern with the nature of the constituents that accumulate in pockets filled with younger material. Given proximity to the source of a titanium or calcium anomaly, for example, the aeolian detritus will be rich in these elements (Fig. G). If the varnish is collected from a desert area that produced abundant barium sulfate, such as a playa surface, barium is found in high concentrations in these erosional pockets (Figs. E, H2, I, J, S, Z4). A geochemical signal such as abundant barium indicates that a sample should not be used for dating.

We see no evidence that the constituents of the varnish are derived from the rock immediately underlying the varnish (Figs. E, I2, P, Q), as has been postulated by some (Merrill, 1898; Blackwelder, 1954; Smith and Whalley, 1988), although there is occasionally some weathering of rock at the rock/varnish interface and there very well may be occasional inclusions of rock material in the varnish (Figs. Q,R,S). Our elemental analysis of various varnishes (Krinsley and Anderson, 1989) using the electron probe with WDS supports the view that there is no elemental exchange between the varnish and the rock (e.g., Potter and Rossman, 1977, 1979; Allen, 1978; Dorn and Oberlander, 1982; Elvidge and Iverson, 1983; Raymond et al., 1988b).

Cracks Oriented Normal to the Varnish Surface

Such cracks were first noted by Whalley (1983, 1984) and are illustrated here by Figures Q, T, U, V and W. We agree that these may be created by wetting and drying, which could cause expansion and contraction; the same set of processes is linked to fixing manganese and iron oxides with mixed-layer illite-montmorillonite clays in varnish (Potter and Rossman, 1977, 1979). It is also possible that organisms such as microcolonial fungi, cyanobacteria, or lichen thalli could weaken the varnish and promote fracturing during wetting and drying. It is possible that different distributions and abundances of these cracks might influ-ence fluid movement and the cation-ratio dating of varnish. This needs to be assessed under controlled circumstances.

Remobilization of Varnish Constituents

Some of the fractures which are oriented parallel or subparallel to the varnish and the underlying rock may be the result of sample preparation (Fig. Q), but many of these predate sample collection and have partial or complete fillings, and 'bridges' high in Mn and Fe resulting from mobilization and reprecipitation after fracturing (Fig. K,T,U,V2,W). These phenomena have not been reported pre-viously, but are common in selected samples observed thus far from southwestern North America. BSE imagery of highly porous varnish (e.g., Figs. E,H,I,J,K,R,S,T,V) illustrates ready avenues for the movement of fluid through varnish.

It is also possible that thin laminae of Mn-Fe rich layers may represent the mobilization, lateral movement, and reprecipitation of oxides. Here, the authors'

preliminary interpretation diverges. All authors believe the appearance of some discontinuous laminae may reflect diagenetic processes that gradually plug the pore spaces and fractures in the layered varnishes (e.g., smaller arrows in Fig. Q, V2, W). Anderson and Dorn (following Perry and Adams, 1978) believe that the layered laminae that are laterally continuous (Figs. M,N,O,P) are produced by depositional processes. All of the authors agree that the mobilization cannot be over significant distances, or the Mn and Fe would be leached completely out of the varnish, something that clearly does not occur.

There is strong chemical evidence that at least some varnish constituents are mobile, inferentially supporting the BSE observations of constituent mobility. Abundant empirical data indicate that K and Ca are leached from varnish over time (Dorn and Oberlander, 1981; Dorn, 1983, 1989; Glazovskiy, 1985; Harrington and Whitney, 1987; Pineda et al., 1988; Liu and Zhang, 1990). Under certain geochemical circumstances, Ti, which is generally insoluble, may also act as a mobile cation. A few of the acid waters and brines for which analyses were given by White et al. (1963) contain more than 1, 000 $\mu g/l$ of titanium, indicating that Ti is mobile under highly acidic and extremely basic circumstances. Chelation of titanium by organic complexes (organic ligands) might also increase its solubility (Hem, 1985). It is possible that chelating complexes and organic acids, produced by the decay of organisms (Figs. C,D,X), could mobilize titanium in rock varnish on a micron scale. The pH values of bulk samples of black varnishes from 97 sites in western North America average 7.3±0.7 (Dorn, 1990), and therefore Dorn believes that titanium mobility is unlikely to influence the chemistry of bulk samples of black varnish.

For varnish radiocarbon dating to work, the organic matter dated must reflect the time of varnish deposition. Any remobilization would inject younger carbon. Stable carbon isotope analyses of the type of organic matter that yields good radiocarbon dates (similar to control dates) indicate that the dated organic matter is derived from the adjacent plants (Dorn and DeNiro, 1985). Dorn et al. (1989) assumed that the organic matter successfully dated was composed of fragments of organic material trapped mechanically as varnish accumulates (Figs. X, Y) and organic matter locked in the lattice structures of Mn-oxides. In contrast, organic carbon adsorbed to clays appears to move through varnish, and if the sample is not treated with HF to remove the younger organic matter adsorbed to clays, the radiocarbon dates are too young (Dorn et al., 1989).

Our observations reveal it is unlikely that the dated organic matter is derived from Mn-oxides, as speculated by Dorn et al. (1989); instead all the dated material must be from trapped detrital fragments (Figs. X,Y). If Mn is mobilized in the evenly layered laminae used in varnish radiocarbon dating, even for short distances, younger carbon could become incorporated into the reprecipitated oxides. Since the varnish radiocarbon dates processed with HCl, HF, hydroxylamine hydrochloride, and dithionite do match the control dates (Dorn et al., 1989), it means either there is not enough organic carbon trapped in the Mn-oxides to influence significantly the radiocarbon date or that the Mn-oxides in the layered laminae are not remobilized. Preliminary transmission electron microscopic (TEM) data suggest that the Mn occurs as very simple oxides, and is at least partly isolated from the
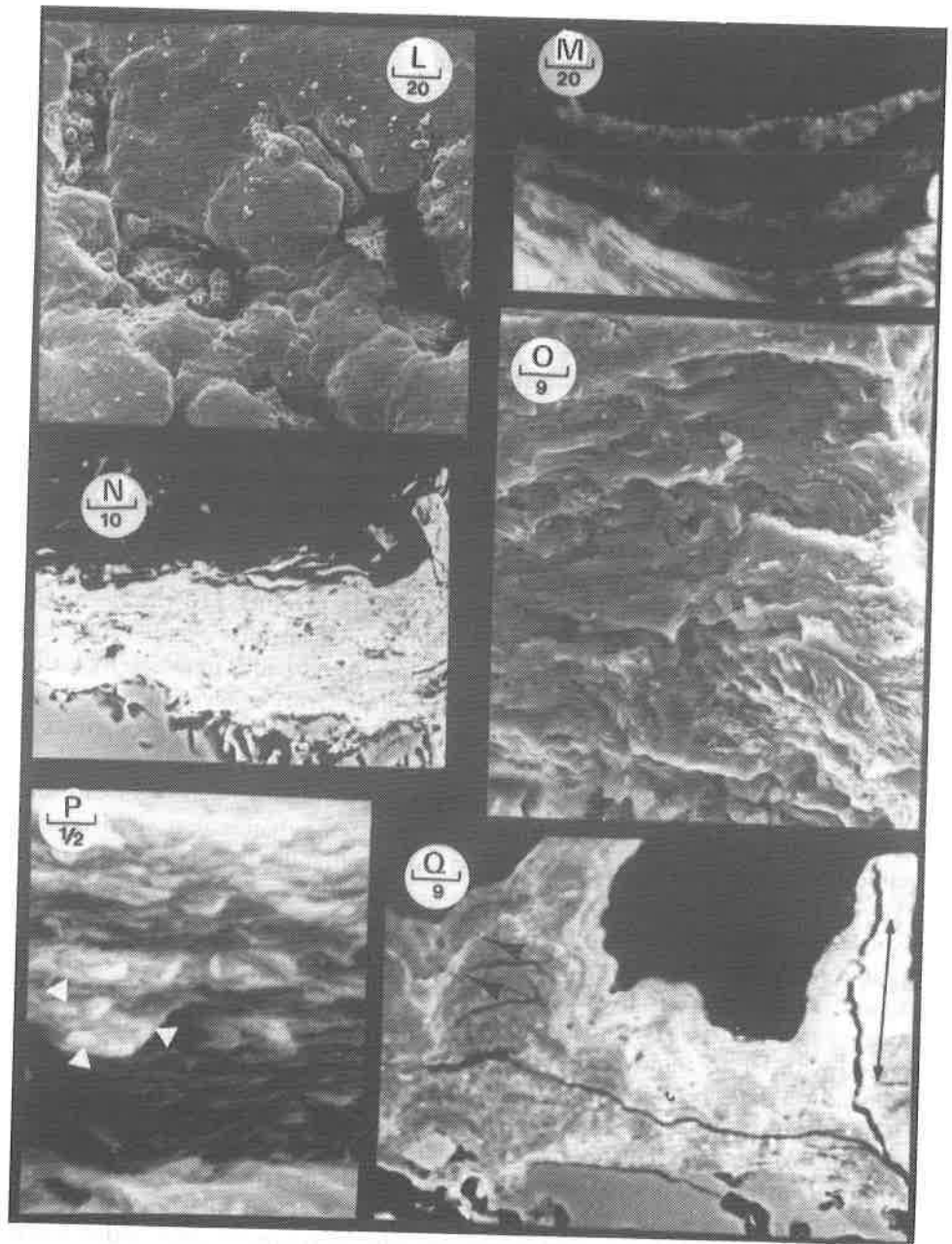
Plate 3.

Fig. L. SE view of the varnish surface from Crater Flat, southern Nevada. The depressions are being made by microcolonial fungi (rounded forms) that secrete acids and chemically erode the varnish. As the Mn and Fe oxides are reduced, they are mobilized and probably reprecipitate in the fractures, as in Figures K,T and V.

Fig. M. Light microscope photograph of a varnish section from Hanaupah Canyon alluvial fan, Death Valley. The uppermost layer of the varnish is lighter in color; it is Mn-poor. The next lowest layer is black and enriched in Mn. The third layer into the varnish is poor in Mn and is lighter. The lowest layer of the varnish is rich in Mn and black. The lighter material beneath this dark layer is the rock. When viewed in color, the lighter layers are orange, reflecting an abundance of iron.

Fig. N. BSE section of varnish from South Mountain Park, Phoenix, Arizona. Note the parallel layers in the varnish, with little deformation. However, there is some fracturing.

Fig. O. SE section of varnish from Little Cones basalt flow, Crater Flat in southern Nevada. Note the parallel layers in the varnish with a little deformation.

Fig. P. SE image of varnish from the Cronese Basin, Mojave Desert. The arrows highlight Mn-oxide crystals imbedded in a matrix of clay minerals, but structurally isolated from the clays and the Fe-oxides, which at least partly confirms the transmission electron microscope data discussed in the text.

Fig Q. BSE image of varnish on Death Valley Canyon alluvial fan, Death Valley. Note the abrupt structural break between the underlying rock and the varnish, but a piece of the rock has been incorporated into the varnish on the lower left part of the image. The double arrow oriented vertically on the right is adjacent to a crevice that may have been created during thin-section preparation. The two smaller arrows on the left side of the image identify discontinuous high-Z laminae that may be from the mobilization and reprecipitation of Mn-Fe oxides. Dorn agrees with Krinsley and Anderson in this situation, that when the high-Z Mn-rich laminations feather out, the Mn-rich laminae may be enhanced by mobilized and reprecipitated Mn.

Scale bar in microns.
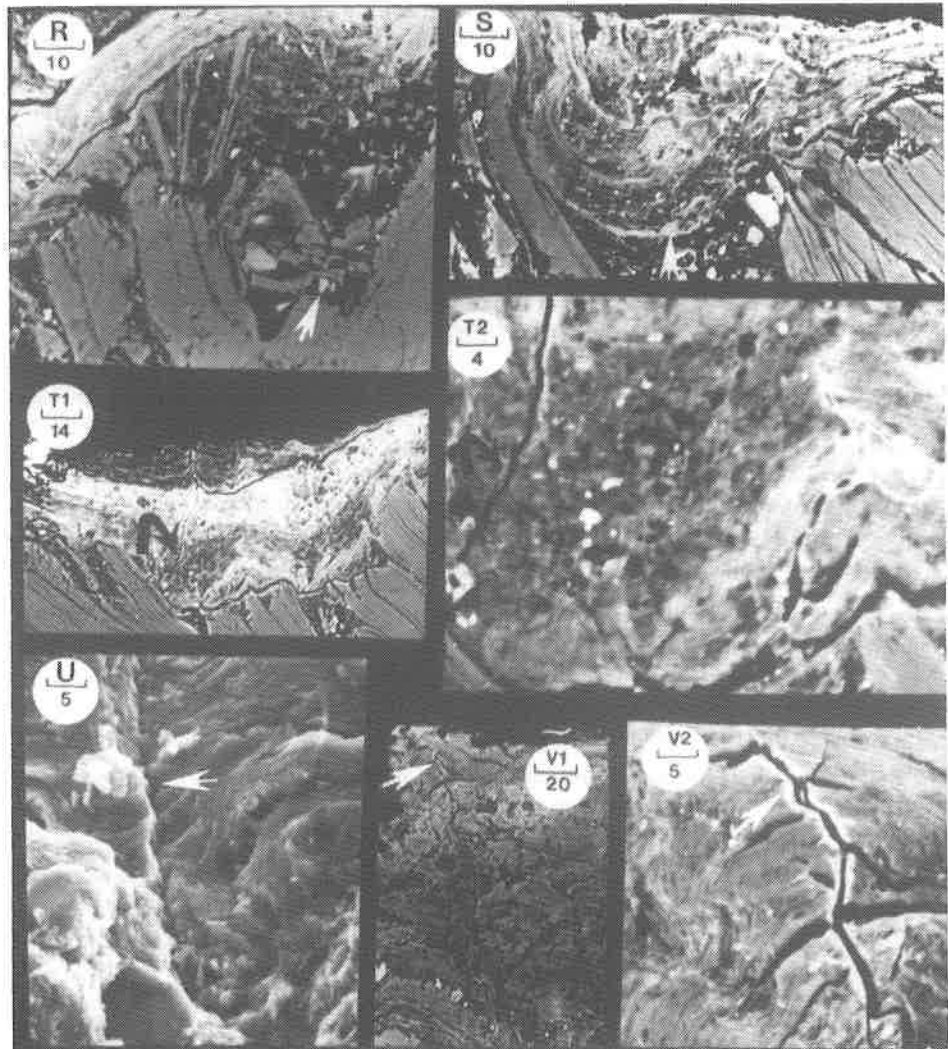
Plate 4.

Fig. R. BSE section of varnish near the rock varnish contact from Hanaupah Canyon alluvial fan, Death Valley, California. Roughly parallel layers of varnish (lighter) are found in the upper portion of the micrograph. Below the varnish on the right side of the image is a depression filled with either rock debris, aeolian fallout debris, or a mixture. This depression probably formed by the weathering of the rock after the varnish started to form. Small, bright minerals scattered throughout the varnish and the rock debris are barium sulfate crystals (e.g., arrow).

Fig. S. BSE section of varnish from Hanaupah Canyon alluvial fan, Death Valley, California. A depression in the rack is bridged by the varnish. The depression was probably not original, since varnish requires a substrate to adhere. It is likely that the rock has weathered, and the varnish is gradually collapsing into the growing depression, accounting for the down-folding of the varnish layers. Note how this growing depression contains more aeolian debris (e.g., bright barium detritus) than the layered varnish on the right part of the image, and is more porous. The growing void under the varnish is a mixture of rock detritus, and varnish, including barium-detritus (see arrow). There are also several vertically oriented fractures that have been filled with Mn-rich high-Z material.

Figs. T1 and T2. BSE images at different scales of varnish cross sections from Hanaupah Canyon alluvial fan, Death Valley, California.
In T1, a depression in the rock has filled with varnish. Note the two fractures roughly perpendicular to the varnish layering. One of the cracks is open; the other (to the right) is filled with high Z (Mn-Fe) material. Note the high Z mound where the left fracture reaches the surface. Also note that this fracture extends down to the rock.
In T2, the depression highlighted by the arrow in T1 is identified by the black curved arrow. The double white arrow points to a fracture filled with Mn-Fe material.

Fig. U. SE image of varnish from Crater Flat, southern Nevada. The arrow highlights a vertical crack in the varnish. Since sample preparation did not involve the preparation of thin sections, but only a very gentle mechanical fracturing of the varnish (in this case, breaking a flaked piece with a fingertip), it is unlikely that the vertical fractures are an artifact of sample preparation.

Figs. V1 and V2. BSE images at different scales of varnish cross sections from Coso basalt flow 28 (see Dorn, 1989). The fracture on the left side of V1 (arrow) is perpendicular to the layering, and extends from the rock surface to the rock/air interface with a mound of high Z material at the top. The poor preservation of the thin section makes the texture difficult to discern in the middle of the varnish, but the layering is easier to observe adjacent to the varnish/rock interface. The arrow in V1 is where the close-up in V2 is located. The arrow in V2 identifies the precipitation of high Z, Mn-Fe rich material, in the vertical fracture, indicating the movement of solutions through the crack. Note also that high Z materials have moved out from this vertical fracture parallel to the layering in a series of stringers.

Scale bar in microns.
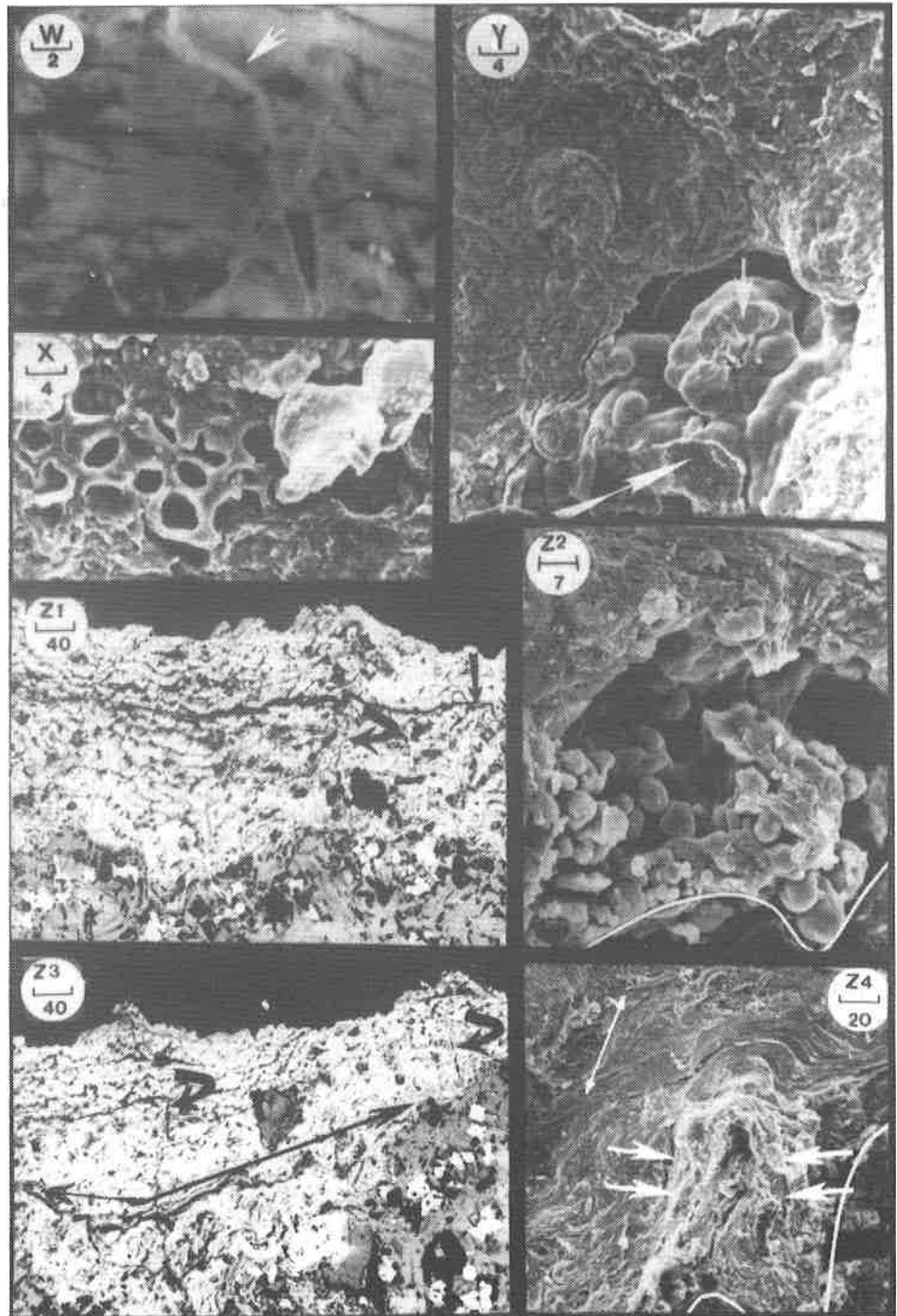
Plate 5.

Fig. W. BSE image of rock varnish from Hanaupah Canyon alluvial fan, Death Valley, California. The arrow details a crack that has been filled with Mn-rich material. The crack is roughly perpendicular to the layering. Note that a portion of the large open crack near the bottom of the image is also partially lined with Mn-rich material.

Fig. X. SE image of cross-section of varnish from Crater Flat, southern Nevada. The honeycombed structures are decayed microcolonial fungi, now partly buried by accreting varnish.

Fig. Y. SE image of cross-section of varnish from Crater Flat, southern Nevada. The smooth-textured mass in the lower right part of the image is unidentified organic matter, encrusted in Mn-Fe oxides. Where the oxide crust has broken off (arrows), the very low counts obtained with EDX indicates it is organic matter.

Figs. Z1-Z4. Deformation structures, illustrated by BSE (Z1,Z3) and SE (Z4). The rock/varnish contact in Z1 and Z3 is represented by a tonal change from bright, high Z varnish to the rock with lower Z values (with scattered high Z iron minerals). The rock/varnish contact in Z2 and Z4 is indicated by the line.

Z1. Section from Coso 28 (see Dorn, 1989 for site description) illustrating "scalloped layers" characterized by wavy layers separated by voids. Also evident are cracks normal to the surface (curved arrow) and interlayer fracturing (the arrow pointing down illustrates the end of a major fracture in the varnish).

Z2. Section of varnish collected from the −180 m shoreline of Lake Lisan, Israel, illustrating lamellate structures on top of rounded botryoidal forms with abundant pore space. Other examples of alternating lamellate and botryoidal layers are found in Dorn (1986).

Z3. Section from Coso 28, illustrating vertical cracks (curved arrows), scalloped structures (above double arrow) and contorted varnish structures (below double arrow). Some of the contortion may be due to infilled paleoerosional depressions, similar to those in Fig. I. Some is probably due to lateral pressures exerted by the wetting and drying of varnish clays. Also note the large mineral fragment (dark, low Z) imbedded in the high Z varnish.

Z4. Section from varnish on an older alluvial fan unit of the Chocolate Mountains, Mojave Desert, California. The four arrows highlight a contorted structure, similar in scale and position to some at the base of the varnish in Z3. An infilled paleodepression with abundant Ba-rich and Ca-rich grains is found to the immediate left of the double arrow (upper left corner of the image).

Scale bar in microns.

iron and clay minerals; manganese oxide diameters range from several unit cells on the order of 12 to 30 angstroms, to diameters of as much as 500 to 600 angstroms (Fig. P). These preliminary TEM data also suggest that these oxides do not include carbon.

Another implication of oxide mobility is the problem of paleomagnetic dating of rock varnish. Potter (1979) first investigated the potential of paleomagnetic variations as an indicator of varnish age. Although Potter concluded that the strength of the signal in the rock underlying the varnish was far greater than in the varnish, new methods of analyzing micron-scale changes in paleomagnetism (Renne and Onstott, 1989) should open varnish Fe-oxides to future investigation. Our results demonstrate that some of the Mn-Fe oxides are remobilized; this would reset at least part of the paleomagnetic clock. Any future paleomagnetic analyses of varnish, therefore, must avoid zones of remobilization.

Deformation of Varnish

A number of varnish cross-sections include evidence of internal deformation; this is particularly true of thicker varnishes. We have classified deformation into three preliminary groups: scallops, contortions and fractures. Scalloped layers (Figs. Z1,Z3) may result from layer deformation and pore enlargement. It is, however, quite possible that scalloped layers separated by pores may represent botryoidal structures (Dorn and Oberlander, 1982; Dorn, 1986), where voids are an intrinsic part of the botryoidal layer (Fig. Z2). Not enough is known about how botryoidal layers are represented in polished thin sections.

Contortion is most commonly found near the varnish/rock contact in thick varnishes (Figs. Z3,Z4). Wetting and drying could cause expansion and contraction of clay-rich layers with time, as Whalley (1983, 1984) speculated. These lateral pressures can cause older layers to be thrust up stratigraphically (Fig. Z4), thereby confusing the dating situation, as older varnish may be found at the same level as the younger material.

Fracturing of thick varnishes occurs mostly parallel to the layers (Figs. F, Z1,Z3). The next most common type is found perpendicular to the varnish surface (Figs. T,U,V,Z1,Z3), while some fractures cut irregularly across the varnish (Figs. F,T2,W). Scallops, contortions and fractures open up pore spaces, and must surely permit relatively large amounts of water to move through the varnish. This must result in solution and reprecipitation, moving material from where it was deposited stratigraphically. If an age determination is to be accurate, the diagenetic history must be worked out in detail for each site to be dated.

CONCLUDING REMARKS

The occurrence of rock varnish on a wide variety of geomorphic and archaeological surfaces in arid and semiarid lands makes it a very valuable dating tool. However, samples must be collected and screened properly. We have documented nine general factors that have been shown to either affect the dating of rock varnish or are likely candidates to influence a varnish date, and hence deserve

further investigation. Some of these factors can be avoided by careful field sampling. Optical and secondary electron microscopy of varnish surfaces will determine whether surface micro-hollows are common and whether biological agencies are eroding the varnish at present. However, examination of varnish cross-sections is necessary to determine whether these and other confounding factors were present in the past. While light microscope analysis of ultra-thin sections yields useful information (Fig. M), the BSE technique produces textural data with a resolution at least 10x greater than light microscopy (less than 200 angstroms as compared to 2000 angstroms for light microscopy), in addition to chemical information with X-ray analysis.

Our BSE observations also lead us to propose a possible new perspective on cation-ratio dating of rock varnish. Instead of scraping square centimeters for a cation-ratio analysis (Dorn, 1989) or using an SEM with energy-dispersive X-ray analysis to examine the top of a varnish sample (Harrington and Whitney, 1987), microtextural areas could be defined in cross-section with BSE. There would be no uncertainty here as to whether the varnish or rock was being analyzed. Also, WDX would separate barium from titanium easily. If certain microtextural areas yield statistically significant correlations between known age and the chemistry of a given texture, there would be considerably greater control over the nature of the varnish which was being sampled. While many have noted extreme chemical variability in varnish on a micron-scale (Dorn and Oberlander, 1982; Dragovich, 1988a,b; O'Hara et al., 1989; Dorn, 1990a,b), it is possible that this variability could be reduced by comparing similar varnish microtextures, for example using only the layered laminae next to the underlying rock (e.g., Figs. I,N). This new approach deserves further investigation.

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