

Chapter Eight

Rock Varnish

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8.1 Introduction: Nature and General Characteristics

Most earth scientists thinking about geochemical sediments envisage stratigraphic sequences, not natural rock exposures. Yet, rarely do we see the true colouration and appearance of natural rock faces without some masking by biogeochemical curtains. Geochemical sediments known as rock coatings (Table 8.1) control the hue and chroma of bare-rock landscapes. Tufa and travertine (Chapter 6), beachrock (Chapter 11) and nitrate efflorescences (Chapter 12) exemplify circumstances where geochemical sediments can cover rocks. Perhaps because of its ability to alter a landscape's appearance dramatically (Figure 8.1), the literature on rock varnish remains one of the largest in the general arena of rock coatings (Chapter 10 in Dorn, 1998).

Rock varnish (often called 'desert varnish' when seen in drylands) is a paper-thin mixture of about two-thirds clay minerals cemented to the host rock by typically one-fifth manganese and iron oxyhydroxides. Upon examination with secondary and backscattered electron microscopy, the accretionary nature of rock varnish becomes obvious, as does its basic layered texture imposed by clay minerals (Dorn and Oberlander, 1982). Manganese enhancement, two orders of magnitude above crustal values, remains the geochemical anomaly of rock varnish and a key to understanding its genesis.

Field observations have resulted in a number of informal classifications. Early field geochemists recognised that varnish on stones in deserts differs from varnish on intermittently flooded rock surfaces (Lucas, 1905). Another example of differentiating varnish involves position on a desert pavement clast (Mabbutt, 1979): black varnish rests on the upper parts of a pavement clast, a shiny ground-line band of varnish occurs at the soil–rock–atmosphere interface, and an orange coating is found on the underside of

Table 8.1 Different types of rock coatings (adapted from Dorn, 1998)

Coating	Description
Carbonate skin	Coating composed primarily of carbonate, usually calcium carbonate, but sometimes combined with magnesium
Case hardening agents	Addition of cementing agent to rock matrix material; the agent may be manganese, sulphate, carbonate, silica, iron, oxalate, organisms, or anthropogenic
Dust film	Light powder of clay- and silt-sized particles attached to rough surfaces and in rock fractures
Heavy metal skins	Coatings of iron, manganese, copper, zinc, nickel, mercury, lead and other heavy metals on rocks in natural and human-altered settings
Iron film	Composed primarily of iron oxides or oxyhydroxides
Lithobiontic coatings	Organic remains form the rock coating, for example lichens, moss, fungi, cyanobacteria, algae
Nitrate crust	Potassium and calcium nitrate coatings on rocks, often in caves and rock shelters in limestone areas
Oxalate crust	Mostly calcium oxalate and silica with variable concentrations of magnesium, aluminum, potassium, phosphorus, sulphur, barium, and manganese. Often found forming near or with lichens. Usually dark in colour, but can be as light as ivory
Phosphate skin	Various phosphate minerals (e.g. iron phosphates or apatite) that are mixed with clays and sometimes manganese; can be derived from decomposition of bird excrement
Pigment	Human-manufactured material placed on rock surfaces by people
Rock varnish	Clay minerals, Mn and Fe oxides, and minor and trace elements; colour ranges from orange to black due to variable concentrations of different manganese and iron oxides
Salt crust	The precipitation of chlorides on rock surfaces
Silica glaze	Usually clear white to orange shiny luster, but can be darker in appearance, composed primarily of amorphous silica and aluminum, but often with iron
Sulphate crust	Composed of the superposition of sulphates (e.g., barite, gypsum) on rocks; not gypsum crusts that are sedimentary deposits



Figure 8.1 This road cut between Death Valley, California and Las Vegas, Nevada illustrates the ability of 10–100 μm -thick rock varnish (darkens debris slope surface on upper half of image) to mask the appearance of the host igneous and metamorphic rocks (light-appearing road cut on lower half of image).

cobbles in contact with the soil (Engel and Sharp, 1958). Detailed discussions also distinguish different relationships among varnish and the underlying rock (Haberland, 1975).

An issue in classification that the introductory reader should be aware of involves the fairly frequent use of the term ‘desert varnish’ or ‘rock varnish’ to describe completely different types of rock-surface alterations (e.g. Howard, 2002). Even experienced desert geomorphologists (e.g. Bull, 1984; McFadden et al., 1989) have mistaken surfaces such as basalt ventifacts and geothermal deposits for varnish. Consider just Antarctic research, which has been consistently unable to distinguish between iron films and weathering rinds usually termed either desert varnish (Glasby et al., 1981) or rock varnish (Ishimaru and Yoshikawa, 2000) from manganese-rich coatings (Glazovskaya, 1958; Dorn et al., 1992).

The problem for any researcher new to the topic of manganese-rich varnish is that the vast majority of papers are written by investigators who collect only a few samples from a few locales and simply assume that their samples, somehow, are equivalent to varnishes collected in completely different biogeochemical settings. The only formal classification of rock varnish thus far presented (Dorn, 1998, pp. 214–224) maintains the goal of forcing varnish researchers to ensure that they have sampled the same variant in any comparisons. For the sake of clarity and brevity, this chapter presents illustrations only for varnishes formed in subaerial settings.

8.2 Distribution, Field Occurrence and Geomorphological Relations

Rock varnish grows on mineral surfaces exposed by erosional processes, either in weathering-limited landscapes such as deserts (e.g. White, 1993), or in settings dominated by rapid erosion such as glaciated terrain (e.g. Whalley et al., 1990). Thus, one first-order control on distribution rests with geomorphological processes exposing rock faces. Another first-order control on distribution rests on whether the varnish formed in a geochemical landscape (Perel'man, 1961) favourable for stability; exposure to minimal acidity helps maintain the manganese and iron in their oxidised and immobile condition in varnish. A second-order issue turns on the nature of the erosional process. Spalling often exposes planar joint faces that already have rock coatings developed in subsurface settings (Coudé-Gaussen et al., 1984; Villa et al., 1995; Dorn, 1998).

Rock varnish exists in geomorphological catenas (Haberland, 1975; Palmer, 2002), much in the way that soils vary along slopes (Jenny, 1941). Taking a simple basalt hill in the western Mojave Desert of California, Palmer (2002) mapped the abundance of black rock varnish, orange iron films, and surfaces experiencing rapid-enough erosion that they lacked field-observable rock coatings (Figure 8.2). Rock varnish occurs more frequently on metre-sized colluvium at the hill crest. In contrast, iron films, that initially formed on clasts formerly buried in soil, increasingly dominate on subaerial slope positions experiencing greater soil erosion from grazing (Palmer, 2002) or Holocene erosion (Hunt and Wu, 2004).

Palmer's (2002) general observation that different geomorphological positions influence rock varnish carries over to a single boulder. Just considering varnish thickness, millimetre-scale topographic highs host thinner varnishes than 'microbasins' or broad depressions a few millimetres across (Figure 8.2). Depressions more than a few millimetres deep favour retaining enough moisture to host varnish-destroying microcolonial fungi (Figure 8.3), cyanobacteria, or even lichens. Granodiorite boulders on a moraine in the Karakoram Mountains, for example, illustrate the importance of aspect where varnish grows on south-facing surfaces, while lichens and salt efflorescences occupy north-facing surfaces (Waragai, 1998).

The varnish literature is filled with misunderstandings surrounding its distribution, field occurrence and geomorphological relations. Consider one of the most common errors, equating darkness in a field sample with age, a generalisation derived from observing the darkening of alluvial-fan units over time. If geomorphological units darken over time, would not individual hand samples? This is not necessarily the case. The darkest varnishes are usually those that grow first in rock crevices (Coudé-Gaussen et al., 1984; Villa et al., 1995) and are then 'born dark' as spalling exposes

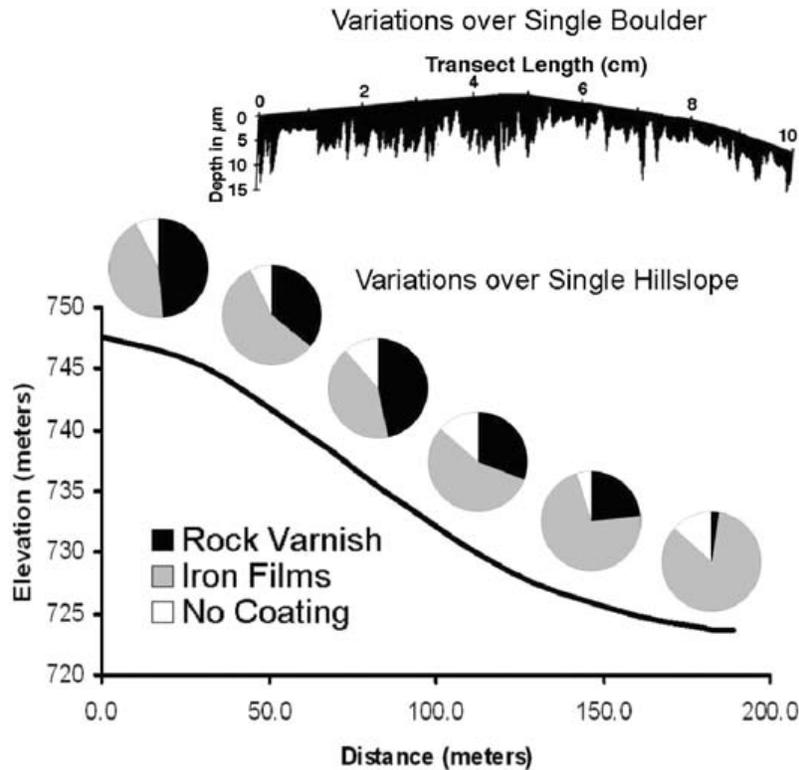


Figure 8.2 Rock varnish varies considerably over short distances, over a single boulder and over a single hillslope. The upper part of this figure illustrates that varnish thickness varies considerably over a single granodiorite boulder on the Tioga-3 moraine at Bishop Creek, about $19 \pm 1 \text{ ka } ^{36}\text{Cl}$ years old (Phillips et al., 1996). The thickest varnishes grow in shallow 'dish shaped' microbasins. Deeper rock depressions typically host varnishes experiencing erosion from acid-generating fungi and cyanobacteria. The lower portion of this figure presents a rock coating catena (adapted from Palmer, 2002) for three rock coating types, and shows variability on a basaltic hillslope in the Mojave Desert, California. Note that rock varnish dominates the more stable hill crest; iron films increase in abundance towards the slope bottom, and rock surfaces mostly lacking either coating occurs in a similar abundance on all slope positions.

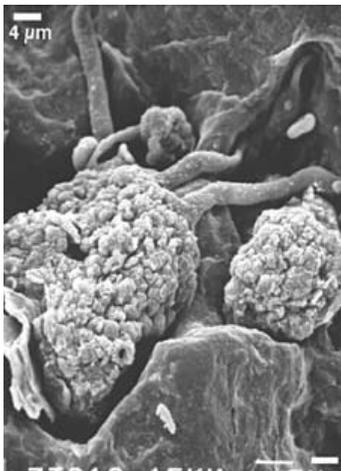


Figure 8.3 Originally named black globular units (Borns et al., 1980) for their appearance under a hand lens, microcolonial fungi are common inhabitants on desert rocks (Staley et al., 1982) that experience warm season convective precipitation. Originally thought to be agents of varnish (Staley et al., 1983) formation, the lack of manganese-enhancement by these and other fungi (Dorn and Oberlander, 1982) and their ability to dissolve varnish (Dorn, 1994) makes these organisms either adventitious or destructive agents, but not formative (Dragovich, 1993).

fracture varnish. Rather than detail each misunderstanding here, Table 8.2 summarises these peculiar components of the literature.

8.3 Macro- and Micromorphological Characteristics

Regions with abundant vegetative cover do have rock varnish on bare-rock surfaces, but these are too small in extent to alter signatures in remotely-sensed imagery. That is why arid regions host a large number of remote-sensing investigations about the macromorphological characteristics of varnish (Kenea, 2001). Alluvial fans are favourite study sites (White, 1993; Farr and Chadwick, 1996; Milana, 2000), in part because of the dramatic colour changes produced by progressive increases in the aerial extent of varnishing (Figure 8.4) and increasing darkness as fracture varnishes are exposed by boulder spalling (Villa et al., 1995).

Regional climatic variations alter the micromorphological character of rock varnishes, where abundance of aeolian dust appears to be a key factor. The vast majority of rock varnishes have micromorphologies that range between lamellate and botryoidal (Figure 8.5). A paucity of dust allows a clustering of varnish accretion, thus producing botryoidal forms. An abundance of dust smothers the tendency of Mn accumulation around nucleation centres, producing lamellate micromorphologies. A variety of other factors, however, can influence micromorphology, including: clay mineralogy, manganese abundance, epilithic organisms such as microcolonial fungi, morphology of the underlying rock, varnish thickness, aeolian abrasion, proximity to soil, and other microenvironmental factors (Dorn, 1986).

The dominant cross-sectional texture of rock varnish is layering (Figure 8.4C, E). Even the highest resolution transmission electron microscopy (HRTEM) views of varnish consistently show layering textures (Krinsley et al., 1995) imposed by its clay mineralogy (Figure 8.4E). Even when the surface morphology is botryoidal, cross-sectional texture remains layered internally within each botryoidal mound (Figure 8.5B). All meaningful theories of varnish genesis must explain varnish textures as well as varnish chemistry.

8.4 Chemistry and Mineralogy

Analytical chemist Celeste Engel completed the first Masters thesis research on rock varnish and teamed up with geomorphologist Robert Sharp to write a seminal paper on rock varnish in the Mojave Desert (Engel and Sharp, 1958). The major elements are O, H, Si, Al, and Fe in approximately equal abundance with Mn. The key mystery of varnish formation (von Humboldt, 1812; Lucas, 1905; Engel and Sharp, 1958; Jones, 1991) is

Table 8.2 A few of the misunderstandings in the literature surrounding rock varnish and its environmental relations. See chapter 10 in Dorn (1998) for a more detailed account of the history of thought on varnish

Topic	Misunderstanding	Resolution
Accretion or rock weathering	A century of debate exists on whether varnish accretes on (Potter and Rossman, 1977) or derives from the underlying rock (Hobbs, 1918)	Low- (Dorn and Oberlander, 1982) and high-resolution (Krinsley, 1998) electron microscopy and trace element geochemistry (Thiagaran and Lee, 2004) fails to show evidence of anything other than an accretionary process
Adventitious organisms	Varnishes host a wide array of organisms (Kuhlman et al., 2005, 2006; Schelble et al., 2005) such as lichens (Laudermilk, 1931), microcolonial fungi (Borns et al., 1980; Staley et al., 1983; Gorbushina et al., 2002) gram-positive bacteria (Perry et al., 2003), cyanobacteria and other organisms (Krumbein, 1969)	The simple presence of organics in association with varnish bears little importance to varnish genesis, unless biotic remains explicitly link to varnish-formation processes. Spatially precise geochemical analyses reveal the difference between adventitious organisms (Dragovich, 1993) and those bacteria that can be seen to enhance Mn and Fe through <i>in situ</i> analyses (Dorn and Oberlander, 1982; Krinsley, 1998)
Case hardening	Rock varnish is too thin to be an effective case hardening agent	Cation leaching (Dorn and Krinsley, 1991) from varnish provides materials for redeposition within the weathering rind – thus case hardening the outer shell of rock (Haberland, 1975)

Darkness shows time	Darker appearing surfaces are older than younger appearing surfaces (McFadden et al., 1989; Reneau, 1993)	This misunderstanding causes a number of errors in geomorphological analyses. Eleven factors other than time influence darkness (table 10.7 in Dorn, 1998)
Desert restriction	Desert varnish occurs in deserts and not elsewhere, and this distribution somehow relates to mode of formation	Rock varnish occurs in every terrestrial weathering environment (Dorn and Oberlander, 1982; Douglas et al., 1994; Lucas, 1905; Whalley et al., 1990). More frequent occurrence in deserts relates to greater landscape geochemical stability (Perel'man, 1961) for Mn and Fe cements
Lithology preference	Rock varnish grows best on certain lithologies such as fine-grained extrusive rocks	A more important issue is host rock stability. Rock varnish forms on all lithologies whose surface stability exceeds rates of varnish formation
Lustre	The shiny appearance of varnish relates to age or wind abrasion	Neither is true. Some sheen derives from very smooth and Mn-rich varnishes. The shiniest varnishes, found at the ground line on desert pavement cobbles, are only a few microns thick and intercalate with silica glaze
Manganese and iron abundance	When averaged over an area, the total accumulation of manganese and iron increases over time	Major problems confound this naïve belief, including exposure of manganese-rich fracture coatings (Douglas et al., 1994), erosion of faster-forming varnishes (Dorn and Oberlander, 1982), and role of microenvironments (Whalley et al., 1990)

Table 8.2 *Continued*

Topic	Misunderstanding	Resolution
Mars analog	Assuming that varnish is a biogenic rock coating, the occurrence of Mn-rich varnishes on Mars provides evidence of life or former life	The use of varnish as a bioindicator of Martian life is untenable until abiotic origins of Mn-enhancement are falsified for Martian conditions
Surface stability	Since cosmogenic nuclide analyses show erosion of rock surfaces (Nishiizumi et al., 1993), and geomorphological surfaces hosting varnish such as desert pavements experience instability (Peterson, 1981), how can varnish exist for 10^5 years (Liu and Broecker, 2000; Liu, 2003)?	Rock surface erosion rarely occurs in a linear fashion. Larger clasts can host zero erosion rates, while adjacent clasts experience much more rapid erosion. Linear rates of boulder erosion remain unusual. Similarly, landforms can exhibit signs of instability such as erosion of fines, even though particular rock faces can remain stable
Thickness	Thickness increases over time	The thickest varnishes grow in wetter micropositions that foster erosion of the underlying weathering rind or on spalled fracture faces. Thus, although varnish does thicken over time if all other formation factors are held constant, the thinnest varnishes can be the oldest at any given site

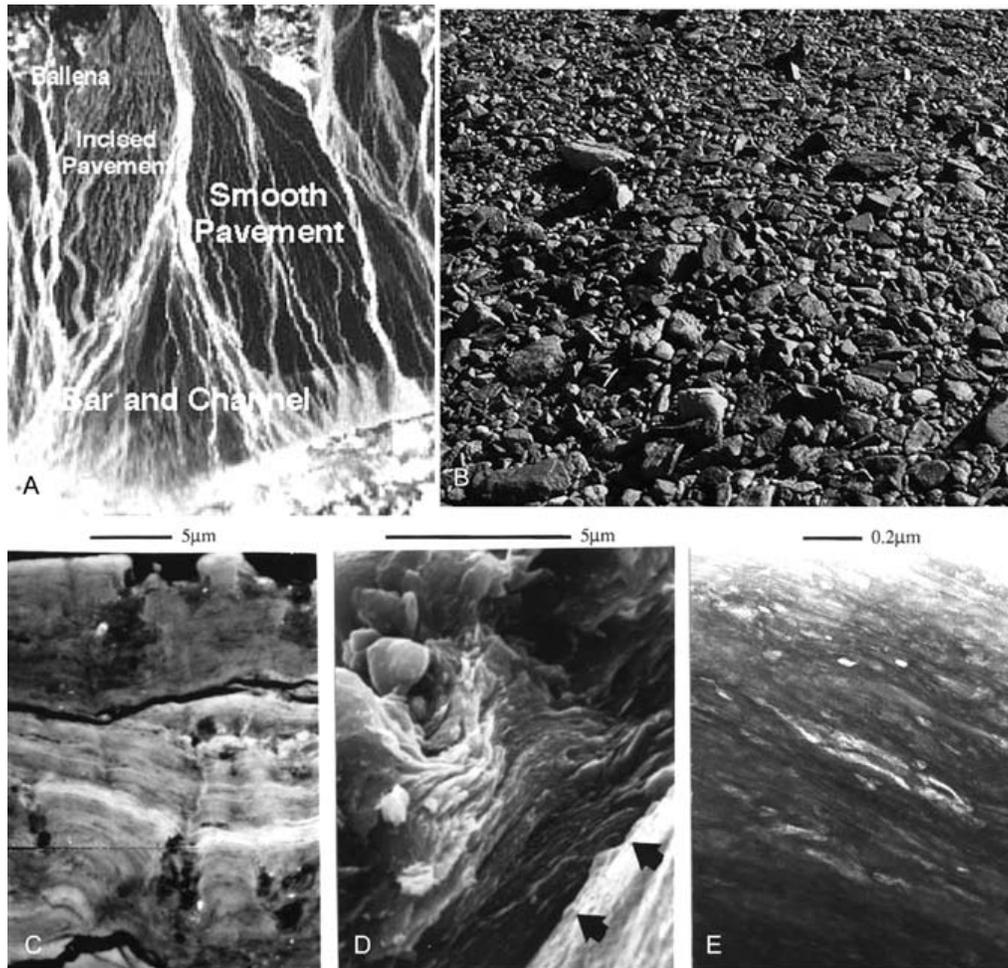


Figure 8.4 Rock varnish on Hanaupah Canyon alluvial fan, Death Valley, viewed at different scales. (A) SPOT satellite image where darkness first increases and then decreases with age. As varnish coverage increases, older sections of the Bar and Channel segment darken, reaching maximum darkness on the smooth pavement (B) segment. Channel incision starts to lighten appearance as varnished cobbles erode into gullies, with lightening increasing as channel incision progresses to the point where rounded ballenas expose a mix of calcrete and varnished cobbles. (C–E) Electron microscope imagery all revealing layering patterns in rock varnish, collected from Hanaupah Canyon alluvial fan, Death Valley. (C) Back-scattered electron image reveals average atomic number, where the bright layers are rich in manganese and iron and the darker layers are richer in clay minerals. (D) Scanning electron microscopy image shows shape, with the arrows identifying the contact between the rock in the lower right and the layered varnish. (E) High resolution transmission electron microscopy image is at a much greater magnification, showing that there are layers within layers, where the layered nature of clay minerals (Potter and Rossman, 1977) imposes the basic texture.

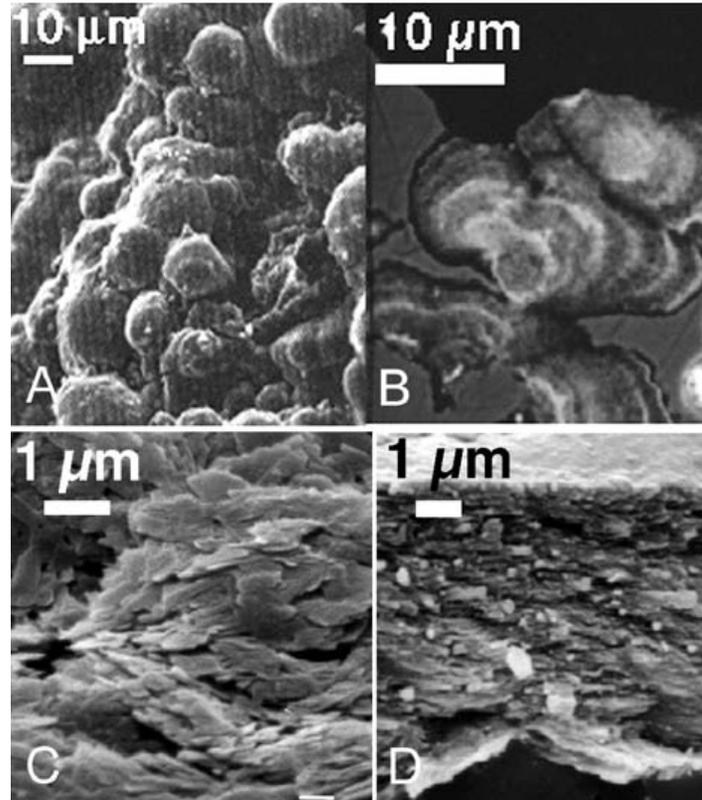


Figure 8.5 Varnish micromorphology form ranges from botryoidal to lamellate (A and C). Two types of imagery show botryoidal varnishes from Kitt Peak, Arizona: (A) the topography by secondary electrons; (B) the same structures from the bottom upwards with back-scattered electrons – showing the layering structures inside each nucleation centre. (C and D) Scanning electron microscopy images of lamellate clay minerals accreting on rock varnish in Death Valley, California. (C) Individual clay platelets overlap as they cement onto the surface. (D) The clays impose a lamellate structure in cross-section, as first noticed by Potter and Rossman (1977).

how to explain the great enrichment in Mn, normally a trace element in soils and rocks. Varnish Mn:Fe ratios vary from less than 1:1 to over 50:1, in contrast with Mn:Fe ratios of about 1:60 in the Earth's crust. Early microprobe analyses showed measurements higher than 15% Mn (Hooke et al., 1969). Concentrations of >80% Mn in focused spots occur on budding bacteria forms (Dorn, 1998).

Mn (II) is the most important soluble form, generally stable in the pH range 6–9 in natural waters (Morgan and Stumm, 1965). Since Mn (III) is thermodynamically unstable in a desert environment lacking abundant humic acids, Mn (IV) is the primary insoluble oxyhydroxide found in varnish, with average valencies of about +3.8 to +3.9 (Potter and Rossman, 1979a; McKeown and Post, 2001). The general Mn (II) oxidation reaction is:



for an oxidation state of (IV).

The inherent heterogeneity of varnish becomes abundantly clear in analyses of minor elements. In order of decreasing concentration, these tend to be: Ca, Mg, Na, K, Ti and P. Like Mn, minor elements vary considerably (0.5–1.5%), with Ba and Sr as the most abundant trace elements, along with Cu, Ni, Zr, Pb, V, Co, La, Y, B, Cr, Sc and Yb found in all varnishes in order of decreasing concentration (Engel and Sharp, 1958). Elements Cd, W, Ag, Nb, Sn, Ga, Mo and Zn were found in some, but not all varnishes (Lakin et al., 1963). With the acquisition of data from newer techniques using electron microprobes (Liu, 2003), neutron activation (Bard, 1979), particle induced X-ray emission (PIXE; Dorn et al., 1990), inductively coupled plasma mass spectrometry (Thiagarajan and Lee, 2004), and ion microprobes (O'Hara et al., 1989), heterogeneity remains the rule of chemical composition at all spatial scales: from micron to micron within a single depth profile or chemical transect, between locations on the same rock, between different rocks from the same area and between different areas (Table 8.3). The palaeoenvironmental significance of variations in varnish chemistry with depth are discussed in section 8.6.

The following generalisations remain unchanged from the original observations of Engel and Sharp (1958).

- 1 Silica and aluminum, taken together, comprise the bulk of rock varnish – consistent with clays being the dominant mineralogy.
- 2 Manganese and iron oxides typically comprise one-quarter to one-third of rock varnish with high point-to-point variability at scales from nanometres to kilometres.
- 3 Minor elements display variable patterns. Elements Mg, K and Ca are correlated with clays in cation-exchange positions. Barium often correlates with S in barium sulphates (O'Hara et al., 1989; Dorn et al., 1990; Cremaschi, 1996). In other cases, Ba correlates with Mn (Liu, 2003). Ti can correlate with Fe in titanomagnetite detrital grains (Mancinelli et al., 2002), but more often Ti is not well correlated with any major element (Dorn, 1998).
- 4 Trace heavy metals generally correlate with Mn abundance, and sometimes with Fe, due to the scavenging properties of these oxyhydroxides (Jenne, 1968; Tebo et al., 2004; Thiagarajan and Lee, 2004).

Varnish minerals were originally reported to be amorphous (Engel and Sharp, 1958), with goethite (Scheffer et al., 1963) and ferric chamosite (Washburn, 1969) as important components. Seminal research conducted with infrared spectroscopy, X-ray diffraction and electron microscopy at the California Institute of Technology revealed that the bulk of rock varnish

Table 8.3 Examples of elemental variation exhibited in bulk chemical analyses of rock varnishes found in desert regions. Results are normalised to 100% with measurements by particle induced X-ray emission (Cahill, 1986), with NA indicating not available and BLD below the limit of detection

Site	Position	Element																			
		Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe	Ni	Cu	Zn	Rb	Sr	Zr	Ba	Pb	
Trail Fan, Death Valley	Former rock fracture	BLD	0.14	23.74	39.09	0.49	0.7	3.45	4.87	1.52	10.87	13.47	0.13	0.12	0.27	BLD	BLD	BLD	0.29	0.85	BLD
Manix Lake, Mojave	>1 m above	1.1	3.44	25.77	32.35	1.15	0.3	2.11	1.35	0.84	12.47	18.09	BLD	0.22	0.3	0.25	0.21	0.22	0.19	0.74	
Desert Makanaka	With silica soil skin	0.62	1.98	21.13	29.77	0.69	0.2	3.3	4.89	0.73	13.6	21.13	BLD	0.33	0.49	BLD	BLD	BLD	BLD	0.16	0.98
Hawaii Sinai	>1 m above	0.28	1.5	22.94	32.81	BLD	BLD	2.42	2.91	0.68	11.97	22.94	BLD	0.25	0.42	BLD	0.42	BLD	BLD	0.18	0.27
Peninsula, Egypt	soil	0.17	1.21	22.81	33.34	0.53	BLD	2.79	2.18	0.65	21.7	13.26	BLD	0.44	0.44	BLD	BLD	BLD	BLD	0.14	0.34
Petroglyph, South Australia	>1 m above soil	NA	2.11	20.45	45.88	0.53	1.13	2.91	6.22	0.85	4.94	12.03	BLD	0.04	0.16	BLD	0.11	BLD	2.42	0.22	
Ingenio, Peru Desert	At soil surface	NA	2.11	20.45	45.88	0.53	1.13	2.91	6.22	0.85	4.94	12.03	BLD	0.04	0.16	BLD	0.11	BLD	2.42	0.22	
Ayers Rock, Australia	From rock fracture	NA	1.58	28.77	35.69	BLD	BLD	2.11	1.45	1.19	11.91	16.57	BLD	0.73	BLD						

is composed of clay minerals (Potter and Rossman, 1977), dominantly illite, montmorillonite, and mixed-layer illite–montmorillonite. As previously noted, the layering seen in varnish at all scales reflects this clay mineralogy (Figures 8.4 and 8.6). Subsequent research has confirmed the dominance of clay minerals (Potter and Rossman, 1977, 1979c; Dorn and Oberlander, 1982; Krinsley et al., 1990, 1995; Israel et al., 1997; Dorn, 1998; Krinsley, 1998; Diaz et al., 2002; Probst et al., 2002), although there is some disagreement (Perry et al., 2006).

Clay minerals are cemented to the underlying rock by oxides of manganese and iron. Birnessite ($[\text{Na,Ca}]\text{Mn}_7\text{O}_{14} \cdot 2.8\text{H}_2\text{O}$) and birnessite-family minerals are the dominant manganese minerals in black varnish, and haematite is a major iron oxide in both black varnish and orange iron films (Potter and Rossman, 1977, 1978, 1979a,b,c; McKeown and Post, 2001). Birnessite-family minerals are found frequently in microbial deposits (Tebo and He, 1998; Tebo et al., 2005). McKeown and Post's (2001, p. 712) summary perspective suggests that:

[e]ven if analysis methods are improved, the situation will remain complicated by the flexibility and great variety of Mn oxide structures. The common elements of these structures enable them to easily intergrow with and transform with one another. Furthermore, many of the phases, particularly the layered structures, readily exchange interlayer cations in response to even slight changes in chemistry on a microscale.

Imagery by HRTEM (Krinsley et al., 1995; Krinsley, 1998) reveals that the iron and manganese oxides that cement clay minerals together exist in this layered structure at the nanometre scale, derived from what appears to be sheaths of bacteria (Figure 8.7). The granular texture of the bacteria sheaths can be seen releasing nanometre-scale Mn–Fe that could be unit cells (Figure 8.6) into the weathered edges of the clay minerals (Fig 8.8) (Dorn, 1998). The ability to undergo incomplete transformation between phases at the nanometre scale would certainly be consistent with a disordered todorokite/birnessite-like phase (cf. Potter and Rossman, 1979a; McKeown and Post, 2001).

Detritus, both organic and inorganic, often settles in morphological depressions on varnish. These pieces are sometimes trapped by accreting rock varnish, leading to a wide variety of other minerals that are sometimes found in varnish samples such as quartz, feldspars and magnetite (Potter and Rossman, 1979a; Dorn, 1998, p. 198; Mancinelli et al., 2002).

8.5 Mechanisms of Formation or Accumulation

The genesis of most varnish constituents is explained easily. The clay mineral building blocks of varnish are ubiquitous in terrestrial weathering

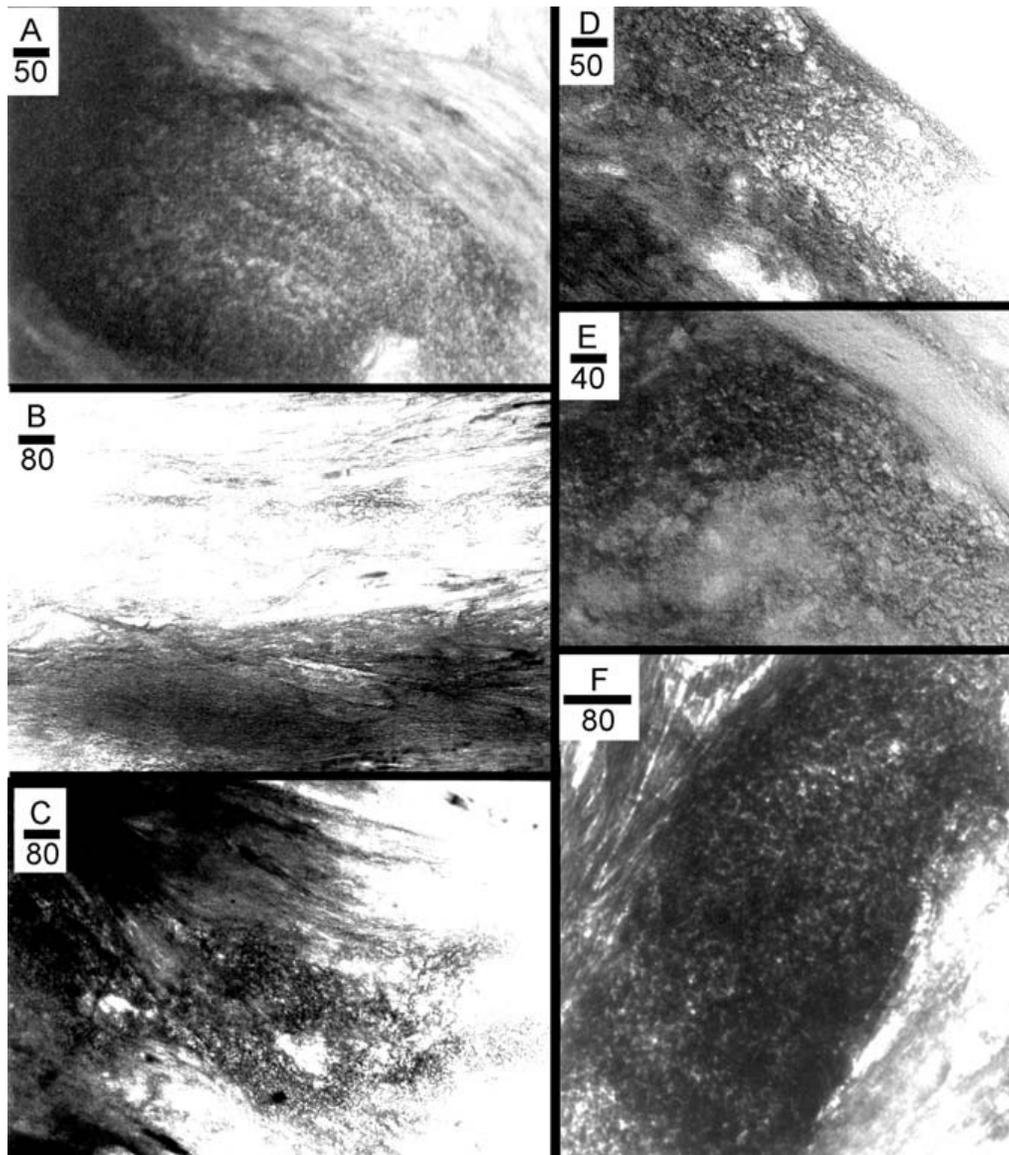


Figure 8.6 High resolution transmission electron microscopy imagery reveals manganese and iron minerals that appear to be moving from the granular remnants of bacterial sheaths into adjacent clay minerals. The granular textures found between layered varnish consist of Mn–Fe precipitates on bacterial remains (Krinsley, 1998). Images are of varnishes from: (A) Nasca, Peru; (B, E) Death Valley; (C, D) Kaho'olawe, Hawai'i; (F) Antarctica. Scale bars in nanometres.

environments where rock coatings are found (Dorn, 1998) and hence require simple dust deposition by aeolian processes. Minor and trace elements come adsorbed to clays, with subsequent enhancement by scavenging properties of Mn–Fe oxyhydroxides (Jenne, 1968; Forbes et al., 1976; Thiagarajan and Lee, 2004).

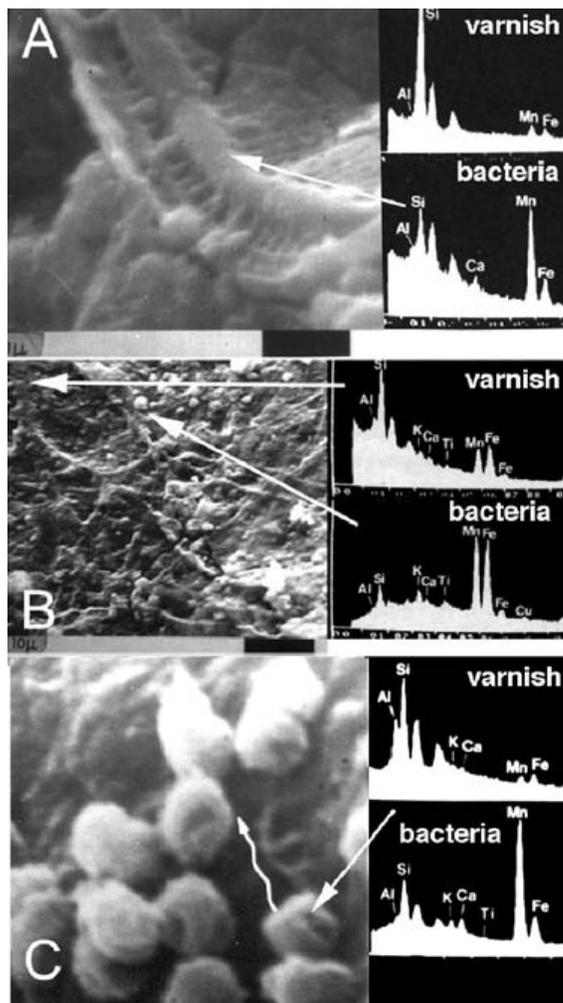


Figure 8.7 Budding bacteria morphologies actively concentrate manganese from (A) Crooked Creek, Kentucky, (B) Negev Desert and (C) Antarctica, as seen by energy dispersive 'spots' focused on the bacteria, compared with defocused analyses on adjacent uncolonised varnish. The Negev Desert hyphae resemble *Metallogenium* in morphology (Perfil'ev et al., 1965). The squiggly arrow in the Antarctica frame shows hyphae extending from bacterial-sized cells, exhibiting a *Pedomicrobium* budding bacteria morphology.

Explaining the great manganese enhancement in varnish (von Humboldt, 1812; Lucas, 1905; Engel and Sharp, 1958) has long been recognised as a key to understanding varnish formation. How clay minerals and manganese selectively interact, however, is just as important a key in discriminating relevant formative processes as concentrating Mn (Potter and Rossman, 1977). The mutual dependency of clay minerals and manganese can be realised by understanding what happens when one is lacking. Dust films, silica glaze and other rock coatings may result from clay mineral accretion without Mn (Dorn, 1998). Conversely, a different type of rock coating, heavy-metal skins, accrete when manganese precipitation occurs without clay minerals (see Chapter 8 in Dorn, 1998). Desert varnish accumulates only when and where nanometre-scale fragments of manganese, as seen in HRTEM imagery, cement broken and decayed fragments of clay minerals to rock surfaces.

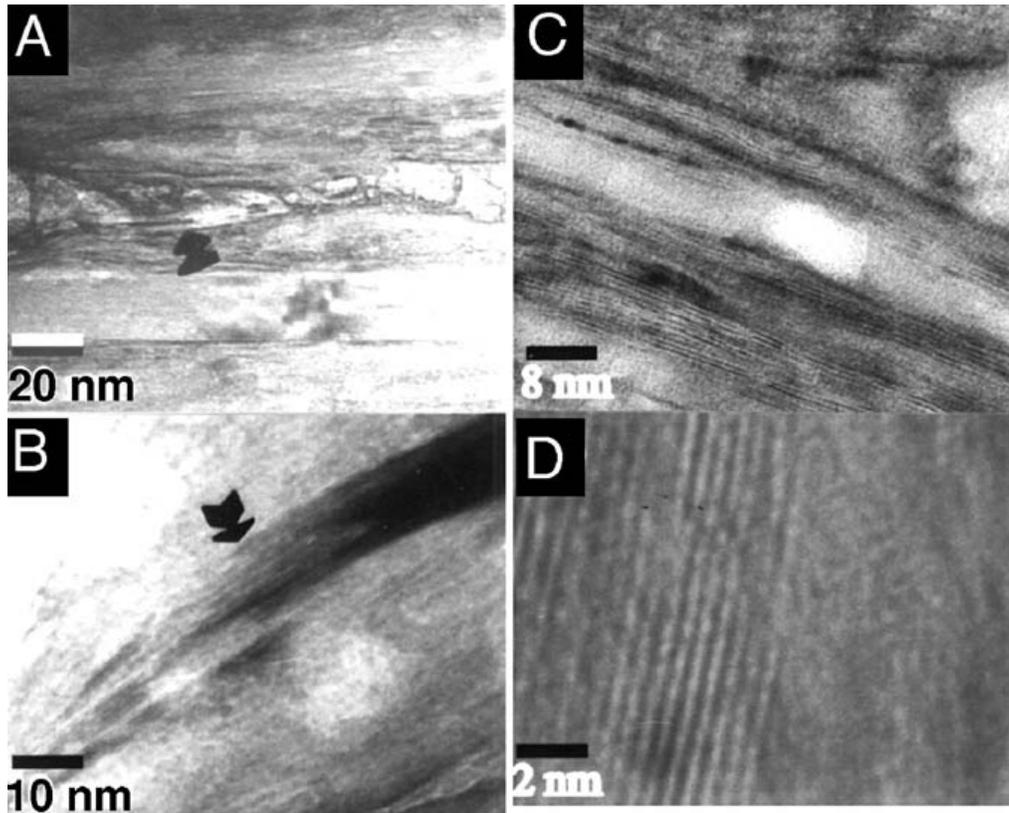


Figure 8.8 Clay minerals appear to be weathering by the insertion of Mn–Fe in samples from (A and B) Antarctica, (C) Peru and (D) Death Valley. Nanometre-scale cells of Mn–Fe appear within detrital clay mineral grains (arrows in A and B), essentially weathering 001 planes of exfoliation (Robert and Tessier, 1992). In many cases, the feathering is associated with granular textures (cf. Figure 8.6). At higher magnifications (C, D), disorganised wavy layers from clay weathering rest next to regularly spaced lattice fringes (with spacing that is consistent with illite, smectite, chlorite and interstratified clay – textural interstratification) (Robert et al., 1990). Scale bars in nanometres.

Four general conceptual models have been proposed to explain varnish formation (Figure 8.9). This section first presents the four proposed hypotheses of varnish genesis and then evaluates strengths and weaknesses.

8.5.1 Abiotic hypothesis of varnish genesis

Proponents of the abiotic hypothesis purport that varnish forms without the aid of biological enhancement of Mn (Linck, 1901; Engel and Sharp, 1958; Hooke et al., 1969; Moore and Elvidge, 1982; Smith and Whalley, 1988). To increase Mn:Fe ratios two to three orders of

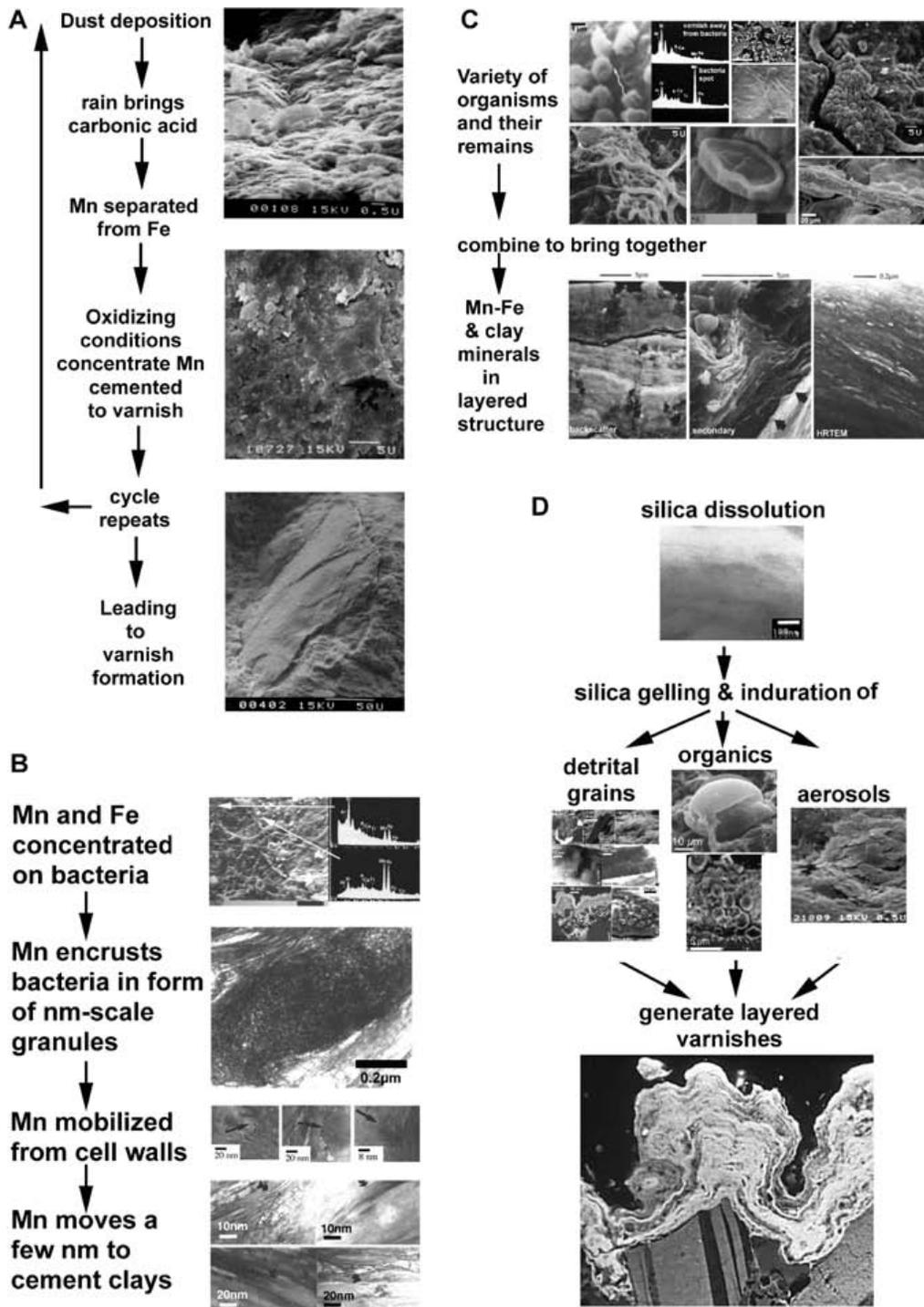


Figure 8.9 Conceptual models of rock varnish formation. (A) Abiotic enhancement by iterations of acid solutions separating Mn^{2+} followed by oxidising conditions concentrates Mn in varnish (Hooke et al., 1969; Smith and Whalley, 1988). (B) Polygenetic clay–bacteria interactions where varnish formation starts with the oxidation and concentration of Mn (and Fe) by bacteria. Wetting events dissolve nanometre-scale fragments of Mn. Ubiquitous desert dust supplies interstratified clay minerals. The Mn-bacterial fragments fit into the weathered edges of clays, cementing clays much like mortar cements brick. (C) Lithobionts or their organic remains (e.g. spores, polysaccharides and other humic substances) play a role in binding varnish and concentrating Mn and Fe oxides and oxyhydroxides. (D) Silica binding of detrital grains, organics and aerosols (Perry and Kolb, 2003; Perry et al., 2006).

magnitude above crustal values, abiotic processes rely on greater mobility of divalent manganese over ferrous iron where small pH fluctuations dissolve Mn but not Fe (Krauskopf, 1957). The Mn released by slightly acidic precipitation is then fixed in clays after water evaporation or change in pH.

Redox reactions between Mn (II) and Mn (IV) are largely governed by pH. In natural waters, Mn (II) oxidation requires pH values >8.5 to oxidise homogeneously within weeks to months without microbial assistance (Morgan and Stumm, 1965). Laboratory experiments reveal that abiotic oxidation from Mn (II) to Mn (IV) requires two steps (Hem and Lind, 1983); Mn first precipitates as an oxyhydroxide (MnOOH) that then forms tetravalent Mn oxides (MnO₂). Abiotic oxidation of Mn (II) may be increased by the presence of abundant Fe oxyhydroxides found in varnish (Junta and Hochella, 1994), but Fe-catalysed oxidation results in Mn (III)-bearing oxyhydroxides (Junta and Hochella, 1994) that are not found in varnish samples (cf. Potter and Rossman, 1979c; McKeown and Post, 2001).

In contrast, microbial oxidation of Mn (II) to Mn (IV) is quite rapid at the near neutral pH values (Tebo et al., 1997, 2004) found on rock varnish (Dorn, 1998). The process appears to be extracellular where Mn oxides create casts on cell walls (Krinsley, 1998). There are both gram-positive and gram-negative bacteria that form a diverse phylogenetic group of sheathed and appendaged bacteria capable of oxidising Mn (e.g. Perfil'ev et al., 1965; Khak-mun, 1966; Dorn and Oberlander, 1981, 1982; Peck, 1986; Hungate et al., 1987). Environmental and laboratory studies suggest that the microbial oxidation of Mn (II) results in the formation of Mn (IV) without lower Mn (III) valences (Tebo and He, 1998; Tebo et al., 2004).

The geography of varnish poses critical obstacles, making purely abiotic formation of varnish difficult to explain. Varnishes found in wetter climates are typically higher in manganese than those in arid, more alkaline settings (Dorn, 1990) – a result that would not be predicted by the high pH requirements of abiotic oxidation. Black, Mn-rich varnishes occur in a host of moist environments such as within joint faces in glacial Norway (Whalley et al., 1990) and Iceland (Douglas et al., 1994). In contrast, hyperarid deserts are dominated by varnishes with a relative paucity of manganese; orange to burgundy coloured varnishes cover rocks in hyperarid deserts, such as the Atacama, and locally alkaline settings such as those adjacent to deflating salt playas in western North America (Dorn, 1998). Repeated oscillations in pH are the key to abiotic concentration of manganese over iron (cf. Engel and Sharp, 1958; Hooke et al., 1969; Smith and Whalley, 1988). However, the very environments where one would expect the least number of these pH fluctuations are the humid environments where

Mn-rich varnishes are most common (Dorn, 1990, 1998) – providing a geographical conundrum for the abiotic enhancement mechanism.

Other geographical problems with the abiotic hypothesis (Dorn, 1998, p. 242–243) include: rapid pH fluctuations in the range to mobilise and oxidise Mn where varnish does not commonly occur (in such as places as the rainshadows of Mauna Loa and Mauna Kea on Hawai'i); purely inorganic Mn fixation experiments yielding too low concentrations of Mn; millimetre-scale distribution of varnish mimicking the pattern of microbial colonisation; an inability to explain botryoidal varnish textures by abiotic processes; and an inability to produce true varnish experimentally without microorganisms.

One of the most serious problems with the abiotic explanation rests in a simple analysis of rates of varnish formation. Based on detailed analyses of over 10,000 microbasins (Liu and Broecker, 2000, 2007; Liu, 2003, 2006), consistent with independent observations (Dorn, 1998), rates of varnish formation are on the order of a few microns per 1000 years. If Mn is enhanced abiotically, there would be no reason for such a slow rate of varnish formation. Multiple dust deposition and carbonic acid wetting iterations take place annually, even in drought years. Under this model, some Mn would be leached from dust with each event and in turn mix with other constituents to accrete in varnish layers. Such progressive leaching would be relentless without a rate-limiting step, and varnish accretion would be from 10^2 to 10^4 times faster than real varnishes, that is if abiotic enhancement led to varnish formation.

Although arguments potentially could be made against each of these problems with an abiotic explanation of Mn-enhancement, such accommodations have not yet been forthcoming in the literature. Abiotic processes are certainly involved in varnish formation (cf. Bao et al., 2001), including trace element enhancement with wetting (Thiagarajan and Lee, 2004) and the process of clay cementation (Potter and Rossman, 1977; Potter, 1979, pp. 174–175; Dorn, 1998). However, these processes alone would not generate a rock varnish.

8.5.2 Lithobionts or their organic remains produce and bind varnish

The general biological argument includes of a number of researchers who report observing microbial remains growing on varnish (e.g. Allen et al., 2004), or report organic compounds such as bacterial DNA (e.g. Perry et al., 2002) within varnish. Lichens (Laudermilk, 1931; Krumbein, 1971), cyanobacteria (Scheffer et al., 1963; Krumbein, 1969), microcolonial fungi (see Figure 8.3; cf. Staley et al., 1982; Allen et al., 2004, pp. 25), pollen

(White, 1924), peptides (Linck, 1928), refractory organic fragments (Staley et al., 1991), gram-negative non-sporulating cocci bacteria (Sterflinger et al., 1999), and amino acids from gram-positive chemo-organotrophic bacteria (Warsheid, 1990; Nagy et al., 1991; Perry et al., 2003) illustrate only spatial correlation with varnish (see Dorn (1998, pp. 238–9, 243) for a more complete list of references). Fatty acid methyl esters analysed from Mojave Desert varnish do not provide any evidence that adventitious gram-positive bacteria responsible for these fatty acids play a role in varnish formation (Schelble et al., 2005). A great leap forward in the study of microbes potentially involved in varnish genesis, however, rests in understanding phylogenetic affiliations and in estimating the total number of microbes actually present – in this case in fracture varnish collected from desert pavement cobbles in the Whipple Mountains of eastern California after winter rains (Kuhlman et al., 2005, 2006). About 10^8 cells of bacteria per gram dry weight of varnish summarises the story: varnish represents a habitat occupied by a plethora of bacteria, with a significant presence of gram-negative Proteobacteria groups and Actinobacteria (Kuhlman et al., 2005, 2006). Spatial contiguity of organisms and organic remains with rock varnish, however, is simply insufficient to explain great Mn-enhancement or clay cementation.

The aforementioned growing number of observations of apparently adventitious organisms and organic matter suffers from a core problem: there is no process by which these observed organisms or their remains produce rock varnish. The most cited of these purported agents – micro-colonial fungi (see Figure 8.3 and Borns et al., 1980; Staley et al., 1983; Gorbushina et al., 2002) – either dissolve or co-exist with varnish (Dragovich, 1993; Dorn, 1998). Even research on cultured Mn-oxidising bacteria (e.g. Krumbein, 1969; Krumbein and Jens, 1981; Palmer et al., 1985; Hungate et al., 1987) miss a key criteria. The bottom line is that seeing is believing, in this case morphologically similar shapes actually seen enhancing Mn *in situ* (Figure 8.7) (cf. Perfil'ev et al., 1965; Khak-mun, 1966; Dorn and Oberlander, 1981, 1982; Peck, 1986). Research into the microbial habitat of rock varnish is just starting, and the future rests in following in the footsteps of Kuhlman et al. (2005, 2006), as long as this research is matched with *in situ* studies.

Rates of varnish formation in desert environments should make readers very sceptical of the growing plethora of biological agents purported to be involved in varnishing. In places where varnishing rates have been measured in warm desert environments, typically one to twenty bacterial diameters accumulate each thousand years (Liu, 1994; Liu and Broecker, 2000). Rates would be several orders of magnitude higher if all of the observed rock-surface organisms, extracted organic matter associated with varnish and rock surfaces, and cultured biological agents actually play a role in making desert varnish. Consider the types of amino acids extracted from

varnishes; the apparent lack of D-alloisoleucine and concentrations of serine suggest that the extracted amino acids are only centuries old – not the thousands of years that would indicate a formative role. If all of the 10^8 microbes per gram are involved in varnish formation, one should be able to see desert rock surfaces encrusted at rates such as seen in travertine contexts (cf. Chafetz et al., 1998). Furthermore, if these commonly seen organisms made varnish, cross-sections would look like biotically generated coatings where fossilised remains are common (Francis, 1921; Ferris et al., 1986; Konhauser et al., 1994; Chafetz et al., 1998; Kennedy et al., 2003).

Fossilised casts of Mn-enhanced bacterial remains are rare in desert varnish; the intra-varnish remains seen in HRTEM and back-scatter electron (BSE) imagery often resemble gram-negative appendaged bacteria in their morphology (Dorn and Meek, 1995; Krinsley, 1998; Dorn, 1998). Simply finding organic remains such as amino acids, DNA or even culturing Mn-oxidisers obfuscates the key question: what is the *in situ* evidence that certain microbes supply the Mn (and Fe) that cement clays to rock surfaces? Researchers wishing to advance any single agent to the role of formative agents must present clear evidence of *in situ* textural connections to formative processes involving Mn enhancement.

8.5.3 Silica binding model

The most recent conceptual model proposed to explain varnish formation focuses on silica as the key agent (Perry and Kolb, 2003; Perry et al., 2006). The hypothesis starts with dissolution of silica from anhydrous and hydrous minerals. The next step has the silica gelling, condensing and hardening. A romantic article title ‘baking black opal in the desert sun’ (Perry et al., 2006) emphasises the importance of the hot desert environment to this model. In the process of silica binding, detrital minerals, organics and dust from the local environment are bound into varnish. There is no ambiguity about the key role of silica in the envisioned process: ‘[s]ilicic acid and (di)silicic acid and polymers form complexes with ions and organic molecules, especially those enriched in hydroxy amino acids . . . The centrality of silica to this mechanism for cementing and forming coatings means that silica glazes and desert varnish should be considered part of the same class’ (Perry et al., 2006, p. 520).

There is no question that the importance of amorphous hydrated silica (opal) and silica minerals (e.g. moganite) have not been emphasised in varnish research. Furthermore, the process of silica binding as envisioned (Perry and Kolb, 2003; Perry et al., 2006) would be compatible with other models of varnish formation. In other words, the movement of water that remobilises varnish constituents (Dorn and Krinsley, 1991; Krinsley, 1998)

would be compatible with and could explain observations of silica (Perry and Kolb, 2003; Perry et al., 2006).

There are, however, multiple fatal flaws with silica binding as the key process in varnish formation. First, the silica binding process does not explain Mn-enhancement seen in varnish or the Mn-minerals seen in varnish. Second, although silica dissolution is slow on rock surfaces, it is not a rate-limiting step capable of slowing varnish accretion to the scale of a few microns per millennia. The formation of silica glaze within decades (Curtiss et al., 1985; Gordon and Dorn, 2005), perhaps from silica binding (Perry and Kolb, 2003; Perry et al., 2006) or perhaps from another process (chapter 13 in Dorn, 1998), indicates that this model cannot explain varnish accretion. Third, the silica binding model rides on the opinion that clay minerals are not a dominant part of rock varnish (Perry et al., 2006), a view incompatible with data sets several orders of magnitude more extensive (Potter and Rossman, 1977, 1979c; Dorn and Oberlander, 1982; Krinsley et al., 1990, 1995; Israel et al., 1997; Dorn, 1998; Krinsley, 1998; Diaz et al., 2002; Probst et al., 2002; Liu, 2003; Liu and Broecker, 2007). Fourth, this model does not accommodate the geography of rock coatings. For example, why would silica glazes dominate on Hawaiian basalt flows (Curtiss et al., 1985; Gordon and Dorn, 2005) and not manganiferous rock varnish? Abundant examples of this juxtaposition exist (e.g. Dorn, 1998), and one of the closest Mars analogue exists on the Tibetan Plateau, where rock varnish rests adjacent to silica glaze and other rock coatings (Dorn, 1998, pp. 367–371). The silica binding model cannot explain this geographical pattern. Fifth, ‘baking’ is a requirement of the silica binding model, but varnish occurs in subsurface and cold-climate settings where the requisite heat and light do not exist (Anderson and Sollid, 1971; Douglas, 1987; Dorn and Dragovich, 1990; Whalley et al., 1990; Dorn et al., 1992; Douglas et al., 1994; Villa et al., 1995; Dorn, 1998). Sixth, the silica binding process does not explain the characteristics of the varnish microlaminations data set discussed in a later section.

8.5.4 Polygenetic model

The polygenetic model of rock varnish formation combines biotic enhancement of Mn with abiotic processes (Dorn, 1998). It builds on the mineralogy research of Potter and Rossman (1979a,b,c) and studies of bacteria fossil remains within varnish layers (Dorn and Meek, 1995; Krinsley et al., 1995; Dorn, 1998; Krinsley, 1998). In brief, weathered remains of Mn-rich bacterial casts (Figure 8.6) cement weathered clay minerals to rock surfaces.

Varnish formation probably starts with ubiquitous dust deposition on rock surfaces; budding bacteria (Dorn and Oberlander, 1982) actively

concentrate Mn and Fe (Figure 8.7). Some of these bacterial ‘sheaths’ become microfossils (Dorn and Meek, 1995; Dorn, 1998; Krinsley, 1998) that then decay (Figure 8.6). Enhancement of Mn by other microbes, such as gram-positive bacteria, could certainly contribute; but *in situ* evidence of Mn-enhancement and preservation of Mn–Fe ‘bacterial casts’ has heretofore been lacking for morphologies other than budding or appendaged bacterial forms. The exact mechanism for oxidation of Mn^{2+} is uncertain, perhaps involving heteropolysaccharides containing the protein that catalyses the oxidation reaction with molecular oxygen. Mechanisms for Mn^{2+} binding and oxidation, however, have yet to be demonstrated for varnish.

Decay of Mn–Fe-encrusted bacterial casts mobilises nanometre-scale Mn and Fe and then cements clay minerals (Figure 8.8). At the highest HRTEM magnifications, irregular layers of Mn–Fe-cemented clays rest next to regularly spaced lattice fringes with spacing that is consistent with illite, smectite, chlorite and interstratified clay – textural interstratification. The reader should note that this discussion is at the nanometre-scale and that the interlayering of different types of rock coatings discussed elsewhere is at the much coarser micrometre scale. Potter (1979, pp. 174–175) argued for this step without the benefit of supporting HRTEM imagery:

Deposition of the manganese and iron oxides within the clay matrix might then cement the clay layer . . . the hexagonal arrangement of the oxygens in either the tetrahedral or octahedral layers of the clay minerals could form a suitable template for crystallisation of the layered structures of birnessite. The average 0–0 distance of the tetrahedral layer is 3.00 Å in illite-montmorillonite mixed-layered clays, which differs only 3.4 percent from the 2.90 Å distance of the hexagonally closed-packed oxygens in birnessite . . .

Varnish formation, then, is a nanometre-scale marriage between clay minerals and the millennial accumulation and decay of Mn–Fe-encrusted bacterial casts. Nanometre-sized Mn–Fe remains of bacteria both feather and cement clay minerals to the rock and to prior varnish.

Any successful model of varnish formation, however, must also explain additional issues associated with varnish chemistry. First, iron is enhanced slightly in varnish over crustal and adjacent soil concentrations. Although most of the iron derives from the clay minerals, some is biotically enhanced (see Figure 8.7 and Dorn and Oberlander, 1982; Adams et al., 1992; Sterflinger et al., 1999) as the nanometre-scale Fe seen in the bacterial casts (Krinsley, 1998) is also found reworked into the weathered remnants of clay minerals seen in HRTEM imagery. Considerable HRTEM work, however, is needed to better document processes of minor iron enhancement.

Second, a number of trace elements are enhanced in rock varnish (Engel and Sharp, 1958; Lakin et al., 1963; Bard, 1979). This enrichment is

explained abiotically by Thiagarajan and Lee (2004); trace element enrichment starts when acidic pH values in rainwater *c.* 5.7 dissolve rare earths, Co, Ni, Pb, Sr, Rb, Cs and other trace elements from dust particles on rock surfaces. Coprecipitation of these trace elements with Mn–Fe oxyhydroxides leaves behind the aeolian dust particles that then blow away. The net process is the sort of concept proposed for the abiotic enhancement of manganese – analogous to a water filter that slowly traps water impurities; in the case of varnish, the dust particles slowly leave behind trace elements trapped by the Mn–Fe minerals. In addition, the opal observed by Perry et al. (2006) could be precipitated as water moves throughout and redistributes varnish constituents (Dorn and Krinsley, 1991; Krinsley, 1998).

8.5.5 Evaluating model strengths and weaknesses

In addition to the great enhancement of Mn, other criteria have been proposed to adjudicate these different hypotheses (Table 8.4). No single model explains all observed aspects of Table 8.4, but three of the proposed models run into severe difficulties when they are tasked to explain key varnish characteristics: abiotic enhancement of manganese; lithobionts or their organic remains produce varnish; and silica binding. These three problematic models, for example, have no severe rate-limiting step. The processes suggested would all produce rock varnish very rapidly, from 100 to 10,000 times faster than the $1\text{--}10\ \mu\text{m kyr}^{-1}$ rates observed in nature (Table 8.4).

The viable polygenetic model, in contrast, turns on the very slow processes by which manganese enhancement takes place and very slow processes by which manganese and iron interact with clay minerals. A significant advantage of the polygenetic model is that it does not suffer from the fatal flaws extant in the other three models (Table 8.5). A minor advantage of the polygenetic model is that it is fully compatible with processes in the silica binding model and the presence of adventitious lithobionts and their organic remains in varnish. An issue for the polygenetic model, however, is that the abiotic enhancement hypothesis has not been falsified – a very difficult task given the rate of varnish formation.

8.6 Palaeoenvironmental Significance

Varnish sometimes serves as an indicator of palaeoenvironments even before the Quaternary (Dorn and Dickinson, 1989; Marchant et al., 1996). A buried Miocene hillslope in southern Arizona, for example, hosts a fossilised debris slope where many of the small boulders are covered by fossilised varnish (Dorn and Dickinson, 1989). Simply finding an isolated clast of rock varnish in buried contexts cannot be used to infer any

Table 8.4 Criteria that have been used to adjudicate competing models of rock varnish formation

Criteria	A successful model must be able to explain . . .
Accretion rate	. . . typical rates of accretion on the order of 1–10 μm per millennia (Dorn, 1998; Liu and Broecker, 2000). Although faster-growing varnishes occur (Dorn and Meek, 1995), such varnish accretion rates (Liu, 2003, 2006; Liu and Broecker, 2007) demand an extreme rate-limiting step for whatever process makes varnish
Clay minerals	. . . the dominance of clay minerals in rock varnish (Potter and Rossman, 1977, 1979c; Dorn and Oberlander, 1982; Krinsley, 1998; Krinsley et al., 1990; Krinsley et al., 1995; Israel et al., 1997; Dorn, 1998; Broecker and Liu, 2001; Diaz et al., 2002; Probst et al., 2002)
Fe behaviour	. . . the differential enhancement of iron in different varnish microlamination (VML) (Liu et al., 2000; Broecker and Liu, 2001; Liu and Broecker, 2007) and different places (Adams et al., 1992; Dorn, 1998; Allen et al., 2004)
Laboratory creation	. . . the creation of artificial varnish coatings (Krumbein and Jens, 1981; Dorn and Oberlander, 1981, 1982; Jones, 1991) may be considered by some to be a vital criteria. However, given the extraordinary time-scale jump between any laboratory experiment and natural varnish formation, and the extreme rate-limiting step involved in natural varnish formation, rigid application of this criteria may be problematic
Lithobionts and organic remains	. . . the occurrence of different types of lithobionts and the nature of organic remains. The plethora of <i>in situ</i> and cultured organisms, as well as spores, polysaccharides and other humic substances associated with varnish (see review in Dorn, 1998; Gonzalez et al., 1999; Netoff, 2001; Gorbushina et al., 2002; Kurtz and Netoff, 2001; Perry et al., 2002, 2003; Perry and Kolb, 2003; Allen et al., 2004; Viles and Goudie, 2004; Kuhlman et al., 2005, 2006; Schelble et al., 2005) must be explained

Table 8.4 *Continued*

Criteria	A successful model must be able to explain . . .
Mn enhancement	. . . the enhancement of Mn typically more than a factor of 50 above potential source materials (von Humboldt, 1812; Lucas, 1905; Engel and Sharp, 1958)
Mn-mineralogy	. . . Mn mineralogy characteristic of birnessite-family minerals (Potter, 1979; Potter and Rossman, 1979a,b; McKeown and Post, 2001; Probst et al., 2001). Very difficult to study because of its small size, Mn oxides range from large tunnel phases to layer phases such as the birnessite family notable in varnish
Not just a few samples	. . . observations at sites around the world. The cost of microanalytical investigations demands analyses of only a few samples at a time. Nonetheless, Oberlander (1994, p 118) emphasises: ‘researchers should be warned against generalising too confidently from studies of single localities’
Paucity of microfossils	. . . the extremely infrequent occurrence of preserved microfossils. Examination of numerous sedimentary microbasins (Liu, 2003, 2006; Liu and Broecker, 2007), and decades of research has generated only a few observations of microfossils (Dorn and Meek, 1995; Dorn, 1998; Krinsley, 1998; Flood et al., 2003)
Rock coating geography	. . . why does rock varnish grow in one place and other rock coatings elsewhere. Over a dozen major types of coatings form on terrestrial rock surfaces (Dorn, 1998). A successful model must be able to why, for example, rock varnish grows with iron films, silica glaze, phosphate skins and oxalate crusts in the Khumbu of Nepal (Dorn, 1998, pp. 360–361) and with dust films, carbonate crust, phosphate film, silica glaze and oxalate crusts in Tibet (Dorn, 1998, pp. 367–369).

Table 8.4 *Continued*

Criteria	A successful model must be able to explain . . .
Rock varnish variety and geography	. . . why different types of rock varnishes occur where they occur. Rock varnish classification must be dealt with, a very complex topic summarised in Dorn (1998: 214–224). Consider just the geography of light. Although light can be a key issue for some rock coatings (McKnight et al., 1988; Nienow et al., 1988), formation of varnish in locales with little or no light (Douglas, 1987; Dorn and Dragovich, 1990; Whalley et al., 1990; Douglas et al., 1994; Villa et al., 1995; Dorn, 1998) places strong constraints on light-related processes.
Varnish microlamination	. . . the revolution in VML understanding. Over ten thousand sedimentary microbasins analysed by Liu (Liu, 1994, 2003, 2006; Liu and Broecker, 2000, 2007; Liu et al., 2000; Broecker and Liu, 2001), a method subject to blind testing (Marston, 2003), reveals clear late Pleistocene and Holocene patterns in abundance of major varnish constituents connected to climate change. The characteristics of this single largest varnish data set must be explained.

particular past climate (Dorn, 1990). However, entire slopes or pavements (Marchant et al., 1996) covered with varnished boulders permits palaeoclimatic inference. In southern Arizona, a reasonable inference is that the occurrence of rock varnish in this buried position (Dorn and Dickinson, 1989) indicates an arid to semi-arid climate.

Microstratigraphic layers in actively forming varnish also provide palaeoenvironmental insights. A wide variety of varnish properties have been used to infer Quaternary palaeoenvironmental change. Micromorphological change (Dorn, 1986), trace element geochemistry such as lead profiling (Dorn, 1998; Fleisher et al., 1999), ^{17}O in sulphates (Bao et al., 2001), organic carbon ratios (Dorn et al., 2000), and interlayering with other rock coatings (Dragovich, 1986; Dorn, 1998) exemplify the potential of varnish microstratigraphy to inform on environmental change.

One key to extracting palaeoenvironmental data rests in sampling the same type of varnishes at sites used to calibrate the varnish proxy record

Table 8.5 Performance of alternative rock varnish conceptual models with respect to adjudicating criteria detailed in Table 8.4

Model	
Criteria	Polygenetic clay–bacteria–inorganic interactions
Abiotic Mn enhancement	Lithobionts or their remains
Accretion rate	Silica binding
<p>There is no rate-limiting step that would slow the accretion rate to fit observations. Even given the lowest dust deposition rates and fewest wetting–acidification events, this process would be 10^2 faster than observed rates</p> <p>Clay minerals are not important, and hence there is no reason why they should dominate in varnish</p>	<p>The rare Mn enhancement by a few budding bacteria, observed <i>in situ</i>, would generate observed rates</p> <p>The silica binding process has no rate-limiting step to slow growth. Under this model, there is no reason why decadal growth rates for silica glazes (Curtiss et al., 1985; Gordon and Dorn, 2005) would not also apply to rock varnish</p>
Clay minerals	<p>Clay minerals are critical to this model, and the model explains their dominance.</p> <p>Mn mobilised from bacteria fit into octahedral positions, cementing clays</p> <p>Proponents assert that clay minerals are not important, and hence there is no reason why they should dominate in varnish</p>

Fe behaviour	Highly oxidising conditions in dry climates or in microsites would lead to the observed Fe behaviour	Different organisms might favour the observed iron behaviour in different conditions and settings	Highly oxidising conditions in dry climates or in microsites would lead to the observed behaviour, since these bacteria do not favour highly oxidising settings	The observed iron behaviour is not important to this process.
Laboratory creation	Replication has occurred with similarities and substantial differences	Replication has occurred with similarities and substantial differences	Replication has occurred with similarities and substantial differences	Replication has occurred with similarities and substantial differences
Lithobionts and organic remains	The occurrence of typically <1% of organic matter is readily explained by purely adventitious incorporation as Mn enhancement occurs	The occurrence is a prerequisite of this model	The occurrence of <1% of organic matter is readily explained by adventitious organics incorporated into varnish	The occurrence of organic matter is predicted by silica binding processes

Table 8.5 *Continued*

Model	
Criteria	Model
	<p>Abiotic Mn enhancement</p> <p>Lithobionts or their remains</p> <p>Polygenetic clay–bacteria–inorganic interactions</p> <p>Silica binding</p>
Mn enhancement	<p>This model was developed to explain Mn enhancement</p> <p>Abundant culturing research documents the presence of Mn-oxidising organisms</p> <p>This model explicitly explains Mn enhancement, followed by clay cementation</p> <p>Mn enhancement is not explained by silica dissolution or reprecipitation</p>
Mn mineralogy	<p>Mn mineralogy is not explained.</p> <p>Mn mineralogy is consistent with biotic enhancement of Mn</p> <p>This model explains the fit of nanometer-scale Mn oxides into clay minerals, with detailed HRTEM observations (Dorn, 1998; Krinsley, 1998) supporting earlier hypotheses (Potter, 1979, pp. 174–175; Potter and Rossman, 1977).</p> <p>Mn mineralogy is not explained.</p>

Not just a few samples	The model's discussion in the literature has been fit to only a few site contexts	Individual studies involve only a very few sites, due to the expenses involved, but cumulative observations have a wide distribution	This model has been applied globally and is consistent with Liu's varnish microlamination (VML) observations of over 10^4 microsedimentary basins	The model is too new to have been assessed at sites globally or articulated to the VML data set.
Paucity of microfossils	This model would predict the paucity of microfossils	Several studies are notable for presence of microfossils, while others are notable for analysis of organic residues only	This model explains the paucity of microfossils, because Mn-encrusted cell walls are redistributed at the nanometer scale	Model proponents hope to use microfossils to explore extraterrestrial life, but this makes little sense given poor preservation
Rock coating geography	The presence of rock varnish in a plethora of settings that lack repeated oxidation cycles challenges this model	This model has not yet explained the geography of rock coatings	This model explains the geography of rock coatings (Dorn, 1998)	This model has not yet explained why rock varnish or silica glazes exists at one locale and not in other geographic settings

Table 8.5 *Continued*

Model			
Abiotic Mn enhancement	Lithobionts or their remains	Polygenetic clay-bacteria-inorganic interactions	Silica binding
Rock varnish variety and geography	This model has not yet explained the variety and geography of rock varnish	This model has not yet explained the variety and geography of rock varnish (chapter 10 in Dorn, 1998)	This model requires light and heat. Yet, both are known to be unnecessary for varnish formation (Anderson and Sollid, 1971; Douglas, 1987; Dorn and Dragovich, 1990; Whalley et al., 1990; Dorn et al., 1992; Douglas et al., 1994; Villa et al., 1995; Dorn, 1998)
Varnish microlamination	This model could explain VML observations, whereby conditions of greater alkalinity and fewer wetting events would generate drier VML events and more wetting events would generate wetter VML events	Model proponents have not yet explored the implications of the VML record	Wording accommodates alternating climatic changes producing VML. However, the silica binding process does not explain VML

and unknown sites (Dorn, 1998, pp. 214–224). Another key rests in avoiding post-depositional modification of varnish strata, such as erosion by microcolonial fungi (Figure 8.3) or cation leaching and redepositional processes (Dorn and Krinsley, 1991; Krinsley, 1998).

Of the variety of potential palaeoenvironmental and dating tools yet proposed for varnish (Table 8.6), the most potent method is varnish microlaminations (VML). Black, yellow and orange layers in varnish reflect regional climatic changes (Dorn, 1990; Cremaschi, 1996; Liu and Dorn, 1996; Zhou et al., 2000; Broecker and Liu, 2001; Diaz et al., 2002; Lee and Bland, 2003; Liu, 2003, 2006), where black layers, rich in manganese, record wet intervals. Orange and yellow layers with less manganese record drier periods (Jones, 1991). A blind test of the VML method (Liu, 2003; Marston, 2003), communicated and refereed by the editor of *Geomorphology*, resulted in this conclusion:

This issue contains two articles that together constitute a blind test of the utility of rock varnish microstratigraphy as an indicator of the age of a Quaternary basalt flow in the Mohave Desert. This test should be of special interest to those who have followed the debate over whether varnish microstratigraphy provides a reliable dating tool, a debate that has reached disturbing levels of acrimony in the literature. Fred Phillips (New Mexico Tech) utilised cosmogenic ^{36}Cl dating, and Liu (Lamont-Doherty Earth Observatory, Columbia University) utilised rock varnish microstratigraphy to obtain the ages of five different flows, two of which had been dated in previous work and three of which had never been dated. The manuscripts were submitted and reviewed with neither author aware of the results of the other. Once the manuscripts were revised and accepted, the results were shared so each author could compare and contrast results obtained by the two methods. In four of the five cases, dates obtained by the two methods were in close agreement. Independent dates obtained by Phillips and Liu on the Cima 'I' flow did not agree as well, but this may be attributed to the two authors having sampled at slightly different sites, which may have in fact been from flows of contrasting age. Results of the blind test provide convincing evidence that varnish microstratigraphy is a valid dating tool to estimate surface exposure ages (Marston, 2003).

The method works in the western USA (Liu et al., 2000), western China (Zhou et al., 2000), North Africa (Cremaschi, 1996) and Patagonia (T. Liu, personal communication, 2001), with the notation that these different regions require different calibrations. Liu's (2003, 2006) calibration for the Great Basin of the western USA extends back to before 140,000 ka. Grey-scale illustrations do not do the method justice, but Figure 8.10 shows that progressively older varnishes display progressively more detailed VML sequences.

The great power of the VML method rests in obtaining two types of information at once: palaeoenvironmental sequence and calibrated age. For

Table 8.6 Different methods that have been used to assess rock varnish chronometry. The refinement of age resolution is either relative, calibrated by independent age control, correlated to discrete events, or numerical based on radiometric measurements

Method and age resolution	Synopsis of method
Accumulation of Mn and Fe: calibrated age	As more varnish accumulates, the mass of manganese and iron gradually increases. Occasionally this old idea is resurrected, but it has long ago been demonstrated to yield inaccurate results in tests against independent control (Bard, 1979; Dorn, 2000)
Appearance: relative age	The appearance of a surface darkens over time as varnish thickens and increases in coverage. However, there are too many exceptions to permit accurate or precise assignment of ages based on visual appearance. For example, varnish can form in under 100 years in selected microenvironments (Krumbein, 1969; Dorn and Meek, 1995). There is no known method that yields reliable results (Dorn, 2000), although individuals have tried to make visual measurements using different techniques
Cation-ratio dating: calibrated age	Rock varnish contains elements that are leached (washed out) at fast rates and elements that are not leached rapidly (Dorn and Krinsley, 1991; Krinsley, 1998). Over time, a ratio of leached to immobile declines over time (Dorn, 2000). While differences in field and laboratory sampling procedures have yielded problematic results in multiple investigations attempting replication (e.g. Bamforth, 1997; Watchman, 2000), if the correct type of varnish is used, the method performs well in blind tests (Loendorf, 1991). It has been replicated in such places as China (Zhang et al., 1990), Israel (Patyk-Kara et al., 1997), South Africa (Whitley and Annegarn, 1994) southern Nevada (Whitney and Harrington, 1993), and elsewhere

Table 8.6 *Continued*

Method and age resolution	Synopsis of method
Foreign material analysis: correlated age	Rock carvings made historically may have used steel. The presence of steel remains embedded in a carving would invalidate claims of antiquity, whereas presence of such material as quartz would be consistent with prehistoric age (Whitley et al., 1999). Meticulous sampling and examination of cross-section with electron microprobe is required to determine if steel remains exist in a petroglyph groove
Lead profiles: correlated age	Twentieth century lead and other metal pollution is recorded in rock varnish, because the iron and manganese in varnish scavenges lead and other metals. This leads to a 'spike' in the very surface layer from 20th century pollution. Confidence is reasonably high, because the method (Dorn, 1998) has been replicated (Fleisher et al., 1999; Thiagarajan and Lee, 2004; Hodge et al., 2005) with no publications yet critical of the technique. The method uses sampling and measurement of chemical changes with depth on the scale of microns or finer, analysed with an instrument such as an electron microprobe, ion microprobe or alpha spectrometer
Organic carbon ratio: calibrated age	Organic carbon exists in an open system in the rock varnish that covers petroglyphs. This method compares the more mobile carbon and the more stable carbon. The method is best used in soil settings (Harrison and Frink, 2000), but it has been applied experimentally to rock varnish in desert pavements (Dorn et al., 2000). The method requires careful mechanical extraction of rock varnish, that is then subjected to basic soil wet chemistry procedures

Table 8.6 *Continued*

Method and age resolution	Synopsis of method
Radiocarbon dating of carbonate: numerical age	Calcium carbonate sometimes forms over varnish, and can be radiocarbon dated, providing a minimum age for such features as rock art. The method has been used in Australia (Dragovich, 1986) and eastern California (Cervený et al., 2006)
Radiocarbon dating of organic material: numerical age	The hope is that carbon trapped by coating provides a minimum age for the petroglyph. First developed in 1986, Watchman (1997) and Dorn (1997) both found the presence of organic carbon that pre-dates and post-dates the exposure of the rock surface — in this case a blind test of petroglyph dating in Portugal. The only person who still uses organic carbon of unknown residues in radiocarbon dating (Huyge et al., 2001; Watchman, 2000), Watchman now admits that he has not tested results against independent controls (Watchman, 2002; Whitley and Simon, 2002a,b).
Radiocarbon dating of oxalate: numerical age	The inorganic mineral oxalate (e.g. whewellite: $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) sometimes deposits on top of or underneath rock varnish. Because this mineral contains datable carbon, the radiocarbon age can provide a minimum age for the underlying or overlying varnish. The most reliable research on radiocarbon dating of oxalates in rock surface contexts has been conducted in west Texas (Rowe, 2000; Russ et al., 2000)
Varnish microlaminations: correlated age	Climate fluctuations change the patterns of layers deposited in varnish. The confidence level is high, because the method (Liu, 2006) has been replicated in a rigorous blind test discussed in the text (Marston, 2003), and the method is based on analyses of over 10,000 rock microbasins

example, research on the alluvial fans of Death Valley (Figure 8.10) permit the first-ever high-resolution assessment of the linkage between fan chronology and palaeoenvironmental fluctuations (Liu and Dorn, 1996). In another example, microlaminations permit explorations of the relationship between archaeology and palaeoclimate (Dorn, 2000, 2006; Dorn et al., 2000).

For those interested in applying varnish to Quaternary research, VMLs offer the ability to link geomorphological and archaeological chronology with regional palaeoenvironmental fluctuations (Liu, 2006). Before they embark on this methodology, researchers should internalise two issues. First, the making of ultra-thin sections is extraordinarily difficult; sections a bit too thick are opaque, whereas sections too thin erode away easily – requiring great patience and a light enough laboratory touch. Second, Marston's (2003) careful handling of this blind test of microlaminations, as well as other blind tests (Loendorf, 1991; Arrowsmith et al., 1998), underscores the importance of understanding classification (Dorn, 1998, pp. 214–224) prior to the sampling phase.

8.7 Relationships to other Terrestrial Geochemical Sediments

Rock varnish rarely exists as a discrete geochemical sedimentary deposit. Aspect (Waragai, 1998) and slope position (Palmer, 2002), for example, influence metre-scale facies changes. Vertical interlayering takes place on the scale of microns with every other type of rock coating (Table 8.1). Examples of interlayering include: with oxalates and lithobiontic coatings in waterflow locales; with nitrate crusts in caves; with silica glaze in desert pavements; with phosphates near locales of decomposition of bird excrement; with carbonate skins in archaeological ground figures; with case hardening agents; with anthropogenic pigment in rock art; or with heavy metal skins in periglacial meltwater streams. At least 102 publications have thus far examined varnish interlayered with other types of rock coatings – thus unknowingly mixing ‘apples and oranges’ in possible misinterpretations.

There have been a number of suggestions in the literature (cf. chapters 10 and 13 in Dorn, 1998) equating silica glazes, coatings of largely amorphous silica, with abiotic formation of desert varnish. In silica glaze formation, soluble Al–Si complexes $[\text{Al}(\text{OSi}(\text{OH})_3)^{2+}]$ are first released from the weathering of phyllosilicate minerals. These Al–Si complexes are then stabilised through very gentle wetting such as dew deposition or movement of capillary water on rock surfaces. Once stabilised, silicic acid and these Al–Si complexes more readily bond the silica glaze coating to the rock (Dorn, 1998, p. 319). In HRTEM imagery, nanometre-scale bands of silica glaze do experience facies changes with varnish, and in BSE imagery,

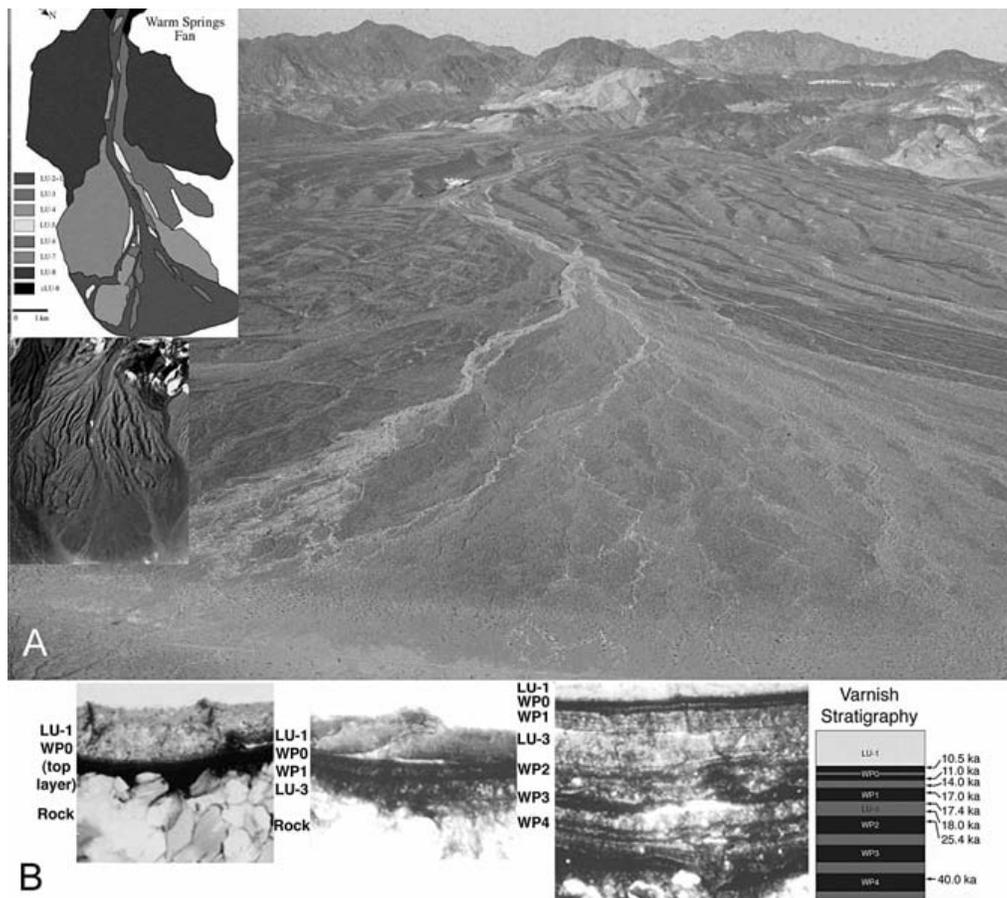


Figure 8.10 Varnish microlaminations (VML) are the most powerful ‘tool’ yet developed in rock varnish research. This figure illustrates the potential of this tool to yield unique insights in geomorphological research. (A) Looking at this oblique photograph of the Warm Springs alluvial fan in Death Valley, there would be a tendency for most of today’s desert geomorphologists to believe in the importance of climatic change in fan development (Farr and Chadwick, 1996; Harvey et al., 1999). Such thinking, however, is not supported by the VML method. Although VML provides the highest resolution palaeoclimatic information yet available for alluvial fans, this detailed mapping fails to reveal a clear relationship between climatic changes and alluvial-fan development (Dorn, 1996). Climatic change may play a role, but this hypothesis is not testable – even with the highest resolution method of VML. High-magnitude and high-frequency palaeoclimatic fluctuations occur with greater frequency than can be related to aggradational events. The inset map is modified from Liu and Dorn (1996), with the inset satellite image from NASA. (B) Varnish microlaminations from Death Valley, California, illustrate progressively more complex stratigraphic sequences in late Pleistocene varnishes. The uppermost LU-1 layer appears yellow in ultrathin section. The other light grey layers appear orange. Dark layers appear black. This figure was modified from Liu and Dorn (1996), with the calibration based on Liu (2003).

micrometre-scale bands of silica glaze interlayer with varnish. Thus, there could also be a cementation role for silica glaze in varnish accretion.

Interlayering of different types of rock coatings, while creating the strong potential for gross misinterpretation, creates excellent opportunities to apply rock coatings to preservation of stone. Natural settings illustrate the importance of mixing different types of cementing agents (Figure 8.11). Iron films play the natural analogue of artificial bonding agents where sandstone grains are held tightly. Iron films create a harder rock face than a more porous cementing mixture of varnish and silica glaze. However, the intercalation of varnish and silica glaze permits much more interstitial water to exit such lithologies as porous sandstone. The stronger cementing agent, iron film, enhances decay in the underlying weathering rind (Tratebas et al., 2004). Whereas spalling under the iron film-hardened sandstone results in rapid erosion of the decayed sandstone, the ‘varnish + silica glaze’ mixture displays slower and less dramatic erosion (Tratebas et al., 2004).

Yet another example of using the interlayering of varnish with other rock coatings is seen in the prehistoric modification of landforms. Consider geoglyphs created by the disturbance of a desert pavement. Boulders are often piled, reorienting the natural varnish sequence. Finding subaerial black varnish shoved into the soil results in the ‘freezing’ of the varnish microlaminations sequence (Liu, 2003) underneath the superposition of a soil-contact iron film. At the same time, subaerial microlaminations form on top of the orange varnish. Boulders thrust far enough into the ground may form calcrete, material with potential for understanding the palaeoen-

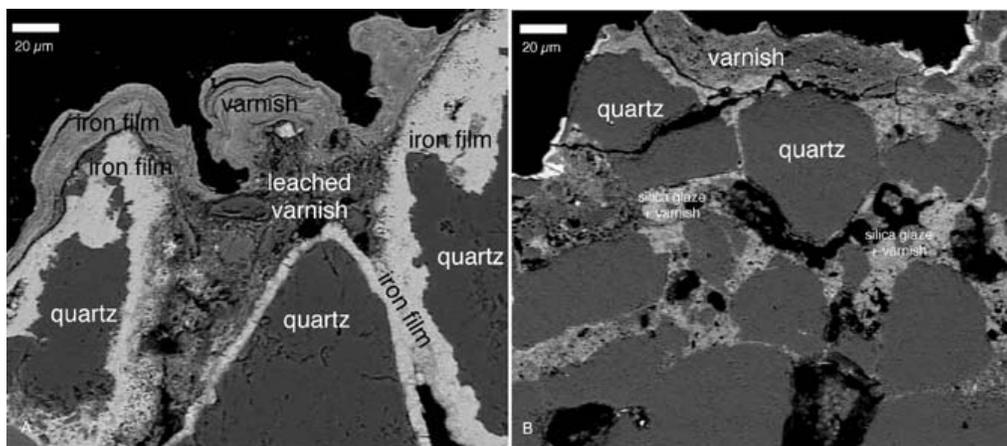


Figure 8.11 Rock varnish interlayers with iron film and silica glaze at Whoopup Canyon, Wyoming. (A) Iron film (back-scatter electron image) acts as a case-hardening agent, and rock varnish accretes on top of the iron film exposed by petroglyph manufacturing. (B) Varnish actively assists in case hardening (back-scatter electron image) when the leached cations reprecipitate with silica glaze in sandstone pores.

vironment (Deutz et al., 2001) and timing (Chen and Polach, 1986) of the disturbance. Thus, understanding all variations of rock varnish and its interdigitation with other rock coatings creates immense possibilities in analysing ancient modifications to stone (N. Cervený et al., 2006).

8.8 Summary and Directions for Future Research

Desert varnish is a rock coating that is brown to black colour and is characterised by clay minerals cemented to rock surfaces by oxyhydroxides of manganese and iron. The individual Mn–Fe minerals are nanometre in size, a result of the decay of bacterial casts. These remnants of bacteria dissolve and reprecipitate in clay minerals – cementing the mix of clays and oxyhydroxides to rock surfaces. Since varnish forms in all terrestrial environments, ‘rock varnish’ is often used as a synonym, but the term ‘desert varnish’ is common because varnishes are most geochemically stable in arid regions. The constituents in varnish accrete on the host rock with thicknesses typically less than 0.1 mm. Usually dull in lustre, its occasional sheen comes from a smooth surface micromorphology in combination with manganese enrichment at the very surface of the varnish. The most useful application of rock varnish rests in the layering pattern of black (manganese-rich) layers and orange (manganese-poor) layers, which reveal past environmental changes experienced by rock surfaces.

Rock varnish is beginning to see an infusion of research funding related to the search for life on Mars by NASA (DiGregorio, 2002), using the assumption that biogenically formed rock coatings on Earth represent a possible Martian analog (Israel et al., 1997; Johnson et al., 2001; Probst et al., 2001; Gorbushina et al., 2002; Wierzchos et al., 2003; Allen et al., 2004; Kuhlman et al., 2005, 2006; Perry et al., 2006). One need in this research arena rests in understanding the transition between Mn–Fe casts of Mn-oxidising organisms on varnish surfaces to their preservation within varnish, and onto their remobilisation into a clay matrix. Cold-dry contexts such as the Tibetan Plateau (Dorn, 1998) and Antarctica (Dorn et al., 1992; Krinsley, 1998) reveal evidence of this process. Simply studying the remains of organisms, most of which are purely adventitious, in warm deserts will inevitably lead to misinterpretation and research dead-ends. Exploring how biogenic remains in the coldest and driest terrestrial settings translate into biogenic coatings, again, requires a penchant towards HRTEM studies. The real key in astrobiology research as it relates to varnish, however, does not rest in understanding terrestrial varnish; the largest gap is the need to falsify abiotic explanations of Mn enhancement on Mars. Imagine when the astrobiology community discovers Mn-rich rock coatings on Mars, claiming evidence of life – only to encounter the

reality that simple mechanisms of abiotic enhancement of Mn have not been falsified for Mars.

The greatest need for future research in terrestrial varnish research rests with individuals who are able to carry out extraordinary care in the preparation of laboratory samples such as microlaminations (Liu, 2003; Marston, 2003). This powerful varnish technique involves Pleistocene (Liu, 2003) and Holocene microlamination sequences (Liu and Broecker, 2007) that exist in rapidly forming varnishes and can be found in microenvironments of greater moisture in a largely arid setting (Dorn et al., 2000; Broecker and Liu, 2001). Robust calibrations of these sequences now provide archaeologists and geomorphologists with a powerful tool to understand the interface of chronology and palaeoenvironmental changes over the past few millennia (Liu, 2006).

Another need rests in linking varnishes seen at the satellite remote sensing scale (White, 1993; Farr and Chadwick, 1996; Milana, 2000; Kenea, 2001) to centimetre-scale remote-sensing sensors placed in such platforms as balloons or helicopters. Bridging scales between ground and satellite (Figure 8.4) remains a giant void. Palmer (2002) illustrates the potential in quantitative landform-scale catenas of spatial variability of rock coatings. Certainly, such field work must be calibrated by textural and chemical analyses using such equipment as an electron microprobe. However, a core research question that remains unresolved is a detailed exploration of spatial heterogeneity of varnish on the scale of single landforms – a topic brought in focus by the realisation that 99% of varnish publications are based on only a few ‘grab bag’ samples. Field-based (with laboratory calibration) studies of varnish spatial heterogeneity will be needed to create the solid backbone of future advances in varnish research.

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