

## Cation-Ratio Dating: A New Rock Varnish Age-Determination Technique

RONALD I. DORN<sup>1</sup>

*Department of Geography, University of California, Berkeley, California 94720*

Received July 1, 1982

Rock varnish coats many surfaces of geomorphic and archaeological interest in arid lands. All varnish dating techniques are limited by the time lag between the exposure of a surface to subaerial processes and the onset of varnishing. They are valid only where manganese is not remobilized after deposition, for example, in most arid environments. The premise of a new age-determination method, cation-ratio dating, is that the ratio of the more mobile cations (e.g., K and Ca) to titanium in varnish decreases with time. Although there are many inherent assumptions and potential limitations, cation-ratio dating has been verified on relative age-sequences from a Death Valley debris cone, Negev Desert talus flatirons, and prehistoric lake levels at Searles Lake in California. Varnish cation ratios have been calibrated to independently dated surfaces in the Coso volcanic field and vicinity in California. Tentative absolute dates have been assigned to geomorphic surfaces in the Coso area. Cation ratios have been used to distinguish relative ages of archaeological artifacts in southwestern North America and to demonstrate that varnish at the South Stoddard locality, Mojave Desert, did not form in 25 yr.

### INTRODUCTION

For over a century natural scientists have speculated on the genesis and characteristics of manganese-rich coatings observed on rocks from tropical environments (e.g., von Humboldt, 1907; Boussingault, 1882) to arid environments (e.g., Blake, 1855; Walther, 1891). Only within the last decade have advances in analytical techniques allowed a more full understanding of these dark films, called rock varnish by Dorn and Oberlander (1980, 1982). Rock varnish is a thin coating of manganese and iron oxides and hydroxides, clay minerals, and trace elements that accrete on rock surfaces.

In the recent literature two dominant theories have been presented on the origin of rock varnish, one physicochemical and the other biological. Adherents of the physicochemical models (e.g., Allen, 1978; Elvidge, 1979; Elvidge and Moore, 1979; Elvidge and Collet, 1981) hold that varnish in arid and humid environments are geneti-

cally dissimilar. Varnishes in mesic environments are not examined by this group of researchers. Varnishes in arid climates, commonly called "desert varnishes," are thought to form by the accretion of airborne material in alkaline environments. The enrichment of manganese in varnish, often 60 times above ambient levels, is thought to result from mobilization of manganese from desert dust by minor pH-Eh fluctuations and wetting associated with summer thunderstorms. When varnish is not in a physicochemical equilibrium with the alkalinity of the environment, it is thought to erode.

Proponents of a biological genesis (e.g., Dorn and Oberlander, 1980, 1981a, b, 1982; Krumbein and Jens, 1981) hold that manganese enhancement in varnish is due to microbial agencies, and cannot be explained by the varnish-surface physicochemical microenvironment. The biogeochemical model forwarded by Dorn and Oberlander (1981b, 1982) accounts for the occurrence of rock varnish in both humid and arid aerobic environments. The arguments in favor of a biological genesis are too lengthy to detail here; however, they

<sup>1</sup> Current address: Department of Geography, University of California, Los Angeles, Calif. 90024

are presented by Dorn and Oberlander (1981a, b, 1982) and Krumbein and Jens (1981, pp. 34–35). Some of the reasoning in this paper assumes a biological origin for rock varnish.

Rock varnish coats man-made and natural surfaces of various ages, and it has long been hoped that some characteristic of rock varnish would provide an age-determination technique. Rock varnish characteristics, such as darkness (e.g., Heizer and Baumhoff, 1962; Hooke, 1967), thickness (e.g., Hume, 1925; Hayden, 1976), and manganese concentration (e.g., Bard, 1979) have been used by archaeologists and geomorphologists to estimate the relative ages of lithic surfaces. However, these traits are not dependent only on time. They are more influenced by microenvironmental factors affecting microorganisms that concentrate manganese (Dorn, 1981).

For example, Bard (1979) proposed that total varnish manganese concentrations relative to iron could be used as a relative dating method. However, chemical analyses of varnish at several sites with relative-age controls in this study indicate that bulk iron:manganese ratios are not related to the age of the underlying surface (Table 1). Still other proposed dating techniques are based on implicit assumptions that varnish constituents come from the underlying rock (e.g., trace-element concentrations by

Bard (1979)) or from depositional solutions (e.g., uranium-series dating by Knauss and Ku (1980)), both of which are incompatible with current concepts of varnish accretion of airborne detritus (e.g., Potter and Rossman, 1977; Perry and Adams, 1978; Allen, 1978; Elvidge, 1979; Dorn and Oberlander, 1981b, 1982).

A new varnish age-determination technique, called here cation-ratio dating, is proposed. It is based on minor elements in varnish that are not overly sensitive to factors that affect manganese deposition. The premise of cation-ratio dating is that with time the leachable cations in varnish, such as Na, Mg, K, and Ca, are gradually replaced by and/or depleted relative to less mobile cations, such as Ti. The decreasing cation ratio of  $\text{Na}^+ \text{Mg}^+ \text{K}^+ \text{Ca}:\text{Ti}$ , or any component thereof (e.g.,  $\text{Ca}:\text{Ti}$ ), provides an indication of the length of time that the varnish has been exposed to cation leaching. Titanium is used here, rather than aluminum or iron, because (1) Ti is less mobile (e.g., Colman, 1982), (2) Fe concentrations are probably influenced by varnish microorganisms (Dorn and Oberlander, 1982), and (3) Al abundance is affected by clay mineral concentrations in varnish, which is probably influenced by eolian dust levels and varnish microorganisms (Dorn and Oberlander, 1981b, 1982).

Cation ratios of varnishes from similar

TABLE 1. MEAN IRON: MANGANESE RATIOS OF BLACK VARNISH ON SURFACES OF KNOWN RELATIVE AGE<sup>a</sup>

Relative age	Location				
	Pyramid Lake		Death Valley <sup>b</sup> (Fe:Mn)	Searles Lake	
	Fe:Mn	Altitude (m)		Fe:Mn	Altitude (m)
Oldest	3.20	1344	5.36	6.3	686
	6.00	1330	8.57	17.7	674
to	3.68	1292	2.39	1.6	597
	6.47	1234		9.1	579
Youngest	3.01	1192		4.0	561

<sup>a</sup> Elemental analyses are by the PIXE technique for Pyramid Lake and Death Valley and by XRF for Searles Lake (Cahill, 1981). The Searles Lake shoreline and Death Valley debris cone sites are discussed in this paper. The relative ages of prehistoric shorelines at Pyramid Lake were discussed by Benson (1978, 1981).

<sup>b</sup> From darkest, moderate, and lightest scrapable deposits.

microenvironmental settings at a given site should indicate a relative-age sequence. Further, if the absolute ages of different surfaces can be determined (e.g., K/Ar dated volcanics), then an empirical relationship between age and cation ratios (called here a "cation-leaching curve") can be established to provide estimates of the absolute ages of varnishes in the region where the relationship has been established. The purpose of this paper is to present the basic theory and limitations of cation-ratio dating, and to illustrate its use in determining the absolute or relative ages of geomorphic and archaeological surfaces.

#### GENERAL LIMITATIONS OF ALL VARNISH-DATING TECHNIQUES

The biological model of rock varnish formation adopted here (Dorn and Oberlander, 1980, 1981a, b, 1982) has important implications for all rock varnish age-determination techniques. It should be stressed that age-determination techniques apply only to initiation of varnish formation, not necessarily to the age of the surface on which the rock varnish is deposited.

The most important limitation is that the start of varnishing is not necessarily coincident with the exposure of the rock surface to subaerial processes. Too much alkalinity, too much acidity (e.g., from lichens), low concentrations of ambient clay minerals, high levels of organic matter, and/or competition from non-varnish-forming microorganisms may halt or impede the colonization of a rock surface by microorganisms that concentrate manganese. Some of the inconsistency in varnish development from outcrop to outcrop and from stone to stone may be the result of the different times of onset of microbial colonization.

Another important factor is the nature of the underlying substrate. The rate of varnish development on a smooth quartz or chert surface is slower than on more porous substrates (Fig. 1). Weathering of quartz and chert does not produce clay minerals that

are favorable for the initial colonization of varnish microorganisms (Dorn and Oberlander, 1981a). A smooth quartz or chert surface also does not favor the accumulation of clay minerals in microdepressions, a more suitable environment for microbial colonization (Dorn and Oberlander, 1982).

Eolian abrasion can totally remove varnish from surfaces. The presence of wind-blast characteristics on the underlying rock (e.g., Whitney, 1979), therefore, suggests that any date obtained for a varnish probably represents a minimum age of the underlying surface.

One critical assumption implicit in all varnish-dating techniques is that rock varnish is a sink for manganese and that manganese is not subsequently remobilized after deposition. If manganese is reworked after deposition in rock varnish, all dating methods are invalidated, because every technique (except the use of color changes in orange bottom varnish) assumes the stability of the manganese-clay cemented varnish. A variety of data suggest that manganese is not reworked after deposition (and subsequent clay fixation) in most varnish-forming environments. Crerar *et al.* (1980) argued that manganese in desert varnish has little mobility because of the lack of acidity, low organic content, and slow decay of organic matter in arid environments. Data on the pH of varnish surfaces indicate that varnish varies in alkalinity from near neutral values on black surface varnish to alkaline values on orange varnishes (Table 2). The widespread occurrence of arid rock varnish is associated with high alkalinity in arid regions, partly because a lack of acidity is required to preserve varnish. However, the pH conditions on black surface varnish are not usually high enough to oxidize mobile Mn(II) to immobile Mn(IV), which is the form present in varnish (Jenne, 1968; Muir, 1978; Uren and Leeper, 1978); thus, a biological mechanism is required to oxidize manganese. Black varnish pH conditions are not low enough to reduce Mn(IV), and manganese-reducing bacteria are probably

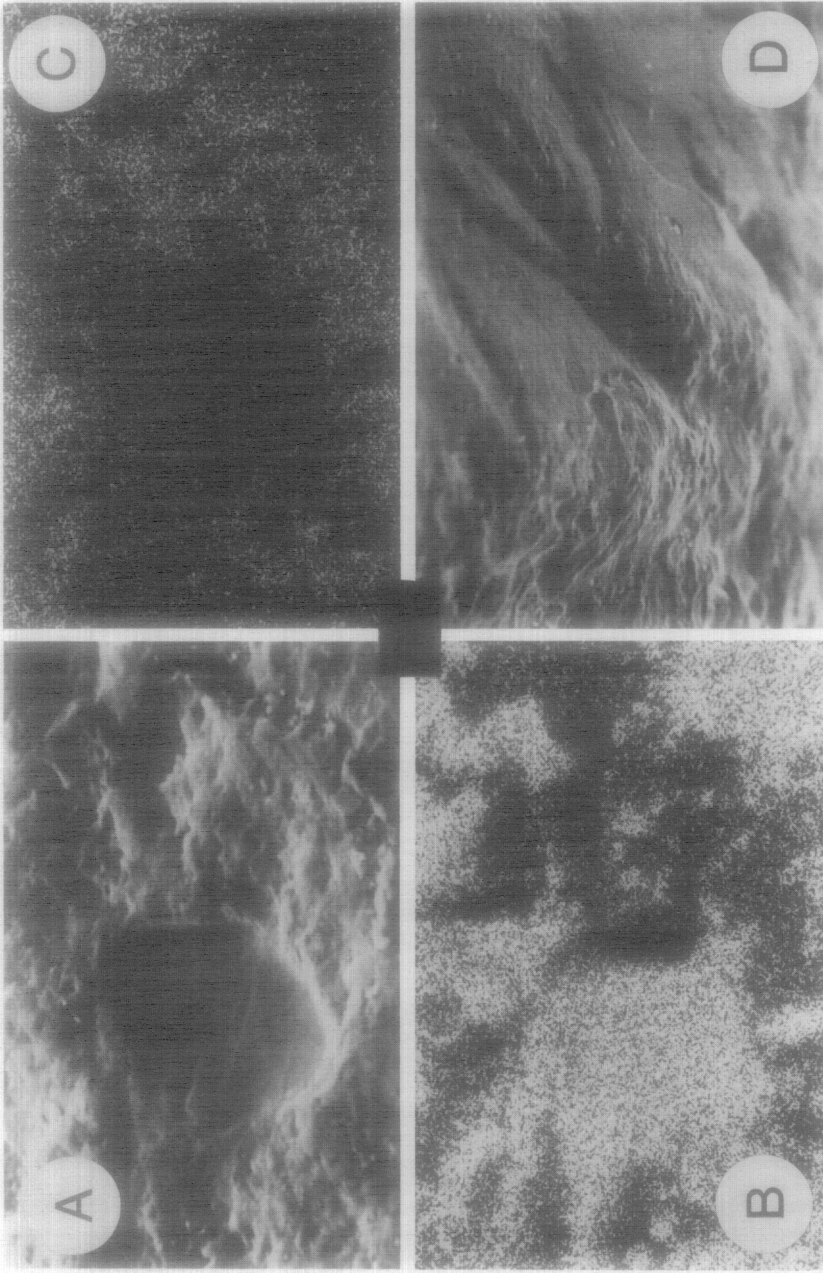


FIG. 1. Varnish "avoidance" of quartz, relative to more porous surfaces. (A) Lamellate rock varnish avoiding smooth quartz grains in granodiorite, Joshua Tree National Monument, California. (B) X-ray map of silica, showing the match of the higher silica concentrations with the exposed quartz and thin varnish in A. Dot density is proportional to concentration. (C) X-ray map of manganese, illustrating the inverse of B, where manganese concentrations are lowest at the exposed quartz and thin varnish. (D) Varnish on a gneissic substrate from a debris cone in Death Valley National Monument, California. Varnish (left side of image) is slow to "colonize" the smooth quartz vein on the right side of this micrograph. Scale bar = 20  $\mu\text{m}$  for A-C, and 40  $\mu\text{m}$  for D.

TABLE 2. PH VALUES AND SD OF ROCK VARNISHES FROM LOCALITIES IN THE WESTERN UNITED STATES<sup>a</sup>

Varnish position	Varnish color		
	Black	Dusky brown <sup>b</sup>	Orange <sup>c</sup>
Surface	7.1 ± 0.4 (53) <sup>d</sup>	7.8 ± 0.6 (29)	8.2 ± 0.3 (19)
Crack	7.4 ± 0.4 (18)	—	8.4 ± 0.3 (19)
Bottom	6.7 ± 0.3 (2)	—	8.6 ± 0.2 (8)

<sup>a</sup> The varnish coatings were first scraped under 45× magnification with a tungsten-carbide needle. Measurements were then taken with a Beckman pH meter (1:1 paste with varnish and deionized water) and with a Hellige-Truog test kit.

<sup>b</sup> Munsell color designation: 10R 3/3 to 4/4, to 2.5YR 3/2.

<sup>c</sup> Munsell color designation: 10R 4/8, 2.5YR 4/6 to 5/6, to 5YR 7/6 to 7/8.

<sup>d</sup> Number of localities sampled in parentheses.

not present on arid-environment rock varnish (Dorn and Oberlander, 1981c).

An important aspect of manganese stability is the clay mineralogy of varnish. Reddy (1973, p. 46) demonstrated that fixation of tetravalent manganese occurs in montmorillonite and illite, noted by Potter and Rossman (1977, 1979) to be the dominant clays in varnish. These clay minerals strongly hold Mn(IV), even under acidic conditions (Reddy, 1973; Glover, 1975; El-rashidi *et al.* 1978). The strong attraction of Mn(IV) to varnish clays tends to stabilize manganese in rock varnish.

The only condition where manganese appears to be mobilized in arid rock varnish is where the varnish is near rock surface microorganisms or organic materials that secrete or produce organic acids. Lichens seem inimical to rock varnish in the western United States and Israel. T. M. Oberlander (personal communication, 1982) noted that lichens preclude formation of varnish in the fog belt in Chile. Weathering of particular minerals, such as pyrite crystals, may also produce enough acid to mobilize rock varnish manganese.

#### ASSUMPTIONS OF CATION-RATIO DATING

There are several theoretical assumptions that must be met in order to determine accurately the ages of rock varnishes using cation ratios.

(1) *Varnish constituents are derived from*

*the same sources, and the ambient "airborne fallout" cation ratio has remained relatively constant during the Quaternary.* This assumption may not be valid over short time periods. Short-term localized shifts in fallout ratios, however, should not significantly disturb the overall input ratio, because varnish accretion is a very slow process in arid environments, taking thousands of years to form a complete coat (Dorn and Oberlander, 1982).

The constituents of most subaerial varnishes are derived from airborne material, usually derived from desert soil surfaces (Elvidge, 1979; Péwé *et al.*, 1981; Dorn and Oberlander, 1982), ultimately derived from the local geology and long-traveled aerosols. The geology of most desert environments has been similar throughout the Quaternary, and Péwé *et al.* (1981, p. 182) proposed that the rate, amount, and source of dust deposition in the central Arizona desert during the Pleistocene has been similar to what it is today. Cation ratios of varnishes intermittently receiving waterborne material cannot be directly compared with varnishes accreting only airborne detritus.

(2) *Rock varnish serves as a cation-exchange complex, and the cation-exchange capacity is similar in all varnish samples being compared.* This assumption is supported by laboratory experiments. Potter and Rossman (1977, 1979) found that black varnish is composed of as much as 70% clay minerals, mostly illite-montmorillonite mixed-layer types. Potter (1979, pp. 45-46)

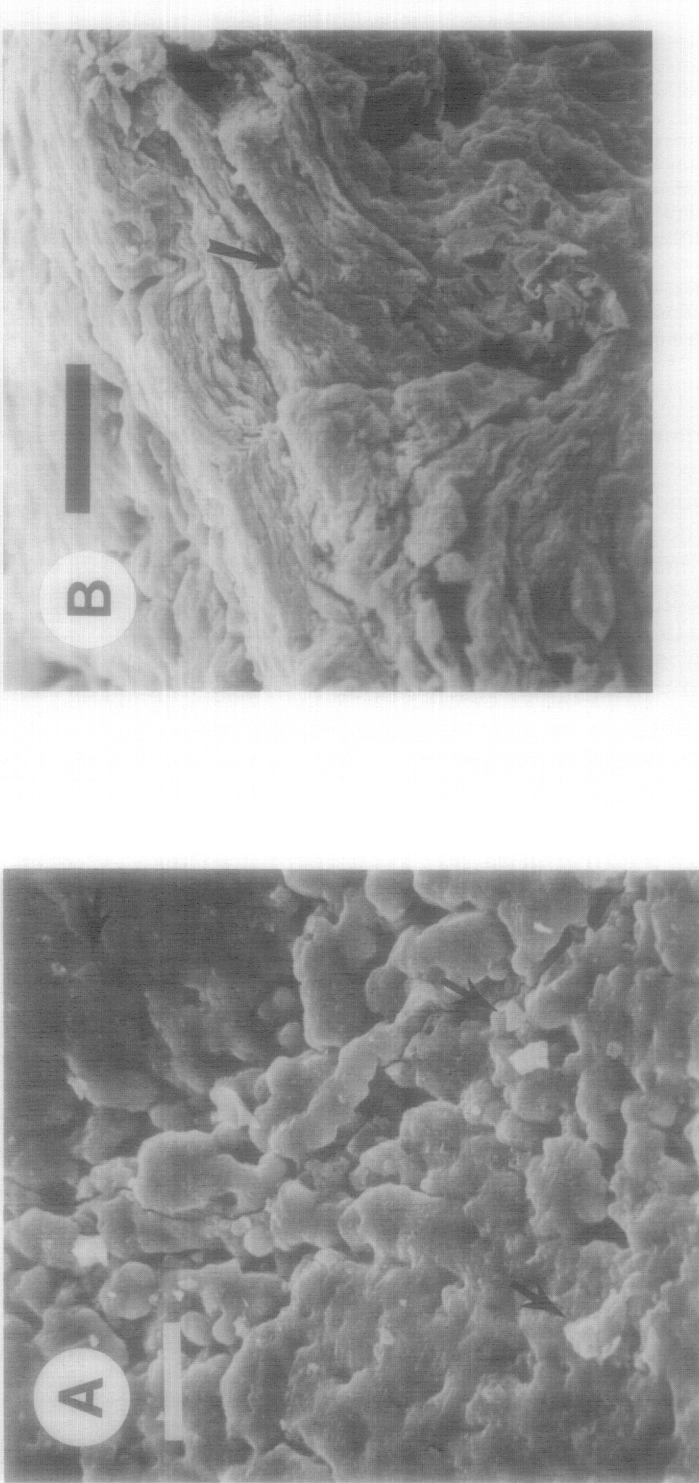


FIG. 2. Incorporation of eolian detritus and clays into varnish. (A) Small detritus (arrows) on varnish. Collected from Salt Springs, Mojave Desert, California. Scale bar = 10  $\mu\text{m}$ . (B) Subsurface lamellate layers and detritus (e.g., arrow) are visible in this cross section of black varnish from the oldest flatiron at Timna, Negev Desert, Israel (Fig. 6). Detritus is incorporated into varnish as clays accrete onto varnish and are cemented by varnish oxides. Scale bar = 10  $\mu\text{m}$ .

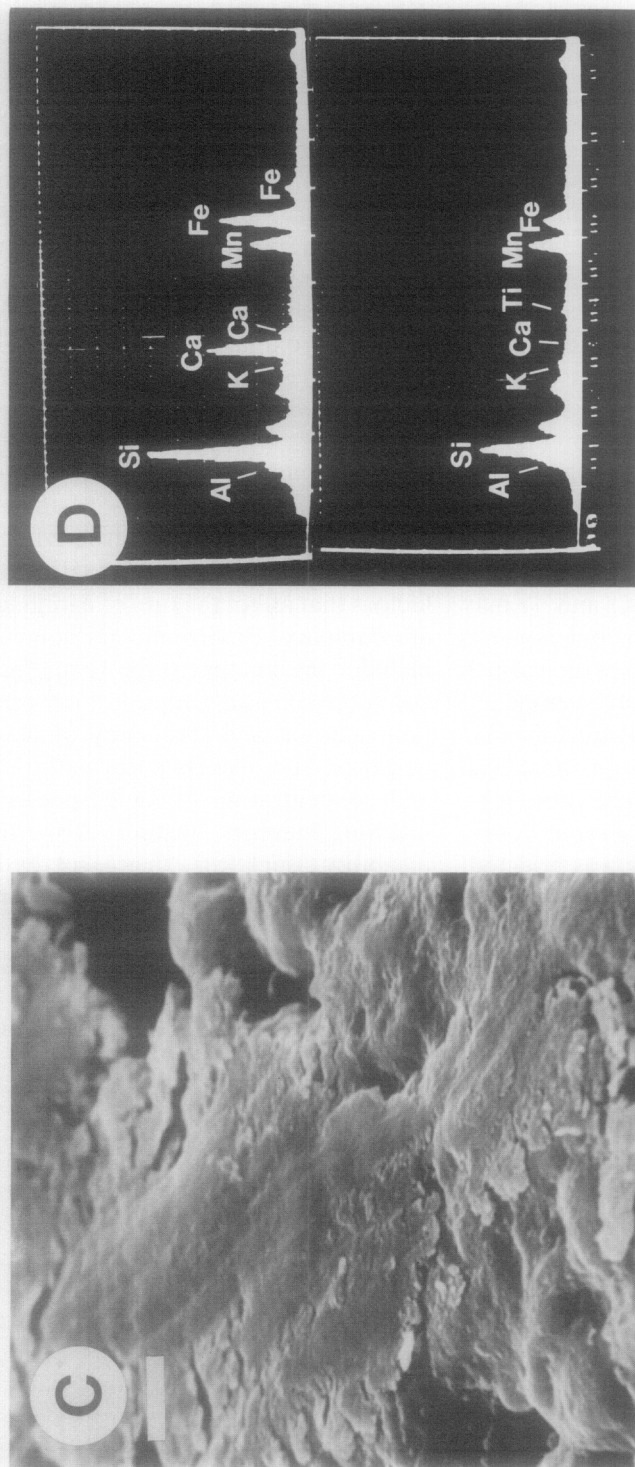


FIG. 2.—Continued (C) Close-up of an accreting lamellate layer on varnish from Salt Springs, Mojave Desert. Scale bar = 2  $\mu\text{m}$ . (D) Energy dispersive analyses of X-rays (EDAX) of a subsurface layer in B, identified by the arrow. The upper panel is a spot EDAX analysis on the detritus and the surrounding varnish at the tip of the arrow; it shows that the detritus is rich in calcium and the varnish immediately surrounding the detritus has a relatively high Fe:Mn ratio. The lower panel, an analysis of the remaining varnish in the same layer as the detritus, has a relatively lower Fe:Mn ratio. This illustrates the reduction in manganese enhancement that occurs around alkaline particles; alkalinity inhibits manganese concentration by varnish-producing bacteria (Dorn and Oberlander, 1982). Unidentified peaks are coating emissions and trace elements.

estimated the cation-exchange capacity of varnish clays for three arid sites, and concluded that the varnish capacities are consistent with that expected from illite-montmorillonite mixed-layer clays. Cation exchange may also occur on manganese and iron oxides (Jenne, 1968).

The concentration of manganese in samples should remain within the same order of magnitude, because the degree of manganese cementation probably affects the cation-exchange capacity of varnish. This was found to be the case in comparisons of orange and dusky-brown varnishes (poor in manganese) with black varnishes (rich in manganese) of similar ages from prehistoric shorelines of Pyramid Lake (Nevada), where the cation ratios are strikingly different (R. I. Dorn, unpublished data).

Occasionally, detrital minerals containing high concentrations of Ca, K, and Ti may be incorporated into varnish, but not into the cation-exchange complexes in varnish (Fig. 2). These particles usually average out to similar proportions in different varnishes. However, when nonproportional concentrations were found to be present by microprobe or energy-dispersive X-ray analysis (EDAX), the sample was rejected. Infrequently, "domes" of mostly titanium and some iron (Fig. 3) are observed on varnish surfaces with scanning electron microscopy (SEM) and EDAX. They could be detrital titanomagnetites. However, they are usually found in clusters, and within these groups the domes are often observed at different stages of burial by the varnish. If they are only detrital, such clustering would not be expected. Sometimes, the domes may go undetected and may be included in a bulk chemical analysis, leading to much lower cation ratios than what would be representative of the true age of varnishes. When anomalously low ratios are found to have titanium domes, as the probable cause, the low ratios are rejected, because varnishes with domes have higher "input" levels of titanium and probably have different cation exchange capacities than varnishes without domes.

(3) *Na, Mg, P, K, and Ca are more mobile than Ti in the varnish cation-exchange complex.* The relative immobility of titanium, compared to Na, Mg, K, Ca, and other bases, is well established in literature about soils (Yaalon *et al.*, 1974; Aubert and Pinta, 1977), weathering geochemistry (Marchand, 1974, p. 402; Chesworth *et al.*, 1981; Colman, 1982), and landscape geochemistry (Polynov, 1951; Karavinov *et al.*, 1966; Lukashev, 1970). Titanium is essentially immobile, except where pH values are under approximately 4.5 (Gardner, 1980).

(4) *The rates of leaching of varnish cations are similar for compared samples, or the changes affecting the leaching rate are synchronous in time and amplitude for compared samples.* This assumption is likely valid in similar microenvironments from the same general area. However, the factors that affect the rate of cation leaching are complex. Environmental controls may include: the amount, type (e.g., frontal or convective), and frequency of precipitation; amount and frequency of dew; temperature; and aspects such as the pH, Eh, and concentration of ionic species in the leaching meteoric waters. Also, the permeability, thickness, degree of hydration, and micromorphology of varnish probably affect the rate of leaching.

In comparing the cation ratios of varnish, all of the above assumptions require verification by field-sampling and laboratory analysis.

## METHODS

Only black surface varnish formed by sub-aerial accretion of airborne material was sampled. Varnishes were collected from surfaces exposed to similar microenvironmental factors: aspect, microslopes of the rock surface, amount of surface available to generate runoff above the varnish, height above dust-generating surfaces such as soil, varnish location relative to rock cracks, position with respect to flora and sources of alkalinity, and other relevant site factors. Surface soils, dust in rock surface depressions, and, at some sites, airborne fallout



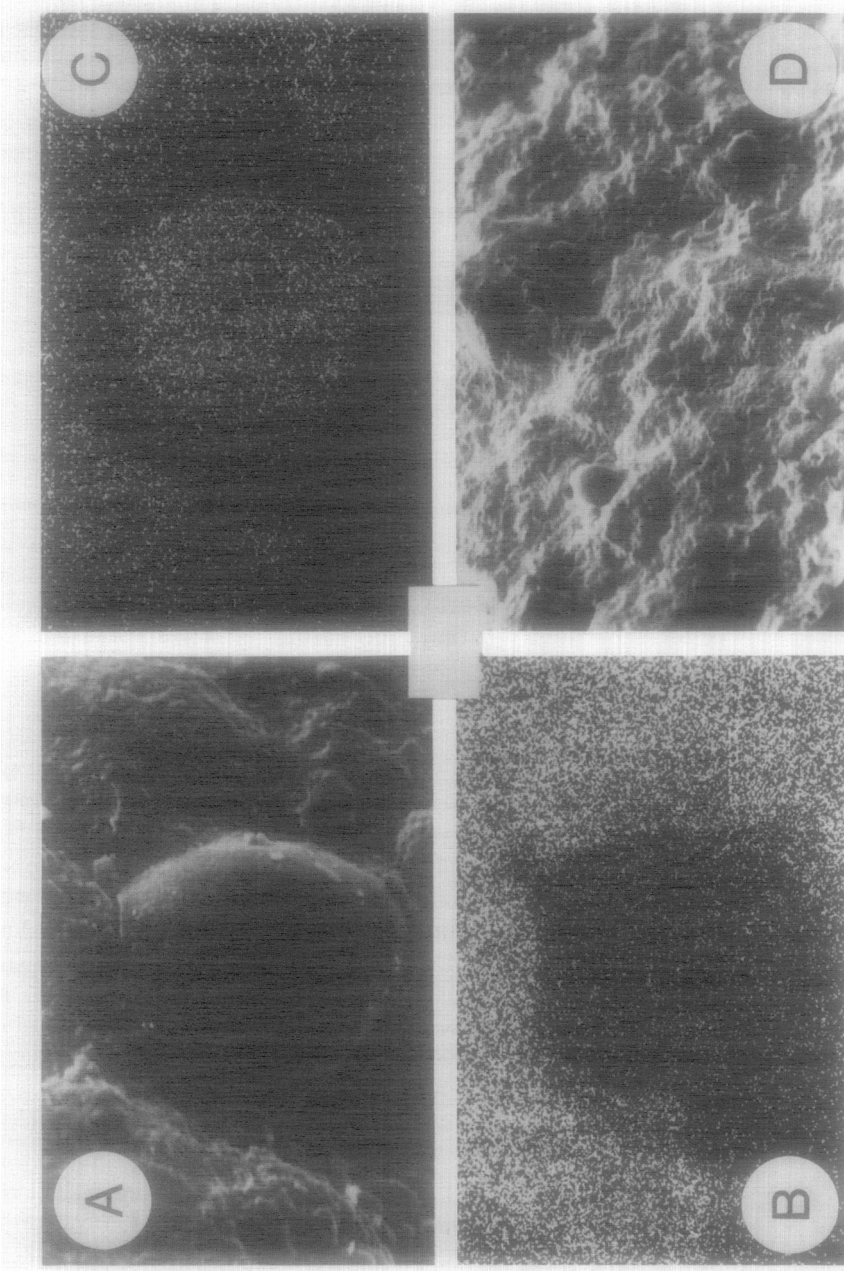


FIG. 3. Titanium domes. (A) Dome of mostly titanium oxide partly buried in black varnish. Sample collected near Park City, Utah. (B) Manganese X-ray map of A, showing an enrichment of manganese in the varnish surrounding the dome. Dot density is proportional to concentration. (C) Titanium X-ray map of A, illustrating a strong enhancement of titanium in the dome and a lesser concentration in the surrounding varnish. (D) Overall view of titanium domes on the black varnish from near Park City, Utah. Most domes are well exposed, but some are almost completely buried by the accumulating varnish. Scale bar = 20  $\mu\text{m}$  for A-C, and 200  $\mu\text{m}$  for D.

were collected and analyzed by size class to estimate the input cation ratio, that is, the cation ratio of the eolian material accreting onto varnish.

To prepare varnish samples for bulk chemical analysis, uncemented detritus was removed from varnished rocks with pressurized air. The rocks were then lightly agitated, scrubbed in deionized water to remove remaining detritus, and allowed to dry for a few hours. Under 10 to 45 $\times$  stereomagnification, varnish was detached from the underlying rock by careful scraping with a tungsten-carbide needle. At 30 to 45 $\times$  magnification fragments of the underlying rock were conspicuous amid varnish scrapings and were extracted. The average rock contamination in scrapings from a well-developed varnish is estimated to be less than 1% by volume. As varnish thickness decreases and the surface roughness of the underlying rock increases, the purity of the scrapings decreases.

The bulk chemical analysis method used almost exclusively in this paper is particle-induced X-ray emission (PIXE) analysis, performed at UC Davis, Crocker Nuclear Laboratory (Cahill, 1981). Any number of readily exchangeable cations could be used for cation-ratio dating, but the PIXE technique gives the most reliable results for potassium and calcium (and occasionally sodium), relative to titanium (T. Cahill, personal communication, 1982). X-ray fluorescence (XRF) analysis, by the Air Quality Group at Crocker Nuclear Laboratory, UC Davis, was used on varnish scrapings from two sites. XRF is only completely reliable for the Ca:Ti ratio (T. Cahill, personal communication, 1982). Unless otherwise specified, the cation ratio used is  $K^+Ca:Ti$ .

The scraping process produces gross samples of varnish coats throughout their depth, which were used for cation-ratio dating. Energy dispersive and electron microprobe analysis of varnish chips and cross sections gave very high local resolution. However, these methods are not useful for establishing bulk cation ratios, because they

include only a small percentage of the varnish, and the representativeness of discrete points within different varnishes is uncertain.

Cation ratios presented in this study represent an average (and standard deviation) of five PIXE analyses of composite samples obtained from different rock surfaces at a given site, unless otherwise stated. The cation ratio of a single analysis was rejected, if SEM-EDAX or microprobe checks revealed localized anomalies (e.g., titanium domes, abundant calcium detritus). Although PIXE elemental ratios of P:Ti and Na:Ti are not usually reliable, comparisons of trends in these ratios with those for K:Ti and Ca:Ti were used to isolate Ca and K detrital anomalies.

#### VERIFICATION OF CATION-RATIO DATING

Several sites were selected, each having a series of surfaces with known absolute or relative ages, in order to test the validity of cation-ratio dating.

##### *Debris Cone in Death Valley*

Several cones of debris consisting of talus and debris-avalanche deposits mantle the side of a turtleback a few kilometers south of Copper Creek Fan, Death Valley National Monument, California. These debris cones are clearly marked by surfaces with different darkneses of rock varnish. Varnish on gneissic cobbles from different surfaces on one cone was sampled (Fig. 4). Only the three darkest deposits of the talus cone had enough varnish to scrape accurately.

The  $K^+Ca:Ti$  ratios (Fig. 5A) and the  $Na^+K^+Ca:Ti$  ratios (Fig. 5B) for the varnish from the sampled deposits reflect the visible sequence (Fig. 4). A horizontal bench, cut by a high stand of Pleistocene Lake Manly, sits well above the debris cone. The debris avalanches cover lower shorelines traces, so that the deposits are younger than the Holocene desiccation of Lake Manly. The region around the debris cones



FIG. 4. Debris cone in Death Valley, California, illustrating the differential development of varnish on debris avalanche deposits of varying ages. Creosote bushes (*Larrea tridentata*) in the foreground are approximately 2 m high.

is rich in titanium (R. I. Dorn, unpublished data), hence the varnish has very high levels of titanium and correspondingly low cation ratios.

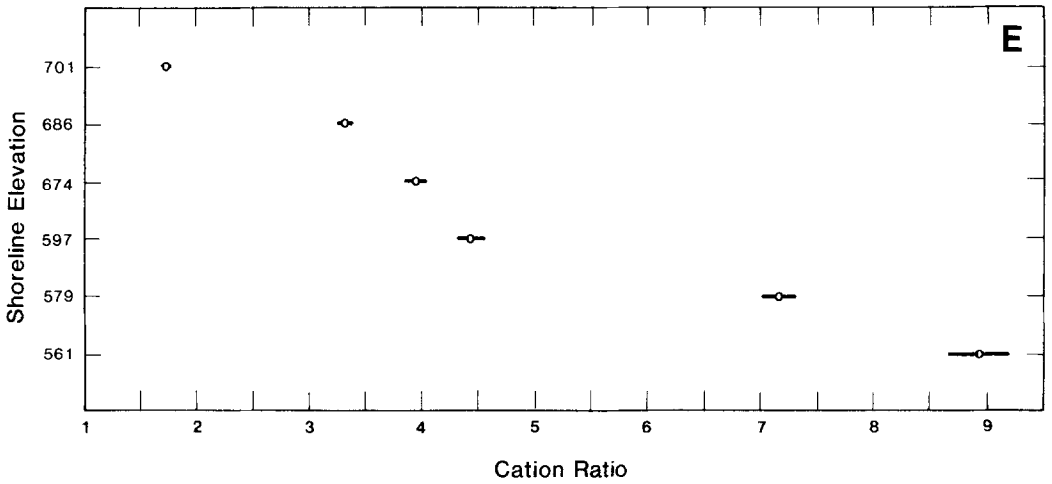
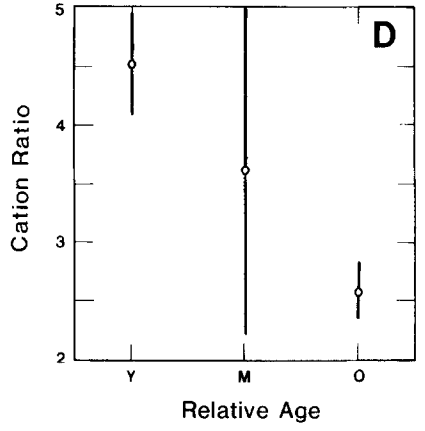
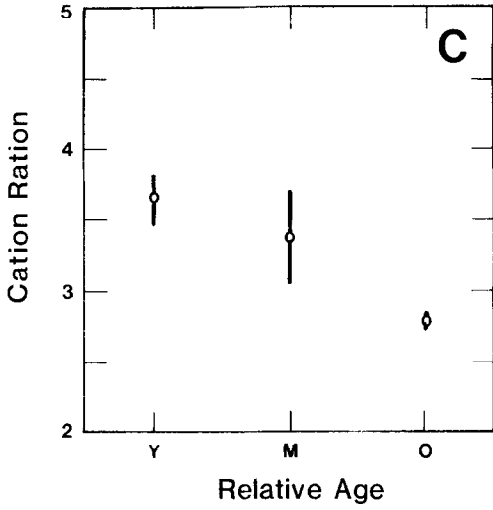
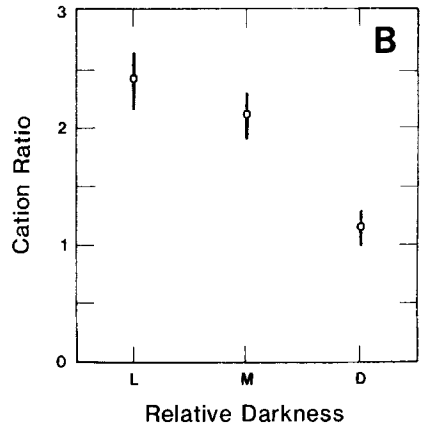
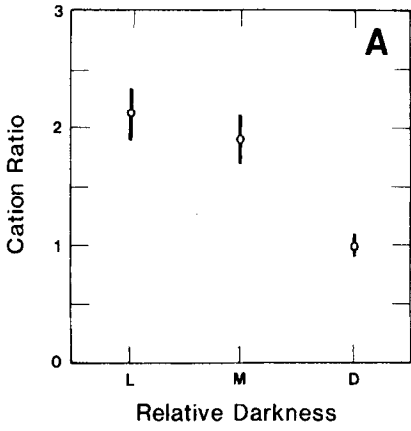
#### *Talus Flatirons in the Negev Desert*

Sequences of talus “flatirons” are present in the arid regions of Israel and in the southwestern United States. Gerson (1981, in press) has proposed a model in which during lengthy pluvial periods hillslopes become mantled with colluvium, remnants of which are preserved as the hillslopes recede during lengthy arid phases. Black surface varnish was sampled from two sequences of three inset flatirons in the Timna region (Fig. 6) and on the south flank of the Arava rift near the small settlement of Paran in the Negev Desert, Israel. In both flatiron sequences cation ratios are lower (more leached) on successively older flatirons (Figs. 5C and D).

#### *Shorelines of Searles Lake*

Further testing was conducted on varnish sampled from prehistoric shorelines of Searles Lake, California, in the Poison Canyon area (NW corner Sect. 25; T. 26 S; R. 24 E; Searles Lake 15' quadrangle, U.S. Geological Survey). The history of fluctuations in the level of Searles Lake has been outlined by Smith (1976, 1979). Smith notes a late high stand at around 690 m about 10,500 yr ago, with a subsequent decline and no stands higher than 550 m in the past 9000 to 10,000 yr. It is assumed that preexisting varnish is eroded by wave action.

Rock varnish was collected from five prehistoric shorelines at 561, 579, 597, 674, and 686 m and on a desert pavement above the 10,500-yr-old high stand at 701 m. All shoreline samples were taken from the lower (outer) third of the wave-cut bench to min-



imize contamination of colluvium from above. A minimum of ten cobbles were sampled at each elevation. The varnish was analyzed with XRF; hence, only the Ca:Ti ratio is available. The ratios for the upper three elevations represent the average (and standard deviation) of three analyses. Because varnish development was minimal, and only enough material was gathered for one XRF analysis at the lower three elevations, the uncertainty reported in Figure 5E for these three sites represents the XRF experimental error. Each successive higher elevation has a lower (more leached) cation ratio (Fig. 5E). This corresponds with Smith's proposed history of early Holocene lake-level fluctuations.

#### *Coso Volcanic Field, California*

The Coso volcanic field was chosen to test the hypothesis that varnish cation ratios can be calibrated with independently dated surfaces to construct a cation-leaching curve for assigning absolute ages to varnishes in a region. The Coso volcanic field, a late Cenozoic veneer on the Coso Range (Inyo County, California), provides a rare opportunity to construct a varnish cation-leaching curve. It is situated in a moderately arid region, with ubiquitous and excellent varnish on stable surfaces. The volcanic rocks are radiometrically dated by the K/Ar technique, providing a range of empirical ages for calibration purposes from 39,000 to more than 3 my (Duffield *et al.*, 1980).

Black rock varnish was collected from the surfaces of 16 K/Ar-dated rhyolite domes and basalt flows. Varnish was sampled from stable outcrops and boulders that receive virtually all detrital input from aerosols.

Figure 7 summarizes the averages (and standard deviations) of varnish cation ratios from sampled volcanics plotted against their K/Ar ages. Each volcanic surface is designated by a number, corresponding to the notation used by Duffield and Bacon (1981). However, the data points designated by stars in Figure 7 were not used in the construction of a final cation-leaching curve. Varnish from 26T (top) was sampled below lichens, which may lower the cation ratio significantly. Varnish from 26N (north), 27, 5, and 60 was collected from talus and other surfaces that are younger than the K/Ar age of the volcanic rocks. Whereas most of the varnishes on the other sampled rocks are not on original flow structures, they have developed on a massive and more stable substructure—the product of initial mechanical weathering of the original surfaces of lava flows and rhyolite domes.

At present there is no way to estimate accurately the time required to weather mechanically an unstable flow surface to the more massive, stable structure. There is no reason to suspect that the rates would vary among the different sites. Therefore, it is assumed that the K/Ar ages of the non-starred volcanic sites (numbered in Fig. 7) are representative of the age of the varnish samples used for calibration. Errors introduced by nonsynchronous varnish initiation and time needed to attain the massive substructure are probably negligible in terms of K/Ar ages and other uncertainties. Additional uncertainty for young samples arises from the fact that the youngest dated volcanic rock (39,000-yr-old basalt flow, 2A) has an age uncertainty of 33,000 yr.

The input cation ratio can be estimated by analyzing soil at the Coso volcanic lo-

FIG. 5. Verification of cation-ratio dating in relative-age sequences. The cation ratios (circles) and standard deviations (bars) for A, and C–E are K + Ca:Ti, and Na + K + Ca:Ti for B. (A) Cation K + Ca:Ti ratios of the three darkest deposits (D = dark, M = moderate, L = light) of a debris cone in Death Valley (Fig. 4). (B) Varnish Na + K + Ca:Ti cation ratios (and SD) of the same deposits as A. (C) Cation ratios of varnish sampled from a sequence of inset talus flatirons at Timna, Negev Desert, Israel (Fig. 6). (D) Cation ratios of varnish from a talus flatiron sequence near Paran, Negev Desert, Israel. (E) Cation ratios of varnish on prehistoric shorelines of Searles Lake (southern California), and a desert pavement (at 701 m) above 10,500-yr-old high stand (690 m).

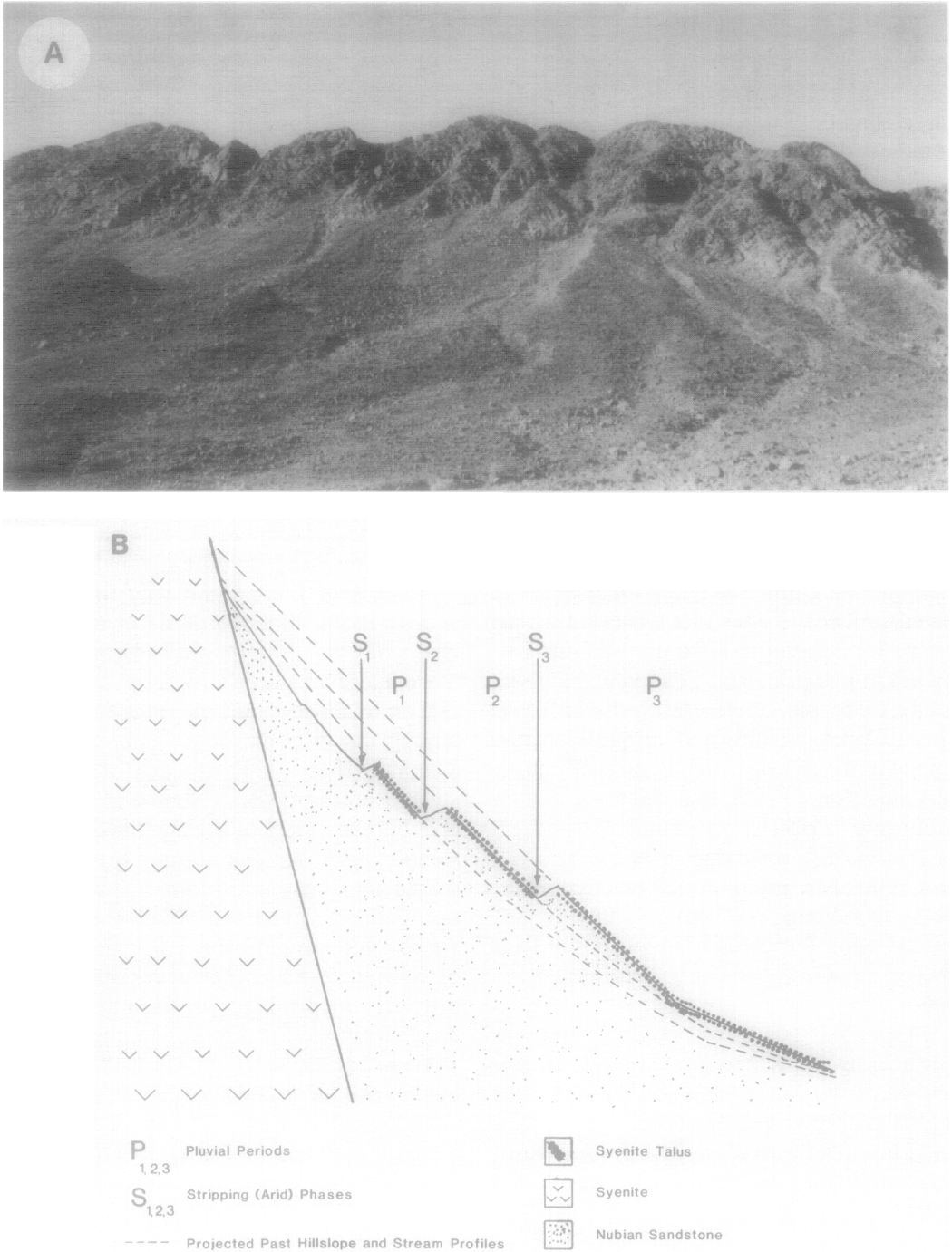


FIG. 6. Talus flatirons from Timna, Negev Desert, Israel. (A) Hillslope in the Timna Basin, Negev Desert, Israel, showing the development of talus flatirons of three ages. (B) Idealized model of the development of talus flatirons at Timna, modified from Gerson (1981). Subscripts 1, 2, and 3 represent successively older phases of flatiron development.

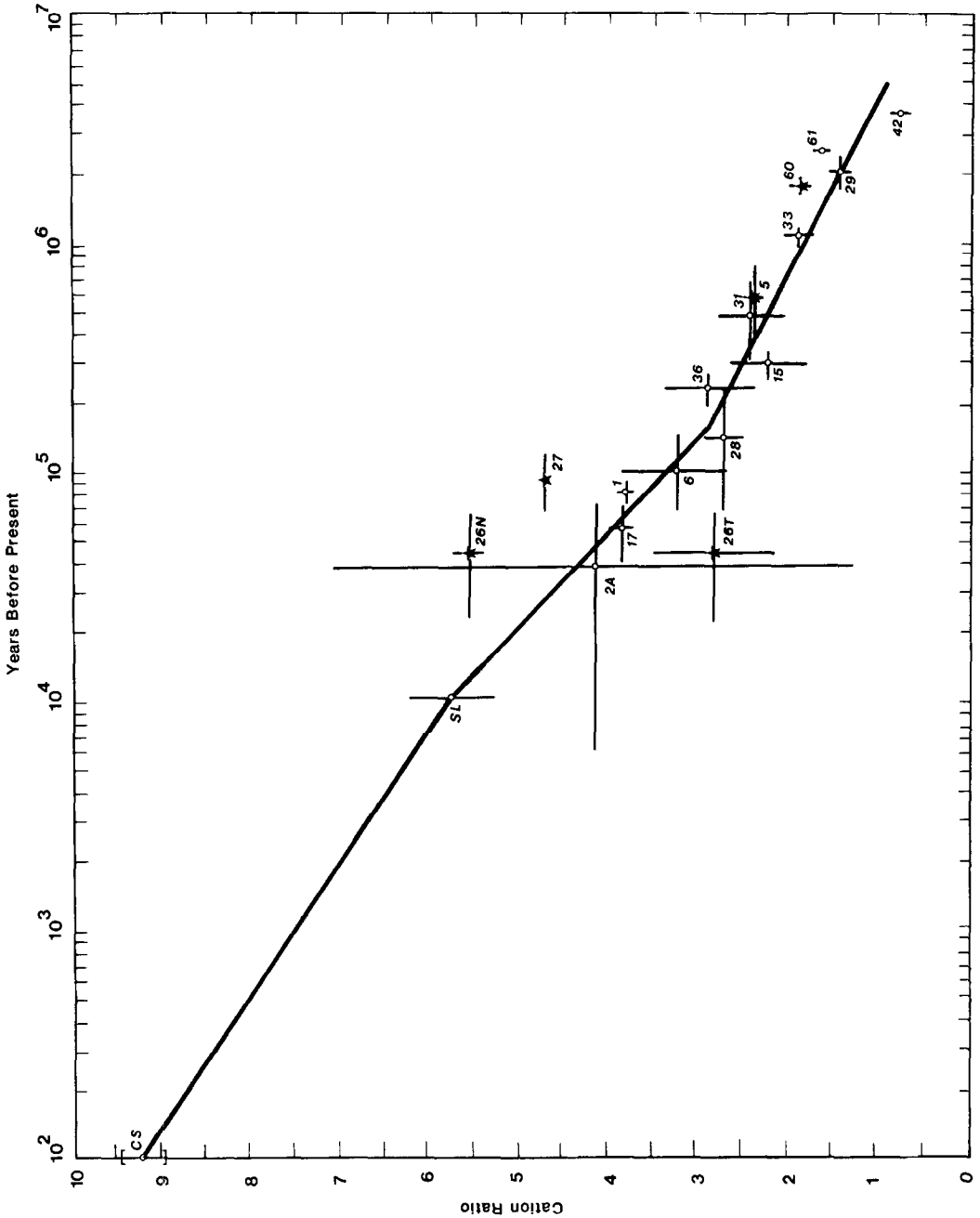


FIG. 7. Varnish K + Ca:Ti cation-leaching curve for the Coso region, southern California. Numbers represent K/Ar-dated volcanic deposits of the Coso volcanic field, identified in Duffield and Bacon (1981). The starred points represent volcanic surfaces that probably do not accurately represent the K/Ar radiometric ages. SL is the varnish ratio for late Pleistocene high stand of Searles Lake. CS is the ratio for the clay-sized Coso Soil material from all 16 volcanic sites. The horizontal and vertical bars represent the K/Ar age uncertainties and the standard deviations of varnish cation ratios, respectively. The brackets on the left margin of the graph show the standard deviation of all 16 soil samples. The lines are semilog regressions, and they indicate the rate of varnish cation leaching in the Coso Range and vicinity, based on the non-starred volcanic rocks and the SL and CS ratios; they are discussed in greater detail in the text.

calities. For the clay-size fraction the average and standard deviation of the K<sup>+</sup>Ca:Ti ratio from 16 Coso Range sites is  $9.17 \pm 0.22$ . For the <120- $\mu\text{m}$  fraction, the average is  $15.56 \pm 4.80$ . Electron microscope observation of varnish surfaces indicate that the particle size incorporated into varnish is usually less than 2  $\mu\text{m}$  in largest dimension (e.g., Fig. 2C). This suggests that the initial cation ratio should be that of the clay-sized fraction. However, it is likely that some K and Ca from the larger particles is included in varnish. Thus, the actual input cation ratio is between 9.17 and 15.56, and probably closer to 9.17. One way to represent the input cation ratio on the logarithmic scale of Figure 7 is to plot the minimum value, 9.17, intuitively at 100 yr B.P. rather than at zero to adjust for the higher ratio in the <120- $\mu\text{m}$  fraction. This procedure probably does not seriously affect the conclusions reached from Figure 7, considering the other sources of error.

The rates of varnish cation-leaching probably were not constant between 39,000 and 100 yr B.P., especially because the southern Great Basin–Mojave Desert region went through a major climatic change to a more arid environment about 11,000 yr B.P. (Smith, 1976, 1979; King, 1976; Mehlinger, 1977; Van Devender and Spaulding, 1979; Wells, 1980; Thompson and Mead, 1982). To fill this gap between 100 and 39,000 yr B.P., the cation ratio of varnish from the high stand of Searles Lake about 10,500 yr ago (Smith, 1976, 1979) was used, even though Searles Lake is about 65 km from the Coso volcanic field.

The varnish K<sup>+</sup>Ca:Ti ratio of the 10,500-yr-old high stand of Searles Lake in the Poison Canyon area (NW corner, Sect. 25, T. 26 S; R. 42 E; Searles Lake 15' quadrangle, U.S. Geological Survey), determined by PIXE analysis, is  $6.03 \pm 0.59$ . The cation ratio of the clay-size fraction of the soil at Poison Canyon is  $9.65 \pm 4.20$ , or slightly more than at the Coso volcanic field. Therefore, the varnish ratio was multiplied by the ratio of the Coso soil to the

Poison Canyon soil (9.17/9.65), giving an adjusted ratio of  $5.73 \pm 0.56$  for the cation ratio of the 10,500-yr-old deposit at Searles Lake.

The cation-leaching curve in Figure 7 represents an empirical relationship between varnish cation ratios and age for the Coso and Searles Lake areas. It includes the cation ratios of the non-starred volcanic flows, the Coso Range soils, and the Searles Lake deposit. The arithmetic scatter plot of the data is nonlinear. Therefore, a logarithmic transformation was performed on the independent variable, age of the surface (i.e., Box and Tidwell, 1962). One least-squares semilog regression could summarize the relationship between cation ratio and time. However, there are nonlinear aspects of the data plotted in Figure 7 that would be disguised by a single regression line. Furthermore, one least-squares line would be of minimal predictive value for the late Pleistocene and Holocene. In order to attempt to account for these nonlinearities, two preliminary least-squares regressions were fitted to the data. The lines in Figure 7 from SL to 36 and from 36 to 42 are semilog least-squares regression lines with correlation coefficients of  $-0.99$  and  $-0.98$ , respectively. The line from SL to CS is drawn between end points. The cation-leaching curve in Figure 7 can be described by the function

$$\begin{aligned}
 &= 7.468 - 0.170\log X \\
 &\quad \text{for } 10^2 < X < 1.05 \times 10^4 \\
 Y &= 8.211 - 2.433\log X \\
 &\quad \text{for } 1.05 \times 10^4 < X < 1.50 \times 10^5 \\
 &= 5.724 - 1.296\log X \\
 &\quad \text{for } 1.50 \times 10^5 < X < 10^7,
 \end{aligned}$$

where  $X$  is in yr B.P. and  $Y$  is the varnish K<sup>+</sup>Ca:Ti cation ratio.

The reasons for selecting the two preliminary break points in this cation-leaching curve may be explained by the following tentative hypotheses. A reduction in the cation-leaching rate about 150,000 to 200,000 yr B.P. may be due to leaching of most of the readily exchangeable cations, or per-



haps to near saturation of the varnish cation-exchange complex with relatively immobile cations. If the break about 10,500 yr B.P. is not an artifact of the assignment of 100 yr B.P. to CS (at 9.17), it is probably due to climatic change. Because climate undoubtedly affects the leaching rate, glacial intervals, such as the Wisconsin, should have more rapid leaching rates. Conversely, the rate of leaching between 10,500 and 100 yr B.P. should be lower because of greater aridity during the Holocene (Smith, 1976, 1979; King, 1976; Mehlinger, 1977; Van Devender and Spaulding, 1979; Wells, 1980; Thompson and Mead, 1982). The varnish cation technique is probably not sensitive enough to record climatic fluctuations in the last 10,500 yr. Similarly, the decreasing rate of cation exchange and/or leaching with time, may disguise the climatic oscillations prior to about 80,000 yr B.P.

#### USE OF CATION RATIOS AS A METHOD OF ABSOLUTE OR RELATIVE DATING

This section presents examples of the assignment of absolute or relative ages to arid-land geomorphic and archaeological rock surfaces.

##### *Surfaces in the Coso Field and Searles Lake Regions*

An undated 4- 10-m-thick intracanyon lava flow of the Owens River Valley (flow Qbr in Duffield and Bacon, 1981), has a varnish cation ratio of  $4.31 \pm 0.56$ . The Coso cation-leaching curve (Fig. 7) suggests an age of 41,000 yr B.P., with an error margin (EM) from 24,000 to 71,000 yr B.P. Radiometric dates for this and other undated volcanic rocks in the Coso field would provide a useful test of the cation-dating method.

Alluvial fans of varying stages of dissection extend out from the Coso Range. Varnished cobbles were collected from loose desert pavement on a relatively undissected surface of a "bajada" near the road on the west side of Sect. 19, T. 24 S; R. 4 E;

Mountain Springs Canyon, 15' quadrangle at about 756 m (2480 ft). The varnish cation ratio of the cobbles is  $4.78 \pm 0.20$ , suggesting an age of about 26,500 yr B.P. (EM 21,500 to 32,000 yr B.P.) (Figure 7). It would be valuable to compare the age of this relatively undissected surface with the ages of more heavily dissected fans farther east.

The Searles Lake basin contains varnished surfaces that, if dated, could provide information on the history of lake fluctuations and tectonism in the area. Rounded cobbles were sampled at 707 m, above the 10,500-yr-old high stand of Searles Lake just south of Gold Bottom Mine (R. 44 E; T. 24 S; Trona 15' quadrangle, U.S. Geological Survey). They appear to have been worked by wave action and are now located on a wide interfluvium. If the varnish cation ratio on the cobbles ( $3.21 \pm 0.61$ ) is corrected for the greater  $K^{+}Ca:Ti$  ratio in the soils near Gold Bottom Mine compared with the Coso soils (9.17/9.78), the adjusted varnish ratio is  $3.01 \pm 0.57$ , suggesting an age of 140,000 yr B.P. (EM 101,000 to 350,000 yr B.P.) (Figure 7). The utility of the Coso leaching curve in this region may be limited by differences between the Searles Lake area and the Coso volcanic field. However, Smith (1976) estimated that a 20,000-yr-long high lake stand started about 130,000 yr B.P., based on extrapolated sedimentation rates. The date for the varnish is close to Smith's age determination, and the difference is well within the error margin of the varnish cation-ratio date.

If these cobbles represent a high stand of the lake, and if high stands of Searles Lake have been controlled by overflow, the relative rate of lowering of the overflow outlet of Searles Lake and/or uplift of the Slate Range can be estimated. From approximately 10,500 (shoreline at 686 m) to approximately 140,000 yr B.P. (shoreline at 707 m), the relative rate of uplift of the Slate Range averaged about 16 cm/1000 yr. Accounting for planimetric distances between the 686- and 707-m shorelines, the average rate of tilt from approximately 10,500 yr B.P.

to 140,000 yr B.P. has been  $0.08 \text{ cm km}^{-1} \text{ yr}^{-1}$ . This figure is similar to the more extreme values obtained by Smith and Church (1980) for surveys taken between 1943 and 1975 in the region.

The application of the Coso cation-leaching curve (Fig. 7) is not limited to geomorphology. Varnished petroglyphs in the Coso Range are also being dated. Nor is the Coso curve necessarily limited to the Coso region. With adequate precautions it may be possible to use it in other regions. Preliminary work on transferring the Coso curve to the Manix Lake basin suggests that varnish on pavement cobbles on top of the Yermo Fan (Sect. 22, R. 2E, T. 10 N; Yermo 7 1/2' quadrangle, U.S. Geological Survey) may be about 100,000 yr old. These cobbles were sampled above Master Pit I of the Calico Archaeological site. The date assigned to the soil at the Calico site by Bischoff *et al.* (1981, p. 579) was between 80,000 and 125,000 yr B.P.

### *Lithic Artifacts*

Most of the lithic artifacts in the western United States observed in this study have little or no black surface varnish on them. Where varnish is present, it is commonly thin and requires careful scraping at  $45\times$  magnification, as is the case for the varnished artifacts from the Manix Lake and San Dieguito industries discussed in this section.

Varnished tools, made of chert from the Manix Lake lithic industry (F. Budinger, personal communication, 1982) were collected on the surface of the Yermo fan, in the Mojave Desert, about 7 km northeast of Yermo, California. Varnish on five sampled artifacts had an average  $\text{K}^+\text{Ca}:\text{Ti}$  ratio of  $5.81 \pm 1.19$ . Black surface varnish on seven cobbles of unworked chert in a nearby desert pavement had a lower (more leached) ratio of  $3.35 \pm 0.32$ . Thus, varnish on the Manix Lake artifacts is considerably younger than that on cobbles in the nearby natural pavement.

Julian D. Hayden contributed varnished artifacts for cation-ratio analysis from the Malpais and San Dieguito I phases of the San Dieguito complex, Sierra Pinacate, Mexico. The Malpais artifacts are thought, on many grounds, to have been made during a pluvial phase beginning ending before about 19,000 yr B.P. (the Malpais pluvial) which preceded a relatively more arid period of unknown duration. Malpais tools usually have a well-developed varnish. Artifacts of the succeeding San Dieguito I phase of the most recent pluvial period usually only have a poor varnish, probably deposited during the early Holocene approximately 9000 to 5000 yr B.P. in the Pinacate (J. D. Hayden, personal communication, 1982).

Cation ratios of varnish from flake scars of these artifacts support Hayden's (1976) relative chronology, although the assignment of absolute dates to the Pinacate cation ratios is not now possible. Three Malpais samples have an average ratio of  $1.59 \pm 0.11$ , with a spread from  $1.51 \pm 0.11$  to  $1.72 \pm 0.07$ . The San Dieguito I sample analyzed has a less-leached ratio of  $1.85 \pm 0.04$ . The cation ratio for each Pinacate artifact represents an average of analyses of three separate scrapings.

### *South Stoddard Locality*

Engel (1957) and Engel and Sharp (1958, p. 515) asserted that desert varnish had formed in 25 yr on an abandoned dirt (power line) road, just off of the Stoddard Well-Barstow road in the Mojave Desert. This claim has been cited often (e.g., Hem, 1964, p. B10; Fairbridge, 1968, p. 280; Goudie and Wilkinson, 1977, p. 18). Field observations of this site, as specified by Engel (1957), make it clear that optically visible revarnishing has not occurred in the last 50 yr (Dorn and Oberlander, 1982; Elvidge, 1982). Additional evidence comes from comparing the cation ratios of black varnish on stones in the road and on cobbles in the surrounding pavement. These varnish scrapings were analyzed by XRF, hence only the

Ca:Ti ratio is presented. These analyses of varnish scrapings of stones from the dirt road and from the surrounding desert pavement produced virtually identical Ca:Ti ratios of  $1.703 \pm 0.035$  and  $1.696 \pm 0.034$ , respectively. This suggests that the occurrence of black surface varnish and orange bottom varnish exposed at the surface of the road has to do with the reexposure of rocks (e.g., through processes described by Springer, 1958), which were driven or plowed under during road construction.

#### DISCUSSION OF THE LIMITATIONS OF CATION-RATIO DATING

Cation-ratio dating has been shown to be a valid age-determination technique for many surfaces when varnishes were sampled from similar environments. However, this study has highlighted some potential problems that require further discussion and study.

##### *Determining the Input Cation Ratio*

The clay-size fraction of soil surfaces has been used in this study to estimate input ratios in the Coso region. While the cation ratio of contemporary airborne fallout might seem more accurate than that of soil, the effect of anthropogenic aerosols (e.g., smog from the San Joaquin Valley or dust from Owens Dry Lake near the Coso Range) would complicate attempts to sample accurately the "natural" and long-term airborne fallout. Cahill *et al.* (1981) concluded that the chemistries of surface soils from remote, arid sites in the western United States are very similar to aerosol chemistries taken from the same sites. The one exception, a potassium anomaly, was attributed to smoke sources. More site-specific research is needed to compare natural airborne fallout with soil material and dust trapped in rock surface depressions. Also, because material larger than clay is occasionally incorporated into varnish, further studies are needed to assess quantitatively its effect on varnish chemistry.

##### *Varnish Cation Exchange*

Little is known about the actual process of varnish cation exchange. The reduction of a cation ratio may be due just to leaching of mobile cations, but it may also result in part from the replacement of leachable bases with less mobile cations, such as Ti. Differential fixation of K in clay lattices (e.g., in illite), the complexing of cations by the organic matter present in varnish (Dorn and Oberlander, 1982), adsorption of H and Al ions, varnish pH-Eh, and other factors may all play a role in varnish cation exchange in different ways at different sites. Laboratory experiments are needed on the process of varnish cation exchange.

The rate of cation exchange has been assumed to be constant for a given sampling area. However, curves of varnish leaching are probably dissimilar, because varnish structures and environmental factors (outlined under assumption 4) may differ from site to site. For example, the cation ratios of the Death Valley debris cone (Fig. 4) are comparatively low, even though the deposits are probably only Holocene in age, because the region is rich in titanium. In a more general example, varnish thickness and micromorphology can vary greatly. This is significant, because both factors affect the accessibility of exchange sites in varnish, a major control of the rate of cation exchange.

Thinner varnishes are probably more easily leached than thicker coatings. This is not a problem for dating, as long as varnishes are sampled where microenvironmental conditions are similar and thickness is time dependent. However, thickness can sometimes be highly variable on surfaces with similar ages: (1) rock surface microdepressions have thicker varnishes than exposed microridges, (2) different aspects on a rock surface may have been subjected to varying degrees of eolian abrasion, (3) some varnishes start in cracks, where thickness is affected by conditions inside the crevice, and (4) varnish growth rates are influenced

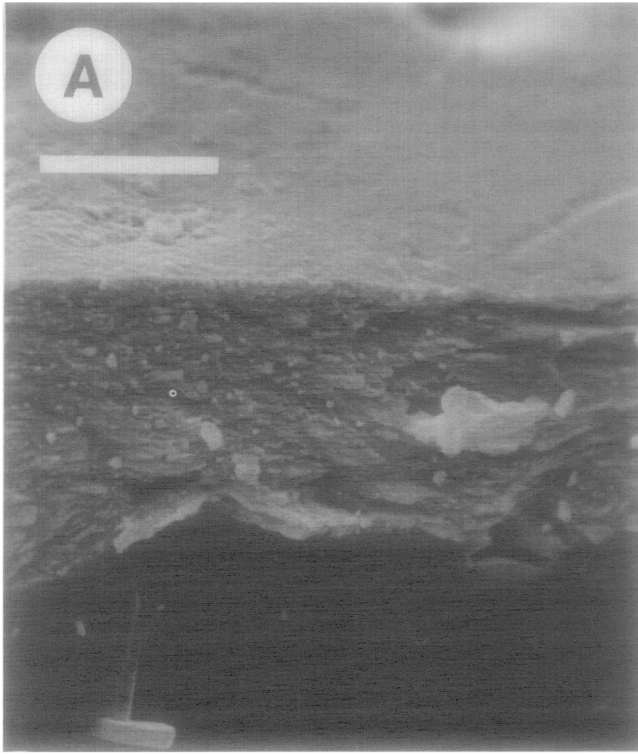


FIG. 8. Micromorphological variations of varnish with depth. (A) Subsurface lamellate layers of black varnish from the darkest deposit of a debris cone in Death Valley (Fig. 4). Scale bar 5  $\mu\text{m}$ . (B) Entirely botryoidal varnish on chert, collected near Amistad Reservoir, western Texas. The morphologic distinctness of the varnish, compared to the underlying rock, is evident in this image and in Figure 8A. Scale bar 10  $\mu\text{m}$ . (C) Micrograph of a broken edge of varnish on Coso flow 28, having a K/Ar age of  $140,000 \pm 89,000$  yr (Duffield *et al.*, 1980). A sequence of four layered varnish micromorphologies is present from the varnish surface down to the underlying rock (lower arrow): surface lamellate, subsurface botryoidal (upper arrow), subsurface lamellate, and indistinct micromorphology just above the underlying rock. Considering the K/Ar age of the basalt flow, the lamellate stratum may be associated with interglacial conditions, and the botryoidal layer may have developed during the relatively moister conditions of the Wisconsin glaciation. Scale bar 20  $\mu\text{m}$ .

by manganese-oxidizing microorganisms, as well as the rate of eolian fallout of manganese and illite–montmorillonite clays.

The subsurface micromorphology of varnish varies from entirely lamellate (Fig. 8A) to botryoidal (Fig. 8B) to a sequential development alternating between the two (Fig. 8C). While the overall structure of botryoids seems more permeable, and therefore more accessible to cation exchange, the individual botryoids observed in this study appear to be more compact than the individual lamellate layers. Thus, the surfaces

in a lamellate varnish are probably more accessible to leaching meteoric waters than in a botryoidal varnish. Although measurements of varnish permeability would be valuable, they might not reflect the accessibility of surfaces within the varnish to cation exchange.

#### *Regional Comparisons of Cation Ratios*

The ultimate goal of this study is to construct a series of cation-leaching curves, calibrated to surfaces of known age, for areas throughout the western United States

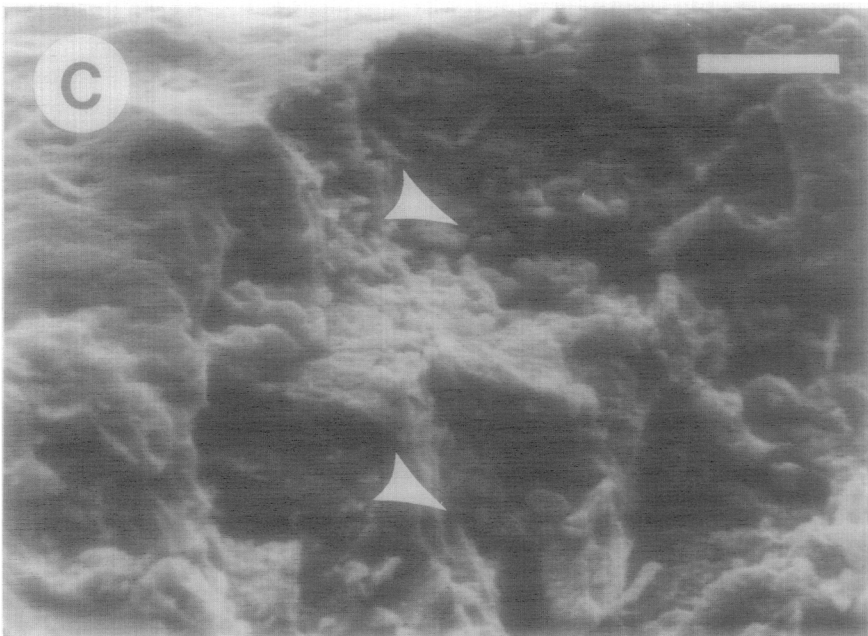
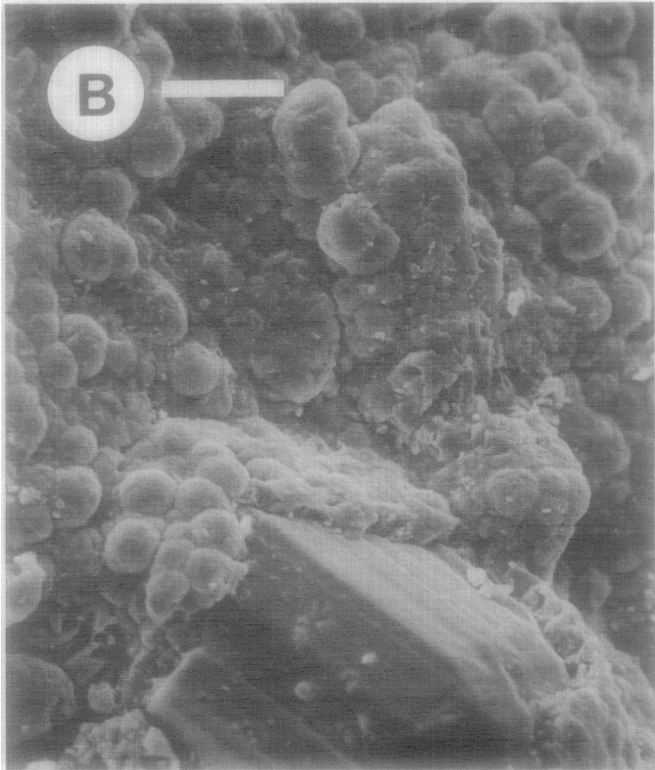


FIG. 8 —Continued.

and other arid regions. One intermediate aim is to apply an established cation-leaching curve to surfaces away from a region where the curve has been established. However, before either of these goals can be achieved, a quantitative understanding of the four previously made assumptions will be required.

### SUMMARY AND CONCLUSION

Many of the previously proposed methods of dating rock varnish are based on untenable assumptions or on characteristics that depend on the manganese concentration of the varnish, which in turn is controlled by microenvironmental factors affecting manganese-oxidizing microorganisms. All varnish age-determination techniques rely on the assumption that varnish is a biogeochemical sink for manganese. Furthermore, all methods date only the onset of varnishing. Hence, factors that inhibit the colonization of rock surfaces by manganese-concentrating microorganisms limit the usefulness of varnish for dating the exposure of the underlying rock to subaerial processes.

Despite these difficulties, the cation-ratio method of dating has been demonstrated to be a valid relative and calibrated absolute varnish age-determination technique. It is based on the concept that a ratio of mobile cations (e.g., Na, Mg, K, Ca) to less mobile cations (e.g., Ti) decreases with time. Cation-ratio dating has been tested on relative-age sequences of colluvial and lacustrine surfaces. Cation ratios were used to verify the relative ages of the San Dieguito (Pinacate, Mexico) and Manix Lake (Southern California) lithic industries and to demonstrate that varnish did not form at the South Stoddard locality (Mojave Desert) in 25 yr, as previously postulated (Engel and Sharp, 1958, p. 515). With the construction of a calibrated cation-leaching curve for the Coso and Searles Lake regions, it was possible to estimate the absolute ages of varnishes on geomorphic surfaces in the area. The rate of cation leaching in the Coso re-

gion is approximately linear on a semilog graph. However, the leaching rate may vary in regions with different precipitation regimes, temperatures, varnish structures, airborne fallout, and other factors. More research on the rate and processes of cation exchange in rock varnish is needed.

One of the greatest advantages of cation-ratio dating is that cation ratios are easily and inexpensively determined by bulk chemical analysis. Important parts of the method are encountered in the sampling stage, where microenvironmental factors can be controlled, and in the sample preparation stage, where contamination of the varnish scrapings by the underlying rock must be avoided. Cation-ratio dating is most effective as a relative-age determination technique when used with varnish paleoenvironmental indicators, such as micromorphological stratigraphy and microchemical laminations (Dorn and Oberlander, 1981b, 1982).

Because varnish is ubiquitous on rock surfaces in desert regions, cation-ratio dating has great potential for archaeological and geomorphological research in arid lands. Cation ratios can be used to date archaeological remains without the traditional restriction of burial by datable deposits. Investigations of alluvial-fan morphogenesis, frequency of deposition, rates of slope retreat, and other problems of desert geomorphology could potentially benefit from cation-ratio dating. Current data on the cation-leaching rates of rock varnish is limited, but with continued research it is hoped that cation-ratio dating can be used in many areas.

### ACKNOWLEDGMENTS

This research was funded by the University of California and by National Science Foundation Grant SES 80-24555 to Dr. T. M. Oberlander. T. M. Oberlander called my attention to the Coso volcanic field and assisted in the collection of varnishes in the Coso region. I thank Julian Hayden for contributing samples for analysis, Ran Gerson for his help in selecting Israeli sampling sites, and Tom Dodson, Glen Roqmore, Carolyn Shepherd, and Dave Whitley for facilitating sam-

pling in the Coso region. I also thank Tom Cahill and Crocker Nuclear Laboratory, University of California at Davis, for providing several PIXE analyses.

## REFERENCES

- Allen, C. C. (1978). Desert varnish of the Sonoran Desert: Optical and electron probe microanalysis. *Journal of Geology* **86**, 743-752.
- Aubert, H., and Pinta, M. (1977). "Trace Elements in Soils." Elsevier Scientific, Amsterdam.
- Bard, J. C. (1979). "The Development of a Patination Dating Technique for Great Basin Petroglyphs Utilizing Neutron Activation and X-Ray Fluorescence Analysis." Ph.D. dissertation, University of California, Berkeley.
- Benson, L. V. (1978). Fluctuation in the level of pluvial Lake Lahontan during the last 40,000 years. *Quaternary Research* **9**, 300-318.
- Benson, L. V. (1981). Paleoclimatic significance of lake-level fluctuations in the Lahontan basin. *Quaternary Research* **16**, 390-403.
- Bischoff, J. L., Shlemon, R. J., Ku, T. L., Simpson, R. D., Rosenbauer, R. J., and Budinger, F. (1981). Uranium-series and soil-geomorphic dating of the Calico archaeological site, California. *Geology* **9**, 576-582.
- Blake, W. P. (1855). "Geological Report. Explorations and Surveys for a Railroad Route from the Mississippi River to the Pacific Ocean." Special Executive Document 78, Vol. 5, Part II, p. 263. 33rd Congress, 2nd Session.
- Boussingault, M. (1882). Sur l'apparition du manganese a la surfaces des roches. *Annales de Chimie et de Physique* **27** (Series 5), 289-311.
- Box, G. E. P., and Tidwell, P. W. (1962). Transformation of the independent Variables. *Technometrics* **4**, 531-550.
- Cahill, T. A. (1981). Ion beam analysis of environmental samples. In "Short-lived Radionuclides in Chemistry and Biology" (J. W. Root and K. A. Krohn, Eds.), pp. 511-522. Amer. Chem. Soc., Washington, D.C.
- Cahill, T. A., Ashbaugh, L. L., Eldred, R. A., Feeney, P. J., Kusko, B. H., and Flocchini, R. G. (1981). Comparisons between size-segregated resuspended soil samples and ambient aerosols in the western United States. In "Atmospheric Aerosol Source/Air Quality Relationships" (E. S. Macias and P. K. Hopke, Eds.), pp. 269-285. Amer. Chem. Soc., Washington, D.C.
- Chesworth, W., Dejou, J., and Larroque, P. (1981). The weathering of basalt and relative mobilities of the major elements at Belbex, France. *Geochimica et Cosmochimica Acta* **45**, 1235-1243.
- Colman, S. M. (1982). "Chemical weathering of Basalts and Andesites: Evidence from Weathering Rinds." U.S. Geological Survey Professional Paper 1246.
- Crerar, D. A., Cormick, R. K., and Barnes, H. L. (1980). Geochemistry of manganese: An overview. In "Geology and Geochemistry of Manganese" (I. M. Varentsov and Gy. Grasselly, Eds.), Vol. I pp. 293-334. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.
- Dorn, R. I. (1981). Observations on the use of "desert varnish" in the age-determination of surfaces. *Society for California Archaeology Newsletter* **16**, 15-18.
- Dorn, R. I., and Oberlander, T. M. (1980). The biological origin of desert varnish. In "Program Abstracts, Association of American Geographers, Louisville Meeting," p. 207.
- Dorn, R. I., and Oberlander, T. M. (1981a). Microbial origin of desert varnish. *Science* **213**, 1245-1247.
- Dorn, R. I., and Oberlander, T. M. (1981b). Rock varnish origin, characteristics, and usage. *Zeitschrift für Geomorphologie* **25**, 420-436.
- Dorn, R. I., and Oberlander, T. M. (1981c). Desert varnish: An example of a terrestrial manganese sink. In "Abstracts: International Conference on Aridic Soils, Jerusalem, Israel, March 29-April 4" (D. H. Yaalon, Ed.), p. 33.
- Dorn, R. I., and Oberlander, T. M. (1982). Rock varnish. *Progress in Physical Geography* **6**, 317-367.
- Duffield, W. A., Bacon, C. R., and Dalrymple, G. B. (1980). Late Cenozoic volcanism, geochronology, and structure of the Coso Range, Inyo County, California. *Journal of Geophysical Research* **85**, 2381-2404.
- Duffield, W. A., and Bacon, C. R. (1981). "Geologic Map of the Coso Volcanic Field and Adjacent Areas, Inyo County, California." U.S. Geological Survey Miscellaneous Investigation Map I-1200.
- EI rashidi, M. A., Shehata, A., and Hamdi, H. (1978). Estimation of Fe and Mn solubility in saline alkali Soils by the use of some chemical solutions. *Egyptian Journal of Soil Science* **18**, 217-231.
- Elvidge, C. D. (1979). "Distribution and Formation of Desert Varnish in Arizona." M.S. thesis, Arizona State University, Tempe.
- Elvidge, C. D. (1982). Reexamination of the rate of desert varnish formation reported south of Barstow, California. *Earth Surface Processes* **7**, 345-348.
- Elvidge, C. D., and Moore, C. B. (1979). A model for desert varnish formation. *Geological Society of America Abstracts with Programs* **11**, 271.
- Elvidge, C. D., and Collet, C. J. (1981). Desert varnish in Arizona: Distribution and spectral characteristics. In "Technical Papers of the American Society of Photogrammetry, ASP-ACSM Fall Technical Meeting, San Francisco, September 9-11," pp. 215-222.
- Engel, C. G. (1957). "Desert Varnish." M.S. thesis, University of California, Los Angeles.
- Engel, C. G., and Sharp, R. S. (1958). Chemical data on desert varnish. *Geological Society of America Bulletin* **69**, 487-518.

- Fairbridge, R. W. (1968). Desert varnish (patina). In "Encyclopedia of Geomorphology" (R. W. Fairbridge, Ed.), pp. 279–280. Dowden, Hutchinson & Ross, Stroudsburg, Pa.
- Gardner, L. R. (1980). Mobilization of Al and Ti during weathering—Isovolumetric geochemical evidence. *Chemical Geology* 30, 151–165.
- Gerson, R. (1981). Geomorphic aspects of the Elat Mountains. In "Aridic Soils of Israel" (J. Dan, R. Gerson, H. Koyumdjisky, and D. H. Yaalon, Eds.), pp. 279–296. Agricultural Research Organization, Jerusalem.
- Gerson, R. (in press). Talus relicts in deserts: A key to major climatic fluctuations. *Israel Journal of Earth Science*.
- Glover, H. G. (1975). Acidic and ferruginous mine drainages. In "The Ecology of Resource Degradation and Renewal Processes" (M. J. Chadwick, and C. T. Goodman, Eds.), pp. 173–196. Blackwell Scientific, Oxford.
- Goudie, A., and Wilkinson, J. (1977). "The Warm Desert Environment." Cambridge Univ. Press, Cambridge, Mass.
- Hayden, J. (1976). Pre-altithermal archaeology in the Sierra Pinacate, Sonora, Mexico. *American Antiquity* 41, 274–289.
- Heizer, R. F., and Baumhoff, M. A. (1962). "Prehistoric Rock Art of Nevada and Eastern California." Univ. of California Press, Berkeley.
- Hem, J. D. (1964). Deposition and solution of manganese oxides. U.S. Geological Survey, *Water-Supply Paper* 1667-B.
- Hooke, R. (1967). Processes on arid-region alluvial fans. *Journal of Geology* 75, 438–460.
- Hume, W. F. (1925). "Geology of Egypt." Vol. 1, pp. 143–161. Government Press, Cairo.
- Jenne, E. A. (1968). Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe oxides. In "Trace Inorganics in Water" (R. F. Gould, Ed.), pp. 337–387. Amer. Chem. Soc., Washington, D.C.
- Karavinov, V. P., Kuntorovich, A. E., and Gerashimova, L. M. (1966). Mechanical and chemical denudation of drainage areas. *International Geology Review* 8, 1199–1207.
- King, T. J. (1976). Archaeological implications of the paleobotanical record from Lucerne Valley area of the Mojave Desert. *San Bernadino County Museum Association Quarterly* 23.
- Knauss, K. G., and Ku, T. L. (1980). Desert varnish: Potential for age dating via uranium-series isotopes. *Journal of Geology* 88, 95–100.
- Krumbein, W. E., and Jens, K. (1981). Biogenic rock varnishes of the Negev Desert (Israel): An ecological study of iron and manganese transformation by cyanobacteria and fungi. *Oecologia (Berlin)* 50, 25–38.
- Lukashev, K. I. (1970). "Lithology and Geochemistry of the Weathering Crust." Israel Program for Scientific Translations, Jerusalem, Israel.
- Marchand, D. E. (1974). "Chemical Weathering, Soil Development, and Geochemical Fractionation in a Part of the White Mountains, Mono and Inyo Counties, California," pp. 379–424. U.S. Geological Survey Professional Paper 352-J.
- Mehring, P. J. (1977). Great Basin late Quaternary environments and chronology. In "Models and Great Basin Prehistory" (D. D. Fowler, Ed.), pp. 113–167. Desert Research Institute Publications in the Social Sciences No. 12.
- Muir, M. D. (1978). Microenvironments of some modern and fossil iron- and manganese-oxidizing bacteria. In "Environmental Biogeochemistry and Geomicrobiology, Vol. 3: Methods, Metals, and Assessment" (W. E. Krumbein, Ed.), pp. 937–944. Ann Arbor Science Pub., Ann Arbor, Mich.
- Perry, R. S., and Adams, J. (1978). Desert varnish: Evidence of cyclic deposition of manganese. *Nature (London)* 276, 489–491.
- Péwé, T. L., Péwé, E. A., Péwé, R. H., Journaux, A., and Slatt, R. M. (1981). Desert dust: Characteristics and rates of deposition in central Arizona. *Geological Society of America Special Paper* 186, 169–190.
- Polynov, B. B. (1951). Modern ideas of soils formation and development. *Soils and Fertilizers* 14, 95–101.
- Potter, R. M. (1979). "The Tetravalent Manganese Oxides: Clarification of Their Structural Variations and Relationships and Characterization of Their Occurrence in the Terrestrial Weathering Environment on Desert Varnish and Other Manganese Oxide Concentrations." Ph.D. dissertation, California Institute of Technology, Pasadena.
- Potter, R. M., and Rossman, G. R. (1977). Desert varnish: Importance of clay minerals. *Sciences* 196, 1446–1448.
- Potter, R. M., and Rossman, G. R. (1979). The manganese- and iron-oxide mineralogy of desert varnish. *Chemical Geology* 25, 79–94.
- Reddy, M. R. (1973). "Fixation of Zinc and Manganese by Clay Minerals." Ph.D. dissertation, University of Georgia, Athens.
- Schweisfurth, R., Jung, W., and Jacobs, M. (1980). Manganese-oxidizing microorganisms and their importance for the genesis of manganese ore deposits. In "Geology and Geochemistry of Manganese" (I. M. Varentsov and Gy. Grasselly, Eds.), Vol. III pp. 279–283. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.
- Smith, G. I. (1976). Paleoclimatic record in the upper Quaternary sediments of Searles Lake, Calif., U.S.A. In "Paleolimnology of Lake Biwa and the Japanese Pleistocene" (S. Horie, Ed.), Vol. 4, pp. 577–604. Kyoto University, Kyoto.
- Smith, G. I. (1979). "Subsurface Stratigraphy and Geochemistry of Late Quaternary Evaporites,



- Searles Lake, California." U.S. Geological Survey Professional Paper 1043.
- Smith, G. I., and Church, J. P. (1980). Twentieth-century crustal deformation in the Garlock Fault-Slate range area, Southeastern California. *Geological Society of America Bulletin* **91**, 524-534.
- Springer, M. E. (1958). Desert pavement and vesicular layer of some desert soils in the desert of the Lahontan Basin, Nevada. *Soil Science Society America, Proceedings* **22**, 63-66.
- Thompson, R. S., and Mead, J. I. (1982). Late Quaternary environments and biogeography in the Great Basin. *Quaternary Research* **17**, 39-55.
- Uren, N. C., and Leeper, G. W. (1978). Microbial oxidation of divalent manganese. *Soil Biology & Biochemistry* **10**, 85-87.
- Van Devender, T., and Spaulding, W. (1979). Development of vegetation and climate in the southwestern U.S. *Science* **204**, 701-710.
- von Humboldt, A. (1907). "Personal Narrative of Travels to the Equinoctial Regions of America during the Years 1799-1804" (T. Ross, Transl. and Ed.), Bell, London.
- Walther, J. (1891). Die Denudation in der Wüste. *Akademie der Wissenschaften Mathematisch-Physikalische Klasse, Abhandlungen* **16**, 435-461.
- Wells, P. V. (1980). Quaternary vegetational history of the Great Basin. *Bulletin of the Ecological Society of America* **61**, 106 (Abstract).
- Whitney, M. I. (1979). Electron micrography of mineral surfaces subject to wind-blast erosion. *Geological Society of America Bulletin* **90**, 917-934.
- Yaalon, D. H., Brenner, I., and Koyumdjisky, H. (1974). Weathering and mobility sequence of minor elements on a basaltic pedomorphic surface, Galilee, Israel. *Geoderma* **12**, 233-244.