

Rock Varnish: Recorder of Desert Wetness?

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ABSTRACT

Rock varnish is a thin coating (<200 μm) of a cocktail rich in Mn, Fe, and clay minerals that is ubiquitous in desert regions. It has become the center of a contentious controversy revolving around its use to date geomorphic surfaces and/or to evaluate past climate conditions. We observe pronounced temporal variations in Mn and Ba concentration that are similar over large regions and that likely relate to variations in paleo-wetness. The mode of formation of varnish remains uncertain, but anthropogenic Pb concentrated in outermost varnish layers indicates its continued formation, and experiments using cosmogenic Be suggest that, while precipitation is a primary control, dust, dew, and aerosols may also be important in delivering the ingredients of varnish. We suggest several steps that may lead to rejuvenation and future breakthrough in varnish studies.

INTRODUCTION

Over the years, the suggestion of a large-scale geographic pattern of planetary wetness has emerged, namely, during glacial time, the extratropical deserts were wetter and at least some tropical areas were drier than they are now. A dramatic switch to present conditions occurred 15 500 yr B.P. at the onset of the Bølling-Allerød warm, a brief return to interglacial conditions preceding the Younger Dryas cold snap (12 000 yr B.P.). For example, at this time, equatorial Africa's Lake Victoria, which was dry during last glacial time, was rejuvenated, and the Great Basin's Lake Lahontan suddenly shrank from its highest shoreline to a size ten times smaller (Broecker et al., 1998). If it could be demonstrated

that this pattern was indeed global, then we would have strong evidence that a major change in the dynamics of the atmosphere's Hadley cell (upwelling of air in the tropical convergence zone coupled with downwelling in the extratropics) occurred. The problem is that detailed and well-dated climate records in desert regions are very hard to come by. This is especially true for times beyond the useful range of ^{14}C dating (i.e., ~30 000 yr). Rock varnish has the potential to yield wetness records extending back to the last interglacial period for each of the world's desert regions.

However, the study of rock varnish has been put in jeopardy by controversies revolving around the reliability of dating rock varnish (Dorn, 1996; Beck et al., 1998) and of correlations among varnish records (Reneau et al., 1992; Reneau, 1993). Radiometric dating of varnish itself has not proven possible. First of all, the varnish contains virtually no carbon. Further, its near-unity ratio of $^{232}\text{Th}/^{238}\text{U}$ activity precludes ^{230}Th dating. The cation-ratio method proposed by Dorn (1983) has received heavy criticism (Bierman and Gillespie, 1991; Reneau and Raymond, 1991). In an attempt to date the geomorphic surfaces on which the varnish forms, Dorn has published 200 or so radiocarbon ages (Dorn et al., 1989; Dorn et al., 1992a, 1992b). But, as shown by Beck et al. (1998), a large number of Dorn's samples are mixtures of a coal-like substance with very little ^{14}C and pyrolyzed wood with an apparent radiocarbon age of several thousand years. Hence, this approach has also fallen into disrepute, as has the cation-ratio method. There also have been claims that no reliable climate signals exist in the chemical stratigraphy of rock varnish (Reneau et al., 1992; Reneau, 1993).

Despite these setbacks, we are convinced that rock varnish does indeed bear an amazing record of wetness in Earth's desert regions. Rather than being measured in centimeters of accumulation per millennium, the sedimentary record in varnish is measured in micrometers of accumulation per millennium. Instead of being found in depositional basins many kilometers wide, varnish records are found in tiny "basins" with spans of only a millimeter or so. The climate record in varnish is contained in

variations of its color and chemical composition. Varnish from Death Valley shows a particularly large range, with MnO_2 concentrations extending from a low of 4% in the Holocene to a high of 40% during parts of the last glacial period (Fleisher et al., 1999; Fig. 1). We suspect but cannot yet prove that the greater the rainfall, the higher the MnO_2 content of varnish. In this paper, we will try to convince the reader of the potential offered by the rock varnish record by attempting to answer questions most often posed by critics.

Is the Record in Varnish Free from Flaws?

The answer to this question is "no." As is the case for most sedimentary sequences, erosional truncations and diagenetic alteration complicate the reading of the varnish record. Extreme care must be taken in order to minimize these imperfections. We have developed our own set of criteria. In the field, we look for the most stable rock surfaces with the highest probability of having the most complete varnish stratigraphy (but not necessarily the most extensive, darkest, or thickest varnish cover). In the laboratory, we look for varnish "microbasins" (i.e., varnish-filled dimples in the rock surface) that have a width-to-depth ratio of ~10, for they contain the most complete varnish microstratigraphy. Thin sections are cut to pass through the centers of selected dimples. A transmitted-light microscope helps in determining whether the varnish has distinct color layers that extend uninterrupted across the entire microbasin. Because accumulation does not necessarily begin at the same time in all microbasins on a given surface, comparisons reveal which of the basins contains the longest sequence of color variations. Element maps and element line profiles are then obtained using an electron microprobe on these thin sections.

Based on the examination of tens of thousands of varnished rocks in the field and thousands of thin sections in the lab, it appears to us that randomly sampled varnish surfaces rarely record reliably the full sequence of chemical events that transpired since the geomorphic surface was created. Further, random sections are often compromised by solution events, erosion, and peeling. Thus, lack of care in the selection of varnish

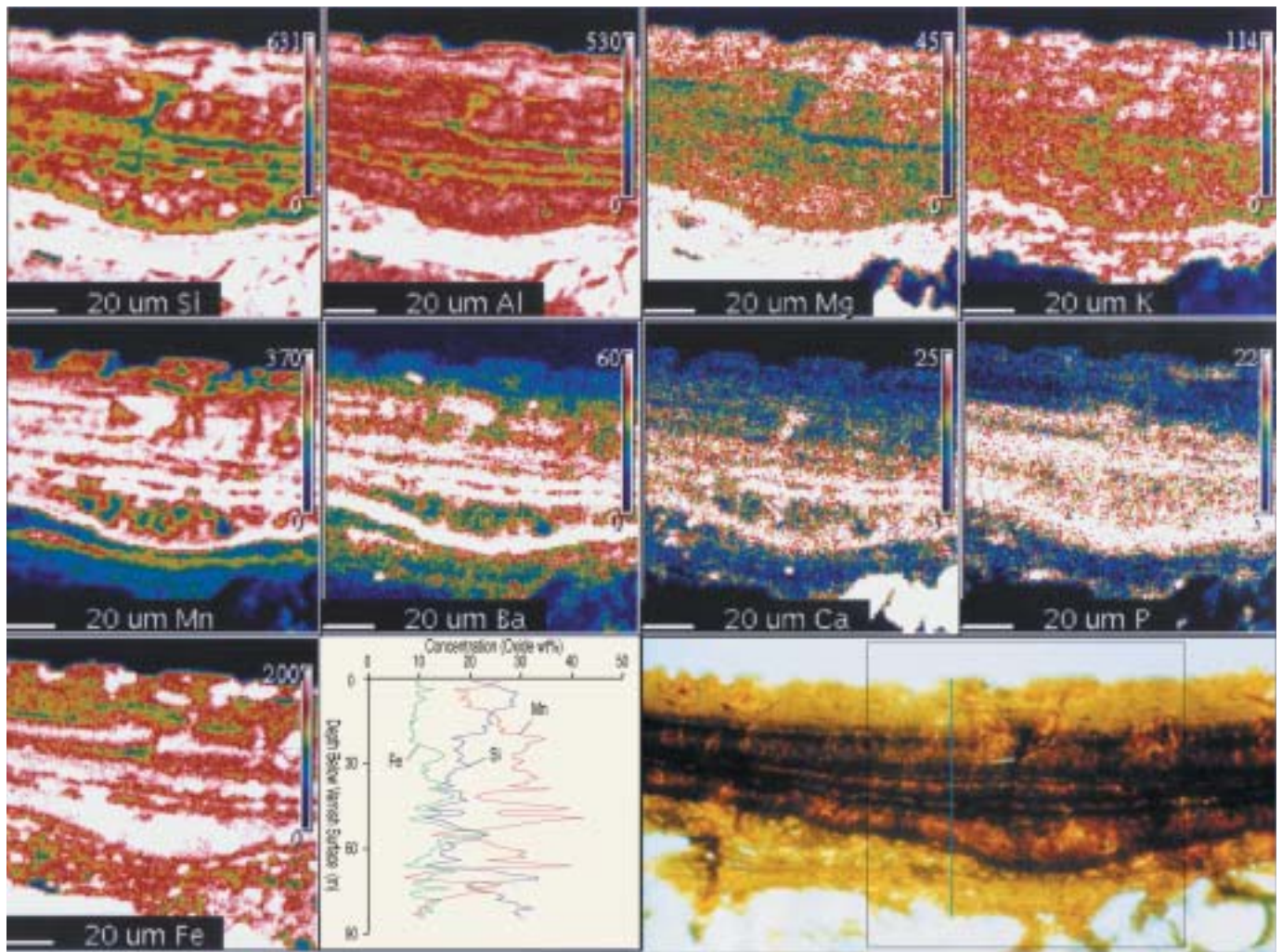


Figure 1. Photograph (lower right) and electron microprobe element maps produced from a varnish thin section from Death Valley, California. Si, Al, Mg, and K achieve their highest concentrations in yellow layer at top of varnish (interpreted to be Holocene) and in yellow layer at base of varnish (interpreted to be last interglacial). In contrast, Mn, Ba, Ca, and P achieve their highest concentrations in dark layers (interpreted to represent last glacial time). Fe shows smallest glacial-to-interglacial change in concentration. Probe-mapped portion of varnish marked by square in photograph. Profile of Mn, Si, and Fe contents was taken along a traverse designated by vertical blue line in photograph. White-blue patches at the base of thin-section photograph are minerals in host rock.

microbasins may have led to many of the negative results found in the varnish literature.

Are Variations in Chemical Composition of Varnish a Reflection of Changes in Regional Environmental Conditions?

One piece of evidence in support of a “yes” answer comes from studies of varnish from throughout the dry regions of the western United States. While the absolute MnO_2 concentrations vary from place to place, the pattern of its concentration with depth in varnish microbasins is similar over the entire region. As shown in Figure 1, the outermost (interpreted to be Holocene) varnish is consistently

lower in MnO_2 than varnish $\sim 10 \mu\text{m}$ down (i.e., glacial age), and when the varnish record extends back into what we consider to be the last interglacial period, MnO_2 contents akin to those for the Holocene are found. Furthermore, during what we consider to be glacial time, a number of fluctuations from high to intermediate MnO_2 are seen. In transmitted light, the low- MnO_2 content varnish is yellow, the intermediate- MnO_2 content varnish is orange, and the high- MnO_2 content varnish is black (Perry and Adams, 1978). The zone in the varnish that we infer to represent the last glacial period is characterized by a series of black bands separated from one

another by orange bands (Fig. 1). While the dating remains uncertain, it is tempting to correlate these black bands with the six Heinrich events and the Younger Dryas (Liu and Dorn, 1996). Although Ba is present in much lower concentrations than is Mn, it may prove to be a better proxy. This is because as the MnO_2 content rises so also does the ratio of BaO to MnO_2 . As a consequence, the BaO concentration has a higher signal-to-noise ratio than does the MnO_2 concentration (Figs. 2 and 3). While for the most part Ba is not present as BaSO_4 (i.e., the SO_4 concentration is far lower than the BaO concentration), there are spikes in the BaO record resulting from

the presence of BaSO₄ (Reneau et al., 1992). These inclusions are rare and can easily be deleted from the record based on the SO₄ concentration.

Independent evidence regarding the wetness record for the western United States drylands comes from reconstructions of the sizes of closed-basin lakes. As the water reaching these lakes must be balanced by evaporative loss, their sizes reflect the excess of precipitation over evaporation in their drainage basins. Over a wide geographic area and regardless of position relative to the source of precipitation (e.g., Lake Lahontan and Lake Bonneville; see Benson et al., 1990; Lake Estancia; see Allen and Anderson, 1993), all the lakes were far larger during glacial time. Further, they achieved their maximum sizes late in glacial time (i.e., ~15 500 yr B.P., just before the onset of the Bølling-Allerød warm in the northern Atlantic region). Then, after shrinking to near their present size, there is some evidence that they were rejuvenated during the Younger Dryas (Smith and Street-Perrott, 1983; Benson et al., 1995). This suggests that the entire Great Basin was somewhat wetter than it is now during late glacial time and probably also during the Younger Dryas.

How Can Time Be Assigned to the Varnish Record?

Because no way has been found to obtain reliable radiometric ages of the varnish itself, it is possible to build a stratigraphy only by compositing varnish records formed on substrates of known age such as from rock surfaces on raised shorelines, basalt flows, alluvial fans, and moraines. Means exist to radiometrically date these geomorphic features. While radiocarbon is the most obvious choice, in desert regions the pickings are slim. Algal carbonates deposited from the waters of expanded glacial-age lakes (Benson et al., 1990) and black mats deposited in springs that were active during wet periods (Quade et al., 1998) are among the few choices. In a few cases, U-series dating has been successfully applied to algal carbonates dating beyond the range of radiocarbon. Basalt flows can in some cases be accurately dated based on the ⁴⁰Ar produced by the decay of radiopotassium. However, it is exposure dating based on the in situ production of cosmogenic

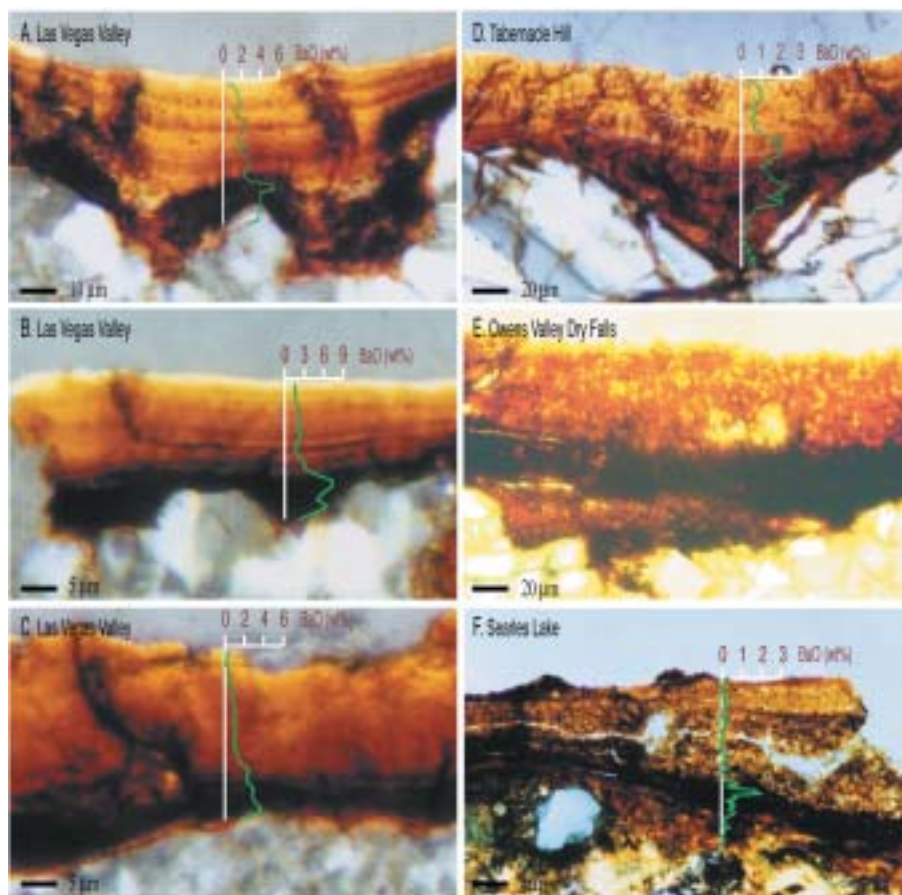


Figure 2. Left: Three varnish thin sections from ~13 ka alluvial-fan surfaces in Las Vegas Valley, southern Nevada. Right: Three varnish thin sections from ~16 ka geomorphic features of Tabernacle Hill lava (Utah), Owens Valley Dry Falls, and Searles Lake high shorelines (California). Also shown are electron microprobe line profiles of Ba concentration in five of these varnish thin sections. Note that high Ba corresponds to dark layers, interpreted to be glacial time.

isotopes that offers the greatest promise. This is especially true for glacial moraines and for lava flows. While potentially also applicable to cobble fans and wave-cut shorelines, all too often the rocks associated with these features have undergone prior exposure to cosmic rays.

Only two horizons in the western United States varnish stratigraphy have as yet been adequately dated. The age for one of these horizons is based on the radiocarbon dating of a fan alluviation and “black mat” episode in the southwestern United States (Haynes, 1967; Bell et al., 1998; Quade et al., 1998). These dates establish this event as a correlative of the Younger Dryas. The synchronous timing of paleo-spring deposition and fan alluviation suggests that the same wet event that supported spring flow also rejuvenated mountain piedmonts leading to the formation of cobble fans over black mats (Bell et al., 1998). The varnish on cobbles from these

now-abandoned fan surfaces yields a record covering approximately the past 12 000 yr B.P. (Fig. 2; Liu et al., 2000).

The second well-dated level in the stratigraphic record kept in varnish is at 15 500 yr B.P. By chance, three well-dated sites in the Great Basin yield age control close to this age: the Tabernacle Hill basalt flow in Utah, the highest shoreline of Searles Lake in California, and Dry Falls, through which the outflow of Owens Lake, California, passed (Benson et al., 1990; Cerling, 1990). Varnishes from all three locales show the same pattern (Fig. 2).

While as yet not directly dated, a third prominent horizon is the sharp upward transition in color from yellow to black, which very likely represents the end of the last interglacial (Figs. 1 and 3). Based on varnish stratigraphies from radiometrically dated lava flows in the Cima volcanic field, California, and the Lathrop Wells volcanic field, Nevada

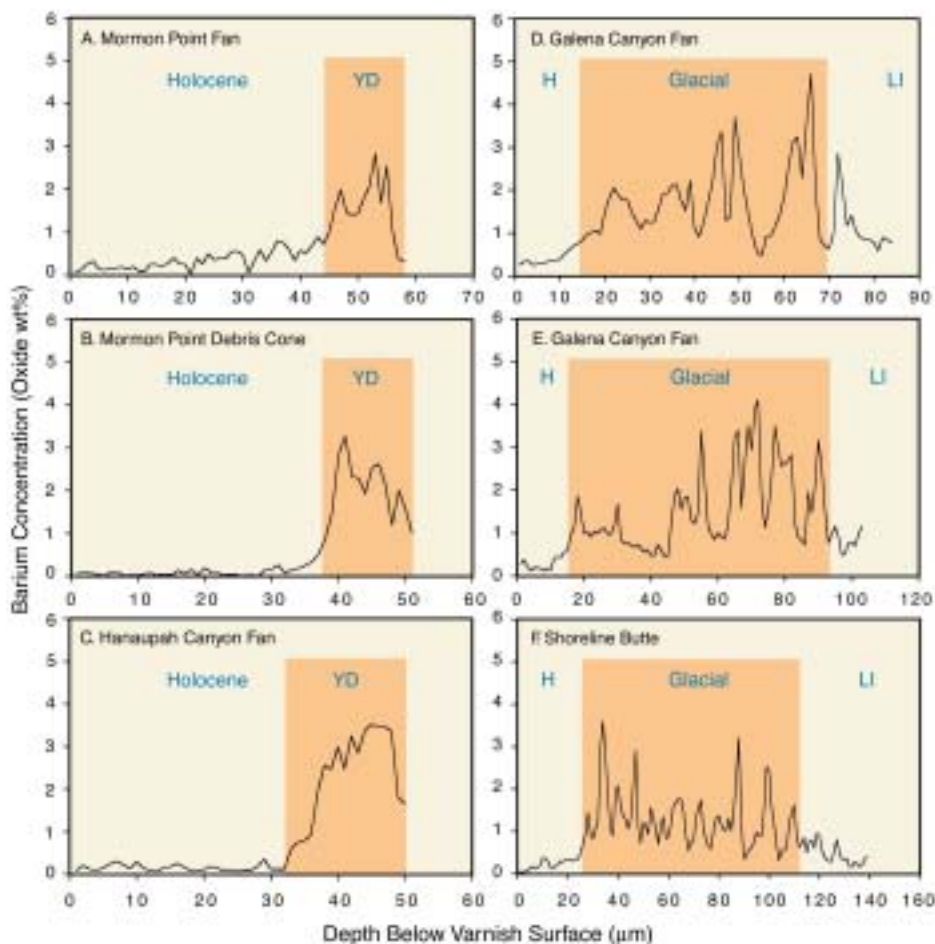


Figure 3. Electron microprobe line profiles of Ba concentration in varnish samples from Death Valley, California, interpreted to extend back to time of Younger Dryas (YD) (left three panels) and of the last interglacial (LI) (right three panels). Mean growth rates in these varnishes are 4–5 μm per millennium (A, B, C) and 1–2 μm per millennium (D, E, F). Note that sample F was from the Blackwelder highstand of Lake Manly in Death Valley that was U/Th dated at between 120 and 200 ka (Hooke and Dorn, 1992). Also note that microprobe element maps and thin-section photograph of sample D are shown in Figure 1. H—Holocene.

(Wells et al., 1995; Heizler et al., 1999), it is reasonable that this transition has an age of roughly 72,000–77,000 yr. Further, as this transition does not show up in varnish formed on ejecta from the well-dated Arizona Meteor Crater (Nishiizumi et al., 1991; Phillips et al., 1991), it is surely older than 50,000 yr. One of the records shown here (Fig. 3F) comes from the Blackwelder highstand of Lake Manly in Death Valley, which, based on U/Th ages, likely formed during the penultimate glaciation (Hooke and Dorn, 1992). We tentatively place this boundary as the equivalent of the end of marine isotope stage 5, approximately 74,000 yr B.P. (Martinson et al., 1987).

The ages of the black layers that lie between layers marking the base of the glacial section and layers at 15,500 yr

B.P. can be very roughly estimated by assuming that the mean rate of varnish accumulation was more or less the same for each orange-black pair. On this basis, the black layers appear to correlate with the pine intervals in the Lake Tulane pollen record and the intervening orange layers with oak intervals (Grimm et al., 1993).

Few varnish records extend back into the penultimate glaciation. As does paint, varnish appears to lose its grip on the host rock with age. This tendency to “peel” seems to correlate with thickness. Wind abrasion also reduces the varnish thickness. Varnish thicker than 200 μm is rarely found.

Some geologists and archaeologists have speculated that the basal age of the varnish can be estimated from its thick-

ness. But as documented by Liu and Broecker (2000), such estimates are extremely misleading. Not only does varnish grow at a wide range of rates, but also, as just mentioned, its ultimate thickness appears to be limited by wind abrasion and its tendency to peel.

Does the Chemical Makeup of Varnish Reveal any Useful Information Regarding its Mode of Origin?

Oxides of Mn, Fe, Ca, Mg, Si, and Al dominate rock varnish. Ca correlates with Mn. Mg, Al, and Si anticorrelate with Mn (Reneau et al., 1992). Only the FeO content of varnish remains nearly unchanged through the entire record (Fig. 1).

One puzzling aspect of varnish chemistry is the enrichment of the large lithophile elements (i.e., Ba, U, Th, and the rare earth elements). Their concentrations are an order of magnitude higher than in shale or average igneous rock (Fig. 4). It is interesting to note that despite the fact that Th is highly particle reactive and U is not, they are not separated from one another in rock varnish. Thus, whatever process is responsible for their enrichment is not influenced by the large difference in their chemical affinities.

The dominance of the element Mn has led a number of authors to propose that the deposition of varnish is negotiated by bacteria that derive their energy by its oxidation (e.g., see Raymond et al., 1992). While this is an appealing hypothesis, direct evidence is lacking. One puzzle in this regard is why the ratio of Mn to Mg + Al + Si differs between times of glacial and interglacial climates. It could be the result of a higher rate of Mn accumulation during the wetter glacial times diluting a more nearly constant accumulation of Mg-Al-Si. If so, the varnish growth rate during glacial time would have been greater than during the Holocene. On the other hand, were the Mn accumulation rate constant and the difference in composition the result of a higher Mg-Al-Si accumulation rate during the Holocene, then the Holocene accumulation rates would be expected to have been higher than those during glacial time. Unfortunately, it is not possible to use the relative thicknesses of Holocene and glacial varnish to reliably distinguish between these two models. Not only does the ratio of the thicknesses

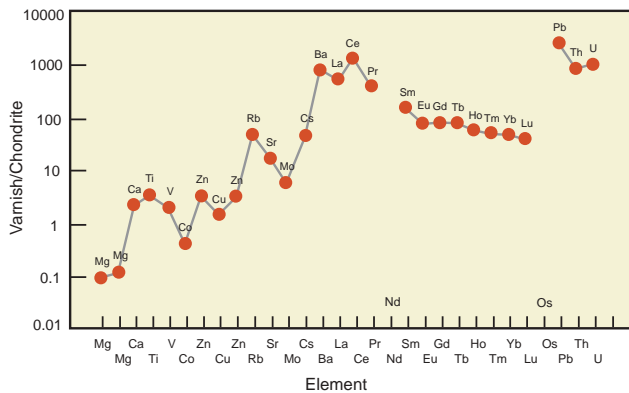


Figure 4. Plot of ratio of concentrations for a series of elements in varnish relative to their concentrations in chondritic meteorites. Large lithophile elements (Ba, the rare earth elements, Pb, U, and Th) are very highly enriched. U and Th in varnish range up to 20 times their concentrations in shale. Measurements made by Bill McDonough using Harvard laser inductively coupled plasma system.

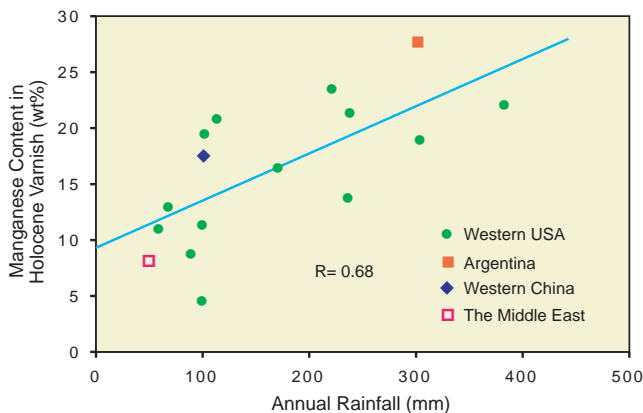


Figure 5. Plot of average Mn content (measured as MnO wt%) of Holocene varnish from western United States, Argentina, western China, and the Dead Sea graben of the Middle East. Nonzero y-intercept of trend line suggests that varnish receives some of its Mn from “dry” fallout and that Mn content increases by 4% per 100 mm of rainfall. But, because the scatter about the trend line is large ($\pm 6\%$), Mn content in varnish cannot be used as an absolute paleo-rain gauge.

vary from microbasin to microbasin on the same rock surface, but also it often changes from one side of a microbasin to the other.

The chemical form of the Mg-Al-Si component of the varnish is the subject of debate. The fact that X-ray diffraction patterns reveal the presence of clay minerals in the varnish suggests that trapped dust grains account for this component (Potter and Rossman, 1977). Because these minerals are not resolved in electron probe maps, they must be sub-micrometer in size. Thus, it is equally possible that these elements are mainly authigenic rather than detrital in origin.

How Do We Know That the MnO_2 Content of Varnish is Related to Wetness?

One way this might be demonstrated is by regressing the mean MnO_2 content of Holocene varnish against today’s mean

annual precipitation. This has been done for a number of sites in the Great Basin of the western United States (Fig. 5). There is a trend toward higher MnO_2 content with increasing precipitation. The best-fit trend line to these results indicates that were there no precipitation, the varnish would contain $\sim 9\%$ MnO_2 . The slope of the mean trend line indicates an increase of $\sim 4\%$ MnO_2 per 100 mm of precipitation.

The nonzero intercept suggests that precipitation is not the only vehicle for delivery of the ingredients of varnish. Perhaps delivery in dust, aerosols, and dew also are important. In order to test whether this might be the case, we created (together with Willard Moore of the University of South Carolina) a varnish garden on Columbia’s Biosphere 2 campus, bringing in varnished rocks from Panamint Valley, California, and from McDowell Mountain, Arizona. These rocks were placed exactly as they were originally situated and were exposed to the elements for eight months. Four of the eight were equipped with rain shields activated to move into place over the varnished rock by the rain itself. The other four had no shields. After the exposure, the varnish was analyzed for the presence of ^7Be , a 53-day-half-life radioisotope produced in the atmosphere by cosmic-ray bombardment. The ^7Be was chosen because it is the only naturally occurring tracer with a half-life short enough to permit interactive experiments. During the exposure period at Biosphere 2 (about 4 half-lives of ^7Be), more than 95% of the ^7Be that accumulated at the original locale would have decayed. Hence, the ^7Be measured must have been added during the exposure at Biosphere 2.

The result of this interactive experiment was that the four varnished rocks that were shielded from the rain accumulated only $38\% \pm 10\%$ the amount of ^7Be as did those that were not equipped with rain shields (W. Moore, 2001, written commun.). Thus, at least to the extent that Be acts as a stand-in for MnO_2 ,

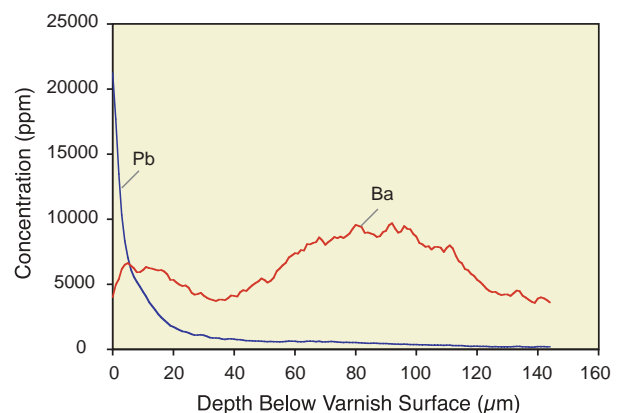


Figure 6. Plot of Pb and Ba concentrations (in ppm) vs. depth in varnish from eastern California indicating anthropogenic sources of Pb. As shown by separate experiments in which varnish was plated with Au and Ag, deep penetration of anthropogenic Pb is an artifact of analysis. Because growth rate of this varnish is only $\sim 10 \mu\text{m}$ per millennium, excess Pb (likely from gasoline) must be contained in a layer $< 1 \mu\text{m}$ thick. Instead (as do the Au and Ag plating), it extends more than $10 \mu\text{m}$ into the varnish.

roughly a third of the accumulation is delivered by some combination of dew, dust, and aerosols. This result is consistent with the relationship between MnO_2 concentration and precipitation (previously discussed). There is, however, a potential flaw in this experiment. Measurements of the integrated inventory of ^{10}Be (half-life 1.6 m.y.) in varnishes of known basal age showed that several percent of the ^{10}Be produced in the overlying air column accumulated (W. Moore, 2001, written commun.). In contrast, several tens of percent of the ^7Be produced in the overlying air column accumulated. One explanation for this difference could be that during its 75-day mean life, ^7Be atoms are merely absorbed on the varnish surface rather than built into it. Were they to have survived longer, perhaps subsequent rains would have removed a sizeable fraction.

Is Varnish Still Forming?

During the past 100 yr, a host of anthropogenic substances have been added to the atmosphere, which might alter the growth rate and chemistry of rock varnish. Manmade acids threaten to dissolve away previously accumulated varnish. On the other hand, excess deposition of dust and aerosols might enhance the growth of varnish. In an attempt to get a handle on these anthropogenic impacts, we have made measurements of short-lived natural radioactivities (^7Be and ^{210}Pb), of nuclides produced during nuclear bomb tests (^{137}Cs and Pu), of Pb released to the atmosphere from automobiles, and of Zn released from smelters. All of these entities have been documented in varnish (Fleisher et al., 1999). Pb shows an amazing tenfold increase in concentration in the outer 1 μm relative to its ambient Holocene concentration, clearly demonstrating the anthropogenic impact on varnish chemistry (Fig. 6). The presence of a large excess of ^{210}Pb (half-life 22 yr) in varnish can only be explained by deposition from the atmosphere. The ^{222}Rn that leaks from soils decays in the atmosphere, producing ^{210}Pb , which is carried back to Earth's surface in rain and in aerosols. Based on the ^{210}Pb inventories in varnish, Fleisher et al. (1999) estimate that the accumulation in varnish represents about 10% of that

produced by the decay of radon in the overlying air column.

Will Rock Varnish Ever Become a Widely Applied Proxy for Desert Wetness?

On the time scale of a decade, the answer is almost certainly "no." Too many questions regarding its mode of origin and the relationship of its chemical composition to local environmental conditions remain unanswered. Further, far too few varnish records are available from well-dated geomorphic surfaces. And last, how long will it be before some young scientist comes along who is brave enough to pick up where we leave off?

Nevertheless, several steps might lead to rejuvenation and breakthrough in varnish studies.

- (1) Continued development of rigorous criteria for the selection of varnished rocks, and the recognition of defects (Liu, 1994).
- (2) Continued efforts to analyze a large number of samples from each area in an attempt to distinguish the regional signal from the local noise. The Ba record seems the most promising in this regard.
- (3) Cooperation with researchers conducting cosmogenic isotope dating of geomorphic features in desert regions, which will allow essential comparison of varnish stratigraphies from a large number of dated surfaces.
- (4) New studies to establish the lag time for nucleation of varnish. Perhaps the best hope will be through studies of geomorphic features associated with the Younger Dryas climate fluctuation.
- (5) Comparisons between varnish records and records from the sediments of desert lakes. While the interpretation of the latter is subject to its own set of problems, ongoing drilling programs will produce a number of detailed lake sediment records spanning the last glacial period.
- (6) Chemical and radiochemical measurements on material leached from the surfaces of varnish samples collected along downwind traverses away from the Nevada

Test Site and away from selected smelters. The strategy would be to compare the relative abundances of anthropogenic entities captured in the varnish with those in soils. Such studies could provide clues to the chemical selectivity of the processes responsible for varnish formation.

- (7) Further efforts to establish whether varnish formation is the product of the activity of living organisms (Taylor-George et al., 1983; Nagy et al., 1991; Staley et al., 1991; Grote and Krumbein, 1992). As part of our Biosphere 2 experiment, we subjected half of the varnished rocks to weekly ultraviolet irradiation, but found that this treatment did not diminish the uptake of ^7Be . However, as the ^7Be may have been absorbed onto the varnish surface rather than incorporated into the varnish, this experiment was likely flawed. If this distinction is to be made, efforts by clever bacteriologists will be required.

CONCLUSIONS

Rock varnish is a substance meriting serious study. Even if its application as a recorder of past desert environments fails to pan out, its mode of origin certainly constitutes a riddle that is bound to captivate inquiring minds. It may also be important for understanding a likely habitat for the most primitive living organisms.

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elements in varnish. Bob Finkel of Livermore National Laboratory conducted the ^{10}Be measurements. Charlie Mandeville of the American Museum of Natural History helped us in electron probe analyses. John Bell of Nevada Bureau of Mines and Geology and Norman Meek of California State University (San Bernardino) assisted us in collecting varnish samples in the field. Lamont-Doherty's Teddy Koczynski aided us in setting up and maintaining our thin section facility. Reviews by Jay Quade, Fred Phillips, and two anonymous readers, plus editorial comments by Karl Karlstrom, helped improve the manuscript. Lamont-Doherty Earth Observatory contribution 6205.

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Notice of Council Meeting

Meetings of the GSA Council are open to Fellows, Members, and Associates of the Society, who may attend as observers, except during executive sessions. Only councilors, officers, and section representatives may speak to agenda items, except by invitation of the chair. Because of space and seating limitations, you will need to notify the Acting Executive Director prior to the meeting if you plan to attend.

The next meeting of the Council will be at 1 p.m., Tuesday, Nov. 6, at the GSA Annual Meeting in Boston.