

Cation-leaching sites in rock varnish

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ABSTRACT

Backscatter electron microscopy of subaerial rock varnish reveals porous textures that are sites of cation leaching with lowered $(K^+ + Ca^{2+})/Ti^{4+}$ ratios and concentrations of manganese and iron. Laboratory studies show that rates of potassium and calcium leaching increase with temperature, time, and surface area, and decrease when varnish interdigitates with coatings of amorphous silica. Only varnishes with continuous layering should be used in paleoenvironmental research and paleomagnetic studies, not textures indicative of postdepositional modifications.

INTRODUCTION

Rock varnish consists of clay minerals that are cemented to the underlying rock by manganese and/or iron oxides (Potter and Rossman, 1977, 1979). With the realization that varnish is an accretion (e.g., Potter and Rossman, 1977; Allen, 1978) with distinctive layers (Perry and Adams, 1978), investigations into its use as a technique for determining past environments and dating began in earnest.

Six distinct types of paleoenvironmental signals have been identified within rock varnishes (Dorn, 1992), and paleomagnetic measurements have been made from iron oxides in varnish (Clayton et al., 1990). For these records to be valid, however, postdepositional modifications must not have occurred where the varnish is analyzed. Cation-ratio dating of rock varnish is based on empirical observations that $(K^+ + Ca^{2+})/Ti^{4+}$ decreases with time (e.g., Glazovskiy, 1985; Harrington and Whitney, 1987; Pineda et al., 1988; Dorn, 1989; Liu and Zhang, 1991). These studies have assumed that potassium and calcium are more mobile than titanium and are preferentially leached over time.

A key piece of theory that has been missing in paleoenvironmental and cation-ratio dating studies of rock varnish is an understanding of why elemental leaching does or does not occur in certain locations.

METHODS

Samples were collected from sites used in previous studies of cation-ratio dating that used only subaerial black (Mn-rich) varnishes. We avoid proximity to the soil surface; crack varnish; former crack varnish; orange varnish; dusky-brown varnish; ground-line band varnish; abundant microcolonial fungi, lichens, filamentous fungi, and cyanobacteria; and where water

or organic matter collects. These and other avoided variables have been described in detail elsewhere (Dorn, 1989; Krinsley et al., 1990).

Two studies were conducted to test the hypothesis of cation leaching: an examination of in situ chemistry, and laboratory studies of factors that influence cation leaching of varnish. In the in situ study, small chips of varnish were mounted in epoxy and polished. Backscatter electron microscopy (BSE) was used to identify different varnish textures, and a JEOL Superprobe electron microscope (wavelength dispersive mode) was used with a spot size of 10 μm .¹

Two laboratory leaching experiments were conducted: exposure of varnish scrapings to leaching solutions, and exposure of varnishes still attached to the rock. These laboratory tests were carried out in less than a year; hence, they cannot be completely analogous to natural processes taking thousands of years. Our initial goal was simply to assess if cation leaching occurred and to better understand some of the variables that influence cation leaching.

To examine the influence of temperature and to compare leaching from varnish scrapings with varnishes attached to the rock, one boulder on the Q3a surface of Hanaupah Canyon fan in Death Valley (Dorn, 1988) was cut into 12 samples with a varnish surface area of $\sim 80 \text{ cm}^2$. Exposed rock surfaces were coated with epoxy, leaving only varnish exposed to 200 ml of deionized water with an initial Ca and K concentration of $<0.2 \text{ mg/l}$. The water was maintained at a pH of 5.5 throughout the experiment; minor amounts of HCl were added in order to simulate

the pH of rainfall. Four subsamples were kept at 5 °C, four at 25 °C, and four at 40 °C. Subsamples within each temperature group were agitated, end over end by hand, five times a day for 5, 20, 50, and 100 days. At the end of each period, the varnish was centrifuged and the water decanted and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Twelve additional subsets of 20 mg of varnish were also scraped from the same Death Valley boulder; the scrapings were cleaned of rock contaminants as described by Dorn (1989). These were subject to the same conditions as the in situ samples.

In order to assess the influence of interdigitation of rock varnish with coatings of amorphous silica, samples were collected from the Puu Waawaa Ranch lava flow of Hualalai, Hawaii (site 10 in Dorn et al., 1992). One group of samples was from varnish interlayered with silica skin (cf. Curtiss et al., 1985) in a proportion of $\sim 60\%$ varnish and 40% silica skin. Another group of samples from the same site was only Mn-rich rock varnish. Each group was divided into six even portions of 20 mg each. Deionized water (200 ml) was added to the varnish; temperature was maintained at 25 °C at a pH of 5.5. They were agitated end over end four times a day for 20, 40, 60, 80, 100, and 120 days. At the end of each period, samples were centrifuged, and the water was decanted and analyzed by ICP-AES.

RESULTS

Figures 1 and 2 present BSE textures of subaerial black (Mn-rich) rock varnish, and Table 1 presents summaries of electron microprobe analyses keyed to numbers that identify transects in the figures. For most numbers there are analyses on layered and porous varnish. For number 10,

¹Electron Microprobe Analyses of Transects Given in Figures 1 and 2, GSA Supplementary Data 9132, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301.

Note: Additional material for this article is Supplementary Data 9132, available upon request from the GSA Documents Secretary (see footnote 1).

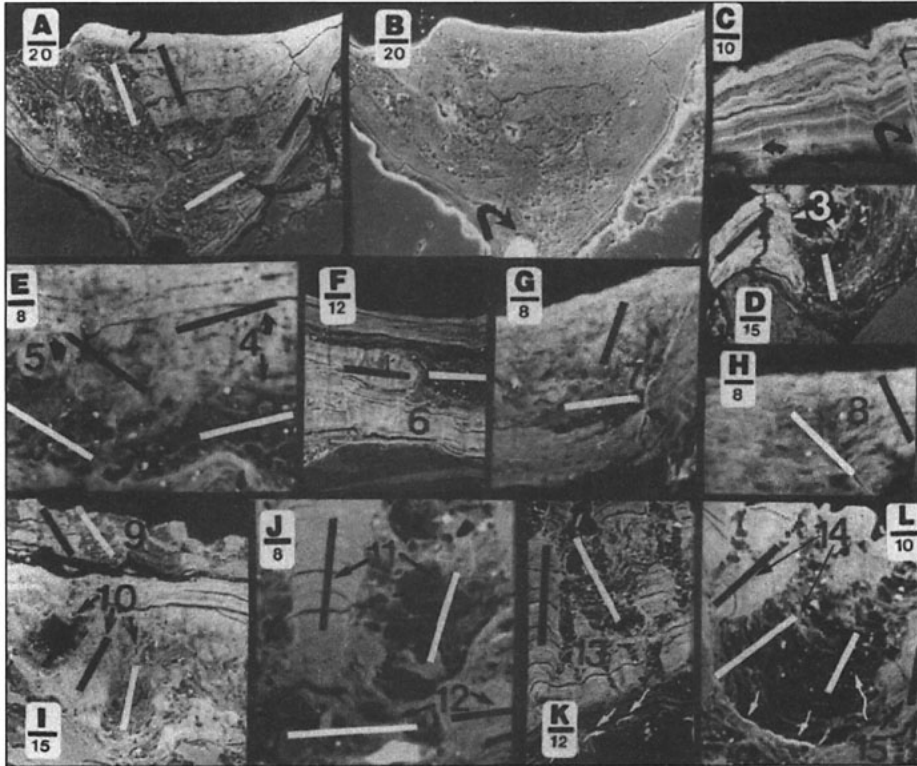
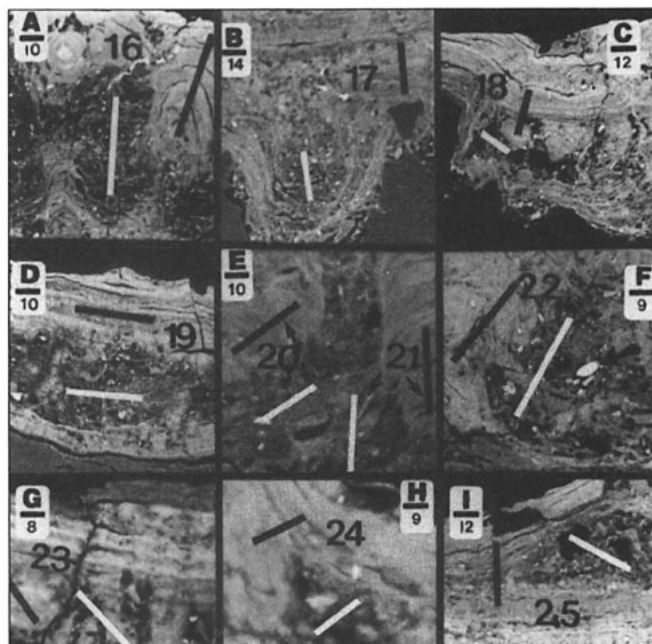


Figure 1. Electron microscope images of rock-varnish cross sections. All micrographs except B were made by means of backscattered electron microscopy, where material with higher net atomic numbers appears brighter (Krinsley and Manley, 1989). Numbers under scale bars are micrometres. Other numbers identify pairs of transects, where electron microprobe analyses were made on layered textures (black lines), leached textures (white lines), and detritus-filled hollows (I and J). A: Wharton Hill petroglyph 5, South Australia, showing layered and leached textures. B: Secondary electron image (showing topography instead of chemistry) of same frame as A. Porous, leached texture is almost impossible to identify with secondary electron imaging. Black particle trapped at base of varnish in A is white in B (arrow) and charging, characteristic typical of organic matter. C: Wharton Hill petroglyph 5, illustrating layered texture appropriate for paleoenvironmental analysis, but no areas of leaching. Arrows indicate cracks refilled with mobilized and reprecipitated Mn and Fe oxides. Large arrow indicates spot analyzed by 2 μm probe with 53% MnO and 31% Fe₂O₃; small arrow indicates spot having 44% MnO and 27% Fe₂O₃. D: Yunta Springs petroglyph 2, South Australia. E: Karolta petroglyph K23, South Australia. F: Desert pavement on Pampa de Los Chinos, near Nazca, southern Peru. G: Petroglyph WP17, Wyoming. H: Petroglyph WP12, Wyoming. I: Artifact, Mojave Desert. J: Makanaka till, Hawaii. K: Little Cone basalt flow, Crater Flat, southern Nevada. L: Perry Aitken till, Chiatovich basin, White Mountains, Nevada.

Figure 2. Backscattered electron microscope images of leached and unleached textures in rock varnish. A: Middle Creek till, Chiatovich basin, White Mountains, Nevada. B and C: Mount Van Valkenberg, Marie Byrd Land, Antarctica. D: Artifact, Mojave Desert. E: Makanaka till, Hawaii. F: Shoreline in Coyote arm of Lake Manix, Mojave Desert. G: Petroglyph PC-40, southeast Colorado. H: Desert pavement, Dunhuang region, western China. I: Beach ridge, Manix Lake, Mojave Desert.



there is a third set of analyses on a pocket of detritus mixed with varnish. For numbers 11 and 12, the paired analyses are on layered varnish (dark line) and pockets of detritus mixed with varnish (white line). (Table A [see footnote 1] contains microprobe analysis results.)

Figures 3 and 4 present results of the cation-leaching experiments. We acknowledge several limitations. Ti concentrations were usually below the limit of detection for ICP-AES (0.2 mg/l), so cation ratios could not be calculated for these samples. We do not know the locations of K and Ca removal in the scrapings, but before and after BSE examinations of the in situ varnish suggest that leaching occurred in the same types of areas as prior natural leaching.

DISCUSSION

Our interpretation of Figures 1 and 2 is that the porous texture is a product of the breakdown of layered varnish. This is indicated by (1) the gradient of increased porosity away from the layered varnish, (2) the apparent disintegration of layering in the porous zones that continues on the other side of the porous area, and (3) the presence of "cracks" running through the porous zones that could channel capillary water. Some of these "cracks" have coatings of Mn-Fe similar to those identified by Krinsley et al. (1990) as deposits of remobilized material (e.g., Fig. 1, G and L). However, we do not understand why leaching progresses sometimes along cracks and other times parallel with laminations.

Table 1 reveals a clear trend of lower Mn, Fe, and cation ratios in porous textures, compared with adjacent layered varnish. This is also indicated by the darker texture on a BSE image, from a lower net atomic number (Krinsley and Manley, 1989) in the porous zone. The simplest explanation is that porous textures are leached of MnO and Fe₂O₃, and cation ratios are lowered by leaching solutions.

An alternative explanation for porous textures is a constructional origin, but this is most unlikely. If porosity is a primary depositional feature, we would expect to see it in surface layers now forming. Other than leaching under lichens and other acid-producing agents, we have found only one sample where a leached zone occurs at the surface (Fig. 1I), after examining hundreds of varnish cross sections with BSE in rock-varnish samples ranging from tropical rainforest streams to hyperarid southern Peru. In this case (Fig. 1I), the porosity is from disintegration of adjacent layered varnish.

In addition to layered and porous textures, there is a "detritus-rich" texture of a chaotic mix of large pieces of rock detritus ($\sim 10 \mu\text{m}$) and Mn-Fe-clay varnish (Fig. 1, I and J). This texture should not be confused with leached varnish. Instead of porosity being created by postdepositional modification, large detrital grains create porosity much like that in sedimentary rocks. The way large pieces of detritus are

incorporated into accreting varnish is encapsulation at the surface (Krinsley et al., 1990). These large fragments should not be confused with micron-size Fe-rich and Ti-rich grains that occur in layered varnish, but become noticeable as bright spots in porous textures after leaching occurs (Figs. 1 and 2).

The generalized explanation for the decline in the rate of cation-ratio change at older sites is that it becomes progressively harder to remove fewer and fewer Ca and K cations, all while Ti remains (Dorn, 1989). This has been found in the leaching experiments (Figs. 3 and 4). The probe data in Table A (see footnote 1) reveal that sometimes K, Ca, and Mg values are lower. In other cases, however, Ti increases in porous zones. This is consistent with the work of Akimoto et al. (1984), who explained Ti enrichment by replacement of mobile cations with highly stable Ti. Morad and Aldahan (1986) found Ti oxides replacing weathered Fe-Ti phases, and Harden (1988) reported a net influx of Ti into soils over time.

Figure 3 illustrates that leaching is influenced by coatings of amorphous silica (cf. Curtiss et al., 1985). In the Hawaii experiment, varnish scrapings interdigitated with coatings of amorphous silica (cf. Curtiss et al., 1985) had less K and Ca in solution than varnish scrapings not associated with silica skins. One explanation is that amorphous silica acts to inhibit leaching of varnish constituents.

Figure 4 illustrates that leaching of Ca and K from rock varnish increases with time and higher temperature, whether the varnish was still attached to the underlying rock or scraped off. Varnish scrapings, however, are leached of Ca and K faster and more extensively than varnish still attached to the rock, probably because more surface area is directly exposed to the leaching

solution. This illustrates that internal fracture systems (Figs. 1 and 2), perhaps initially produced by desiccation of varnish clays (Krinsley et al., 1990), can be critical in opening up areas to leaching.

IMPACT FOR FUTURE RESEARCH

1. Different types of rock varnish produce different results. At first our findings and those of Krinsley et al. (1990) and O'Hara et al. (1990) appear to be at odds with the conclusions of Reneau et al. (1990). Whereas Reneau et al.

(1990) found little evidence of elemental mobility, we find remobilization and leaching to be common.

These differences may be explained by sampling different types of varnishes. Subaerial rock varnishes that we sample for cation-ratio dating have abundant leaching sites (Figs. 1 and 2). However, varnishes that originated in rock crevices and were later exposed by spalling of the overlying rock characteristically have tightly laminated and virtually unleached textures. Whereas subaerial varnishes are exposed to al-

TABLE 1. ELECTRON MICROPROBE (WAVELENGTH DISPERSIVE) ANALYSES OF REGIONS DELINEATED IN FIGURES 1 AND 2.

Transect*	Layered textures			Porous textures			Bulk CR‡ (method)
	MnO (%)	Fe ₂ O ₃ (%)	CR	MnO (%)	Fe ₂ O ₃	CR	
1	23.86 ± 8.22†	16.87 ± 3.71	5.12 ± 0.86	10.26 ± 3.31	13.69 ± 4.26	3.46 ± 0.55	4.33 (Probe)
2	28.76 ± 5.95	16.16 ± 2.20	5.28 ± 0.61	11.77 ± 2.97	14.20 ± 5.24	3.53 ± 0.47	4.33 (Probe)
3	25.43 ± 1.32	9.47 ± 0.73	6.74 ± 0.22	8.76 ± 1.73†	7.90 ± 1.56†	4.10 ± 0.54†	5.88 (Probe)
4†	12.81 ± 2.20	13.37 ± 0.49	7.14 ± 0.99	2.32 ± 1.20	9.93 ± 1.68	3.32 ± 0.44	4.85 (Probe)
5†	16.86 ± 4.20	13.87 ± 1.85	5.74 ± 1.52	10.25 ± 1.62	11.46 ± 2.39	2.93 ± 0.60	4.85 (Probe)
6	12.73 ± 0.73	22.00 ± 5.15	24.14 ± 9.06	2.75 ± 1.17	14.79 ± 10.37	10.11 ± 3.71	13.24 (Probe)
7†	29.17 ± 4.30	17.08 ± 0.94	10.18 ± 0.01	11.23 ± 3.27	15.37 ± 0.81	6.61 ± 1.68	8.80 (Probe)
8†	28.79 ± 1.86	17.52 ± 3.13	10.54 ± 0.41	10.80 ± 3.34	9.75 ± 3.54	7.97 ± 0.98	8.18 (Probe)
9†	10.16 ± 1.28	12.89 ± 0.29	6.71 ± 0.19	3.05 ± 1.33	11.95 ± 1.99	4.09 ± 1.55	3.81 (PIXE)
10	27.83 ± 6.19	16.02 ± 1.03	7.99 ± 0.84	10.84 ± 4.63	16.04 ± 3.00	4.12 ± 0.16	3.81 (PIXE)
11†	16.27 ± 2.53	13.63 ± 1.60	7.04 ± 0.55				6.51 (PIXE)
12†	9.87 ± 4.00	14.51 ± 1.18	6.89 ± 1.11				6.63 (Probe)
13	13.37 ± 3.77	13.37 ± 5.69	2.73 ± 0.18	10.27 ± 2.96	10.90 ± 1.19	1.85 ± 0.37	2.71 (ICP)
14	27.19 ± 2.08	13.44 ± 1.08	5.87 ± 1.28	4.28 ± 2.14†	10.34 ± 1.39†	4.83 ± 0.35†	5.05 (Probe)
15	21.20 ± 4.61	15.36 ± 3.01	5.22 ± 0.17	10.40 ± 2.27†	13.79 ± 0.82†	2.54 ± 0.22†	5.05 (Probe)
16	16.73 ± 3.32	12.24 ± 1.20	5.25 ± 0.65	7.07 ± 1.65	12.57 ± 0.37	1.75 ± 0.32	4.94 (Probe)
17	8.65 ± 0.54	9.65 ± 0.31	6.26 ± 0.19	3.61 ± 1.08	7.90 ± 2.63	4.05 ± 0.49	7.99 (Probe)
18	18.87 ± 3.86	9.91 ± 0.20	3.54 ± 0.21	11.11 ± 1.21	11.46 ± 0.14	2.73 ± 0.05	7.99 (Probe)
19	9.73 ± 0.97	16.42 ± 2.62	5.79 ± 0.24	4.17 ± 1.34	10.65 ± 1.65	3.57 ± 0.34	5.10 (PIXE)
20	15.57 ± 1.26	15.60 ± 1.14	6.42 ± 0.74	8.58 ± 1.09	12.82 ± 0.12	4.55 ± 0.94	6.51 (PIXE)
21	22.25 ± 4.76	15.29 ± 1.84	6.07 ± 0.28	7.90 ± 0.58	14.88 ± 3.47	4.92 ± 0.07	6.63 (Probe)
22	21.15 ± 4.30	14.90 ± 3.17	4.58 ± 0.15	11.66 ± 4.92	12.86 ± 1.57	3.53 ± 0.13	3.90 (ICP)
23†	4.42 ± 0.57	9.70 ± 1.55	10.71 ± 1.16	3.38 ± 1.21	8.86 ± 0.07	6.02 ± 0.16	7.26 (Probe)
24†	4.30 ± 0.90	7.51 ± 0.28	15.17 ± 0.73	1.13 ± 0.10	8.13 ± 0.78	11.52 ± 1.45	not available
25†	8.72 ± 1.97	14.40 ± 0.98	4.72 ± 1.23	3.36 ± 0.68	11.55 ± 0.88	3.27 ± 0.81	4.12 (PIXE)

	Detritus-rich textures		
	MnO%	Fe ₂ O ₃ %	CR
10	5.12 ± 1.17†	11.43 ± 7.64†	4.90 ± 2.16†
11	1.20 ± 1.01	12.35 ± 11.2	6.45 ± 5.46
12	2.28 ± 0.98	16.32 ± 3.81	1.78 ± 0.78

Note: Errors are ± 1 sigma. Table A (see text footnote 1) gives complete details of analysis methods.
 * Numbers correspond to transects in Figures 1 and 2. Five analyses were made per transect with 10 micrometre spot size, except where not possible due to limited area.
 † Only 3 analyses possible, due to minimal length of transect. Overlap was not desired due to loss of K and Na.
 ‡ Bulk CRs are analyses of varnishes from the same sites as the microprobe transects, only on cubic millimeters of varnish.

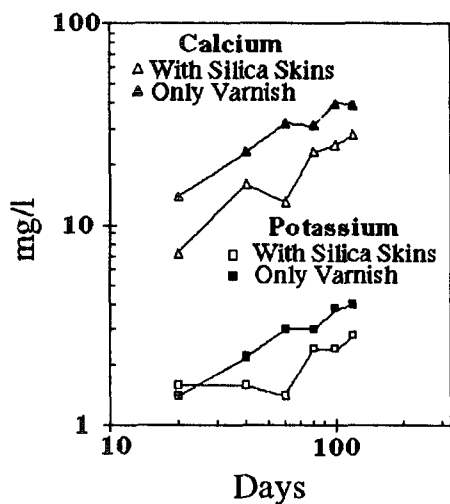


Figure 3. Laboratory leaching experiments on scrapings of Hawaiian rock varnishes. Two types of scrapings were leached: varnishes interdigitated with amorphous silica (cf. Curtiss et al., 1985) and just rock varnish. See text for details.

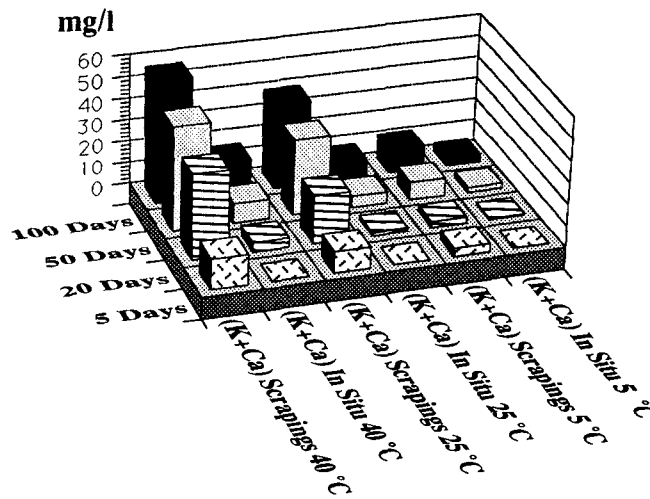


Figure 4. Laboratory leaching experiments comparing Death Valley varnishes still attached to rock with varnishes that were scraped off rock and cleaned of contamination. See text for details.

ternating conditions of dust deposition, water flow, and acid-producing organisms, rock crevices provide an environment of wetting and drying buffered by long-term contact with collected alkaline dust. This promotes superior varnish cementation, while avoiding exposure to the acidity of rainfall and rock-surface organisms in the subaerial environment. Recently exposed crack varnishes and ground-line bands are typically the darkest, best-developed, and smoothest varnishes because growth occurs in such favorable microenvironments.

2. The nonuniform nature of leaching in varnish poses problems and opportunities for cation-ratio dating. Bulk chemical methods used for cation-ratio analysis are based on analyses of cubic millimetres to cubic centimetres of varnish (Pineda et al., 1988; Dorn, 1989; Liu and Zhang, 1991). Although this approach is not spatially precise, it incorporates both leached and unleached textures. Because rigorous tests are used to assess and reduce the amount of rock contamination (Dorn, 1989), the age-dependent trend observed in bulk cation-ratio analyses probably reflects cation leaching.

The scanning electron microscope (SEM) method is based on the penetration of electrons into the upper $<5 \mu\text{m}$ of varnish (Reneau et al., 1991). Because the surface layer of varnish is not where zones of leaching occur (Figs. 1 and 2), our data do not contradict Reneau et al.'s (1990) hypothesis that the time-dependent change they observe with the SEM method is not produced by cation leaching.

The challenge now is to determine how much area/volume is needed to achieve a representative cation ratio. Abundant research with focused electron beams ($\sim 2 \mu\text{m}$) shows great micrometre-scale variability in varnish chemistry (Dragovich, 1988; Dorn, 1989; O'Hara et al., 1990). However, when the beam is defocused to $\sim 10 \mu\text{m}$, chemical variability is decreased somewhat (Table 1). We are investigating whether it is possible to obtain representative cation ratios from cross sections with a wide beam ($\geq 10 \mu\text{m}$) by controlling texture.

3. Those attempting to extract a paleoenvironmental signal from rock varnish must avoid areas of postdepositional modification. This includes leaching, as well as previously documented hazards of aeolian abrasion, refilled pits, remobilized varnish, deformed varnish, and crack-varnish discontinuities (e.g., Krinsley et al., 1990).

The presence of leached and layered textures indicates that different parts of varnish can integrate and accumulate environmental effects;

however, samples with layered textures like those in Figure 1C are most appropriate for paleoenvironmental analysis (e.g., Dorn, 1992). Similarly, information obtained from encapsulated organic fragments or tephra can be interpreted as syndimentary features, even though they may exist in leached zones. Interpretations of Mn:Fe microlaminations or paleomagnetism (Clayton et al., 1990), however, would be void if sampling occurred in leached zones. Of course, all methods will not work if the varnish has undergone erosion (Krinsley et al., 1990).

The challenge is how to recognize and understand this complexity. The key to the use of varnish as a geochronometer or paleoenvironmental indicator is understanding how the analyzed varnish has formed.

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