



Spatial, temporal and geographic considerations of the problem of rock varnish diagenesis

Ronald I. Dorn ^{a,*}, David Krinsley ^b

^a School of Geographical Sciences, Arizona State University, Tempe, AZ 85287-0104, USA

^b Department of Geological Sciences, University of Oregon, Eugene, OR 97403-1272, USA

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ABSTRACT

The rock varnish literature hosts an abundance of *prima facie* contradictory empirical data. Past and perhaps future empirical contradictions, however, can be resolved by theoretical considerations of different spatial and temporal scales of varnish diagenesis, as well as the geomorphic position of different types of varnishes. For example, twentieth-century contamination by lead and other heavy metals has led to claims of accumulation rates in the last century far more rapid than prior published empirical studies. A consideration of spatial scales resolves this contradiction; nanoscale processes allow migration of lead into varnish deposited well before the twentieth century time of heavy metal pollution. Evidence of nanometer-scale disequilibrium in three samples led to claims that varnish cannot be used in paleoclimatic research; these data rest in contrast to replicable patterns in varnish deposition observed by Dr. Tanzhuo Liu and others in over ten thousand micro-sedimentary basins. This contradiction can be resolved by understanding that the types of varnishes studied differ and that processes differ substantially between the nanoscale and the micron scale. A lack of evidence of Mn-oxidizers in genetic analyses contrasts with culturing studies and *in situ* evidence of Mn-enhancement by bacteria. This contradiction has a likely resolution in vastly different temporal scales; DNA material analyzed may be no older than 200 years, but *in situ* fossilized remains of bacteria may be preserved for thousands of years recording palaeoecological conditions favoring growth of Mn-enhancing bacteria.

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1. Introduction

The literature on rock varnish has a long tradition of dozens of *prima facie* contradictions (Dorn, 1998). Prior to World War II, for example, most investigators believed firmly that varnish constituents were sweated out of the rock, and observations of weathering-rinds under varnishes provided the empirical proof (Linck, 1901; Blake, 1905; Hume, 1925); others advocated an accretionary origin based on evidence such as the presence of varnish on rocks without manganese (Basedow, 1914). In another example, the notion that Mn–Fe-rich varnishes were desert phenomena (Loew, 1876; Walther, 1891) reached its pinnacle in the mid-1950s with the observation of varnish formation within 25 years in the Mojave Desert; the interpretation, therefore, was that deserts like the Mojave must be the ideal climate of formation (Engel, 1957; Engel and Sharp, 1958). This was all despite prior observations of very similar coatings in periglacial, crentitic, temperate, tropical, Arctic and Antarctic environments (von

Humboldt, 1812; Lucas, 1905; Linck, 1930; Klute and Krasser, 1940; Longwell et al., 1950; Glazovskaya, 1952; Hunt, 1954). Still others were convinced that the spatial contiguity of lichens and varnish (Laudermilk, 1931) implied some importance for varnish genesis, despite contradictory observations that these organisms were erosional or adventitious (Fry, 1926; Dragovich, 1986).

This paper explores the importance of epistemology in resolving the most recent rounds of *prima facie* contradictions in empirical data on rock varnish. We propose, following a tradition of philosophers of science (Brown, 1996; Rhoads and Thorn, 1996; Fuller, 2000; Inkpen, 2004), that the epistemological (conceptual) framework of the investigator often drives interpretation. Conversely, changing how data are examined can resolve some apparent contradictions. In order to be clear, we acknowledge that this paper represents a critique from the standpoint of the authors. Furthermore, we present our own perspective of interpreting rock varnish data that is similar to the abductive reasoning approach of analyzing “traces of the past” (Inkpen, 2008). We interpret field context and microscope imagery in terms of relationships between ongoing accretion and post-depositional diagenesis (Fig. 1) (Krinsley et al., 1990; Dorn and Krinsley, 1991; Krinsley and Dorn, 1991; Dorn et al., 1992; Dorn, 1998; Krinsley, 1998; Krinsley et al., 2009). In our research, we

* Corresponding author. Fax: +1 480 965 8313.

E-mail addresses: Ronald.dorn@asu.edu (R.I. Dorn), krinsley@uoregon.edu (D. Krinsley).

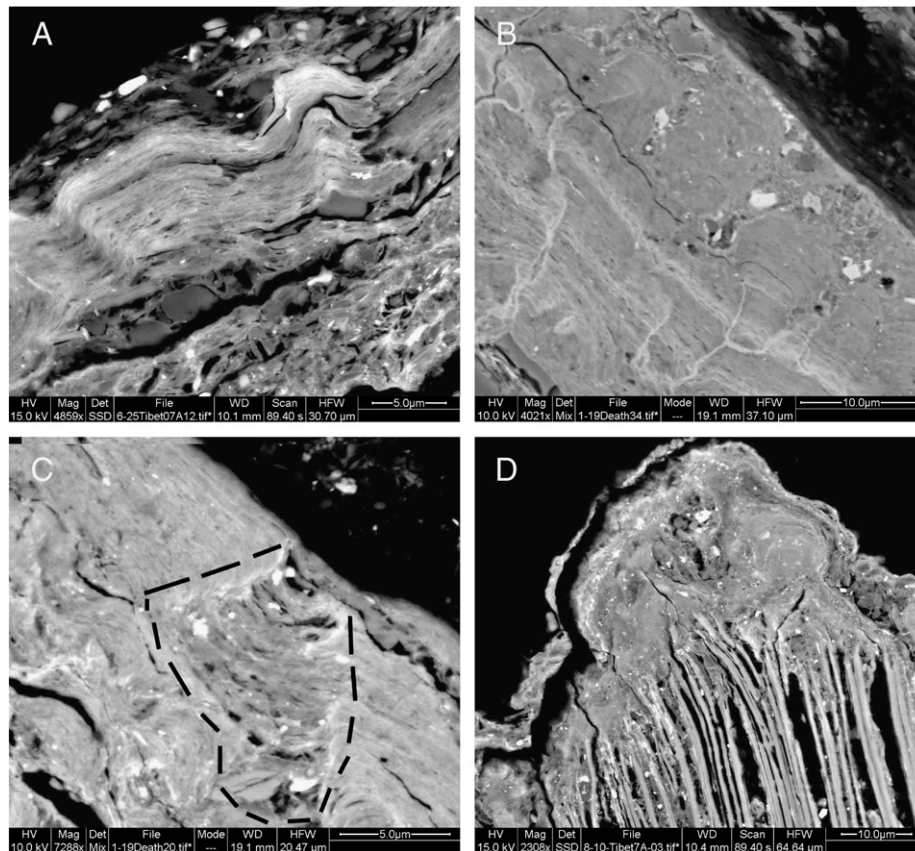


Fig. 1. Examples of an epistemological interpretation of rock varnish in terms of the tension between ongoing accretion and post-depositional diagenesis, using back-scattered electron microscope imagery. Scale bars are indicated. A. Dust particles coming to rest on the surface of subaerial rock varnish from the Ashikule Basin, Kunlun Mountains, Tibet. Diagenesis occurs at the very surface of varnish with mobilization of Pb and other contemporary heavy metals from particulate fallout (Dorn, 1998: 139; Fleisher et al., 1999; Hodge et al., 2005; Wayne et al., 2006). B. Veins filled with Mn-Fe indicate post-depositional leaching and reprecipitation in this Death Valley varnish (cf. Krinsley et al., 1990: Figures K, Q, T2, U, V1 and V2). C. The regular layering of this Death Valley varnish is interrupted by post-depositional cation-leaching (outlined area) that enhances porosity (Dorn and Krinsley, 1991; Krinsley and Dorn, 1991). D. When the underlying surface erodes under accreting varnish, post-depositional mobilization leads to the gradual infiltration of varnish constituents into opening cracks and pores (cf. Krinsley et al., 1990: Figures B), in this example into biotite from the Ashikule Basin, Kunlun Mountains, Tibet.

analyze empirical data in the context of (1) spatial scale, (2) temporal scales of processes, (3) type of rock varnish sampled, and (4) context of the sample with respect to the geomorphic history of the study site.

Consideration of these four perspectives has helped to resolve prior apparent contradictions in the rock varnish literature. For example, secondary (Potter and Rossman, 1977), back-scattered (Krinsley et al., 1990), and high resolution transmission electron microscopy (Krinsley et al., 1995) at different scales all revealed distinct morphologic contacts between subaerial rock varnish and the host rock; along with geochemical studies (Thiagarajan and Lee, 2004), the source of varnish constituents has been resolved as being external. Light and scanning electron microscopic observations of varnish textures and a careful exploration of a site's geomorphic context similarly led to the discovery that the purported 25-year-old varnish was simply a pre-existing desert pavement that partially reformed after road construction (Dorn and Oberlander, 1982; Elvidge, 1982). Careful field, electron microscope, and chemical observations revealed that, despite physical proximity, acid-producing lithobionts are adventitious or erode varnish (Dragovich, 1987, 1993; Allen et al., 2004). However, it wasn't just the presence of empirical observations that led to these resolutions, but rather consideration of spatio-temporal scale, rock varnish type, and geomorphic site context. We further our argument for applying an abductive reasoning (Inkpen, 2008) to varnish research, emphasizing the importance of temporal and spatial scales, in an examination of several *prima facie* contradictions with varnish empirical data that have arisen in the last decade.

2. Towards resolving the contradiction of heavy metal contamination versus slow rates of formation

Rock varnish is known to form within a few decades to centuries in wet locations such as boulders along tropical rivers, periglacial talus, scarps in moist areas, and slag piles that do not host an abundance of acid-producing lithobionts such as lichens (Lucas, 1905; Klute and Krasser, 1940; Buchun et al., 1986; Dorn and Meek, 1995). In warm deserts, however, a century of anecdotal observations of Quaternary and anthropogenic rock surfaces suggests it takes perhaps 10^4 years to coat completely many rock surfaces (Schweinfurth, 1903; Basedow, 1914; Blackwelder, 1948; Iskander, 1952; Denny, 1965; Hayden, 1976). It was not, however, until the compilation of the microlamination data set by Liu and colleagues (Liu and Broecker, 2000; Liu et al., 2000; Zhou et al., 2000; Liu, 2003; Liu and Broecker, 2007, 2008a,b; Liu, 2010) that it was possible to obtain rates of accretion of varnish formed on subaerial surfaces in warm desert environments. Knowing the age of the underlying geomorphic surface and thicknesses of varnishes accumulated in over 10,000 micro-sedimentary basins led to the first comprehensive understanding of accumulation rates; subaerial Mn-rich varnish in the Basin and Range of the western USA, for example, accretes at the order of a few micrometers per millennia (Dorn, 1998; Liu and Broecker, 2000).

In contrast, there has been growing evidence of rapid 20th century formation of varnish through studies of trace metals. A "spike" in lead was first seen in the upper micron of varnishes in the Sonoran Desert

(Dorn, 1998: 139). Then, Cs-137 and Pb-210 were measured in rock varnish samples collected throughout the western USA; since Pb-210 only has a half life of 22 years and Cs-137 was absent prior to nuclear weapons testing, varnish formation would have to be rapid enough to accommodate these observations (Fleisher et al., 1999). Detection of alpha particles from Po-210 coming from the surfaces of rock varnish poses the same problem (Hodge et al., 2005). Finding an abundance of lead in the uppermost varnish collected from the Four Corners region, interpreted to be from recent activity of coal-fired power plants (Wayne et al., 2006) or smelters (Spilde et al., 2007) also points to 20th century varnish accumulation. Similarly, research in metropolitan Phoenix has revealed an abundance of lead in the surface-most micron(s) of varnish (Dorn, 2010), likely from automotive pollution.

For at least three of these metal studies (Dorn, 1998; Fleisher et al., 1999; Dorn, 2010), the same subaerial type of rock varnish was collected and from the similar site context of surfaces exposed by erosion; these are the same sampling considerations as those studied for microlaminations (Liu and Broecker, 2000). Thus, the apparent empirical contraction cannot be explained by analyzing different types of varnishes or by analyzing varnishes collected from different geomorphic contexts.

One potential resolution of this apparent contradiction rests in consideration of spatial scale, in particular processes that occur at submicron scales. Mn–Fe oxyhydroxides are well-known scavengers of trace metals (Gulson et al., 1992; Dong et al., 2002; Thiagarajan and Lee, 2004). As iron oxides are notoriously unstable at the nanoscale (Navrotsky et al., 2008), water moving over the surface of varnish, interacting with dust (e.g. Fig. 1A), could simply supply the trace metals that are then scavenged by Mn–Fe oxides undergoing stability crossovers (Thiagarajan and Lee, 2004). The missing link requires, however, that Mn–Fe oxides in varnish not be in equilibrium at the nanoscale, facilitating ongoing scavenging of trace metals.

The polygenetic model of varnish formation explicitly depends on a lack of equilibrium at the nanometer scale (Potter, 1979; Krinsley, 1998; McKeown and Post, 2001; Dorn, 2007). Using HRTEM imagery for evidence, Mn and Fe appear to be mobilized from bacteria-sized sheaths and into the feathered edges of clay minerals (Dorn, 1998; Krinsley, 1998; Dorn, 2007). Nanoscale alteration, however, does not cease with the initial cementation of clay minerals (Dorn, 2007). As McKeown and Post (2001: 712) explained: “even 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”. Thus, 20th century contamination does not have to require “a growth rate of 36 μm per millennia” (Spilde et al., 2007), but rather just the scavenging of trace elements by Mn–Fe-oxyhydroxides that accreted previously and are in a nanometer-scale disequilibrium. This disequilibrium allows the ongoing addition of heavy metal pollutants into previously accreted varnish.

3. Towards resolving the issue of paleoenvironmental interpretation of varnish microlaminations

The contrast between the light and scanning electron microscope observations of microsedimentary basins (Liu and Broecker, 2000; Liu et al., 2000; Zhou et al., 2000; Liu, 2003; Liu and Broecker, 2007, 2008a,b; Liu, 2010), and the opposing conclusion reached by Garvie et al. (2008) that paleoenvironmental interpretations of varnish are species, exemplify the relevance of an epistemological perspective.

The “Mount Everest” of varnish data sets is the over 10,000 rock varnish-filled millimeter-scale depressions analyzed by T. Liu and collaborators. Using a mix of light microscopy, X-ray mapping, back-

scattered electron microscopy, T. Liu and colleagues only analyzed varnishes carefully sampled from subaerial rock varnishes at the rock–atmosphere interface, well above soil surfaces, and from geomorphic positions that could not have originated in a rock fracture – information provided in their methodological discussions. Liu and colleagues have been careful to point out that they avoided meter-scale geomorphic conditions that would lead to varnish instability, as well as centimeter-scale microenvironmental conditions that would lead to biogeochemical mobilization of varnish constituents (Liu and Broecker, 2000; Liu et al., 2000; Zhou et al., 2000; Liu, 2003; Liu and Broecker, 2007, 2008a,b; Liu, 2010). In other words, Liu and colleagues clearly established the spatial and temporal scales of samples of a specific type of rock varnish collected from very specific geomorphic settings. No other data set published about varnish comes within two orders of magnitude of the number samples studied to reach the conclusion that millennial-scale paleoenvironmental changes are recorded by micrometer-scale rock varnish microlaminations.

To challenge the work of Liu and colleagues, as well as others who similarly advocate the ability to identify paleoenvironmental fluctuations from rock varnish (Drake et al., 1993; Cremaschi, 1996; Patyk-Kara et al., 1997; Plakht et al., 2000; Lee and Bland, 2003; Dorn, 2007; Zerboni and Cremaschi, 2007; Zerboni, 2008), Garvie et al. (2008, 2009) follow the geoscience tradition of using a method “that he or she selects as appropriate to the job at hand” (Frodeman, 1995: 966). The title of Garvie et al. (2009), a “microscopists view of desert varnish from the Sonoran Desert,” acknowledges an epistemology that is personally familiar – in this case interpreting high resolution transmission electron microscopy (HRTEM) – to reach a conclusion that “[o]ur results suggest continuing adjustment of varnish to changing environmental conditions, compromising its reliability as a paleoenvironmental indicator.” Garvie et al. (2008) analyzed only three samples. For these samples, they (1) do not specify the type of rock varnishes they collected, and (2) do not explain whether or not their sample came from a geomorphic position that was formerly a rock fracture (Coudé-Gausson et al., 1984; Villa et al., 1995; Dorn, 1998; Cervený et al., 2006).

The contrast in epistemology could not be greater, and the resolution to this apparent conflict rests in placing empirical data in, its spatial scale, the context of an understanding of the temporal scale of processes, the context of the type of rock varnish sampled, and the context of the sample with respect to the geomorphic history of the study site.

Certainly, everyone cited above sampled some type of rock varnish, but that is not very helpful. This is not a trivial issue. There exists a wide variety of different types of rock varnishes (e.g. see Dorn, 1998: 223). For example, Garvie et al.’s (2008) sample 1 is from a site context that would not be used by Liu and colleagues for paleoenvironmental analysis (Liu and Broecker, 2000; Liu et al., 2000; Zhou et al., 2000; Liu, 2003; Liu and Broecker, 2007, 2008a,b; Liu, 2010), because it derives from too small a desert pavement clast (Garvie et al., 2008). The photograph of varnish shown in Garvie et al. (2009: Figure A) shows ground-line band varnish, a unique type of varnish recognized by Engel and Sharp (1958); such a sample is completely unsuitable for paleoenvironmental analysis because it is heavily influenced by soil effects. Upon visitation to their sample sites 2 and 3, without knowing the exact spot of sampling, we can only state that both sites have varnishes with a large abundance of microcolonial fungi (Dragovich, 1993) and a high abundance of varnishes that originated in rock fractures (Coudé-Gausson et al., 1984; Villa et al., 1995; Dorn, 1998; Cervený et al., 2006).

Consider three reasonable scenarios that are entirely possible given the abundance of these conditions in the general area where Garvie et al. (2008) collected samples 2 and 3. Scenario 1: if the analyzed sections came from a position on the rock within a few millimeters of microcolonial fungi that are ubiquitous at these sampling locales (Fig. 2A), disequilibrium from organic acids

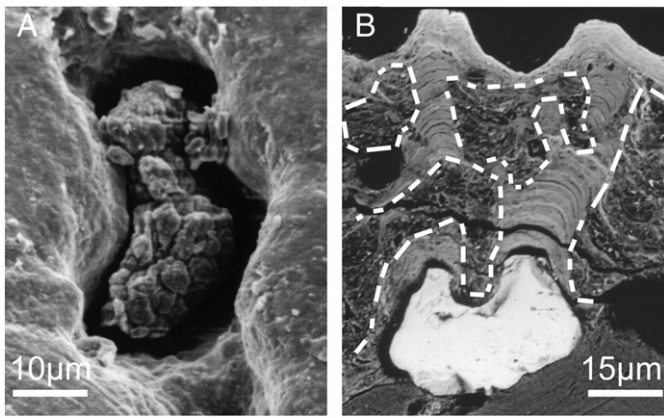


Fig. 2. Reasons why disequilibrium would be an expectation for many rock varnishes at the collection sites of Garvie et al. (2008). (A) SE image of microcolonial fungi, dissolving a pit into varnish collected near Site 3 of Garvie et al. (2008). (B) BSE image of zones of cation leaching, outlined by the dashed lines, indicating more intense water flow in varnish collected near Site 3 of Garvie et al. (2008). In this image, varnish rests on magnetite (bright mineral), and quartz (darker mineral).

(Dragovich, 1993) would be the expectation. Scenario 2: if Garvie et al.'s (2008) sections came from locales within a few millimeters of porous, cation leaching locations (Fig. 2B) (Krinsley et al., 1990; Dorn and Krinsley, 1991), disequilibrium and “Mn-rich rimmed pores” (cf. Garvie et al., 2008) through proximity to excessive intravarnish water flow would be expected (see Fig. J in Krinsley et al., 1990). Since Garvie et al. analyzed samples with “crosscutting Mn-stringers” and “Mn oxides filling cracks”, Krinsley et al. (1990) and Krinsley (1998; Figure 4) established previously that these stringers form in conduits for water flow and reprecipitation of Mn–Fe oxides – thus disequilibrium through greater intravarnish water flow would be expected. Scenario 3: if Garvie et al. (2008) collected varnish that originated in a rock joint, exposed by spalling (Coudé-Gaussen et al., 1984; Villa et al., 1995; Dorn, 1998; Cervený et al., 2006), then disequilibrium through an adjustment to the subaerial environment would be expected. Liu and colleagues are explicit in that they do not interpret paleoenvironmental changes from varnishes in these

contexts (Liu and Broecker, 2000; Liu et al., 2000; Zhou et al., 2000; Liu, 2003; Liu and Broecker, 2007, 2008a,b; Liu, 2010).

Still, if we assume that Garvie et al. (2008) actually collected the exact same type of rock varnish used in paleoenvironmental research, and that they collected samples from a comparable geomorphic context of uncoated rock faces exposed by erosional processes, considerations of spatial scale resolves seemingly contradictory data. The polygenetic model of varnish formation and its supporting evidence (Potter, 1979; Krinsley, 1998; Dorn, 2007) require disequilibrium between Mn, Fe and clay minerals, where nanometer-scale shifting of Mn and Fe is the key in the weathering of clay minerals and cementing clays together. Although not discussed by Garvie et al. (2008, 2009), Krinsley (1998), Dorn (1998, 2007) and McKeown and Post (2001: 712) previously argued for ongoing nanoscale alteration of Mn-oxide structures in varnish. Garvie et al.'s (2008) observations of ongoing nanometer-scale disequilibrium, thus, simply provide confirming evidence of the polygenetic model of varnish formation (Potter, 1979; Dorn, 1998; Krinsley, 1998; Dorn, 2007).

Ongoing disequilibrium inside the micrometer-scale layers of varnish microlaminations analyzed by Liu and colleagues, however, does not invalidate paleoclimatic interpretations of those microlaminations. As Krinsley (1998, p. 721) explained: “at the spatial scale of microns... some varnish appears quite stable with distinct layering patterns... At the spatial scale of nanometers as viewed with HRTEM, varnish appears to be in an open system... This is analogous to automobiles moving in a crowded parking lot, with oxides moving around until they find a suitable parking space in clay minerals.” Just because cars keep moving around inside a parking lot does not mean that the parking lot itself is unstable as evidenced by analyses examining both micrometer and nanometer scales (Fig. 3).

We have not seen in our research (Fig. 3; Dorn, 1998; Krinsley, 1998; Dorn, 2007) or in the literature, nor did Garvie et al. (2008, 2009) present in their papers, evidence that movement of Mn or Fe at the nanometer-scale systematically prevents a replicable interpretation of distinct micrometer-scale layering units identified by Liu and colleagues in their analysis of over 10,000 sedimentary microbasins (Liu and Broecker, 2000; Liu et al., 2000; Zhou et al., 2000; Liu, 2003; Liu and Broecker, 2007, 2008a,b; Liu, 2010). Thus, the empirical data indicating nanometer-scale disequilibrium in rock varnish can be fully

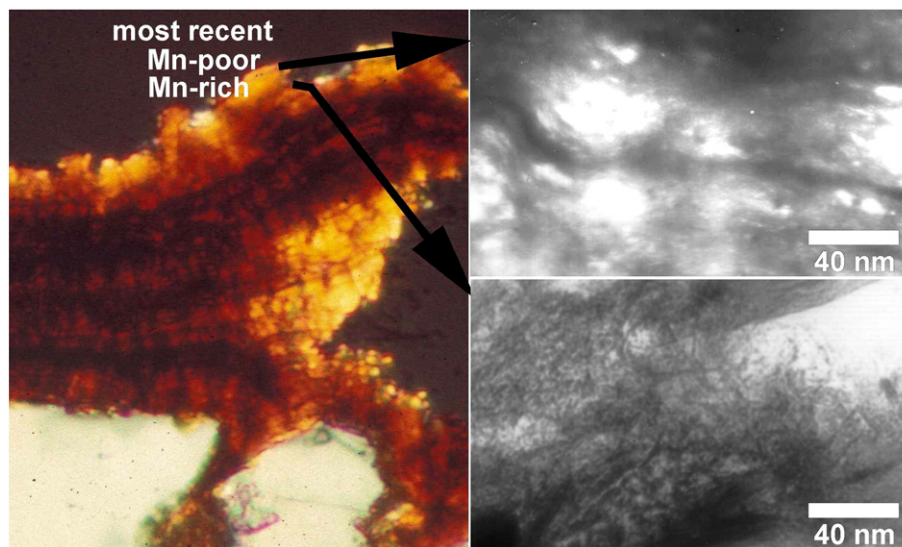


Fig. 3. Mn-rich and Fe-rich microlaminae of rock varnish from the Coso Range of eastern California. The left image is a light microscope image of alternating Mn-rich and Fe-rich layers that are approximately 60 µm thick. The upper right image is a HRTEM view of the most recent Mn-poor layer dominated by clay minerals. In contrast, the most recent Mn-rich layer directly underneath still displays the granular texture of bacterial casts that are nanoscale remobilizing into adjacent clay minerals. Although nanoscale movement occurs within the micrometer-scale microlamination, nanoscale disequilibria do not interfere with the ability to interpret VML using the calibrations of Liu and colleagues.

compatible with paleoenvironmental micrometer-scale interpretations of rock varnish microlaminations.

4. Towards resolving the contradiction of DNA versus cultural and *in situ* studies

Varnish researchers have employed four general types of strategies to understand the role of organisms in the genesis of rock varnish: field observations; culturing; *in situ* observations; and analysis of organics in bulk samples. Prior to World War II researchers used field studies to connect pollen dispersal (White, 1924) and lichens (Laudermilk, 1931) to deduce varnish genesis.

A number of researchers cultivated bacteria and fungi genera from varnish (Krumbein, 1969; Dorn and Oberlander, 1982; Taylor-George et al., 1983; Palmer et al., 1985; Hungate et al., 1987; Staley et al., 1991; Adams et al., 1992; Grote and Krumbein, 1992; Eppard et al., 1996; Sterflinger et al., 1999; Perry et al., 2004; Northup et al., 2010). There have also been some small degrees of success in attempting to use cultivated microorganisms to generate some semblance of laboratory varnish (Dorn and Oberlander, 1982; Perry and Kolb, 2003).

Analyses of 'bulk samples' (i.e., those requiring the scraping of varnish and underlying weathering rind and rock material) have included analysis of amino acids (Warsheid, 1990; Nagy et al., 1991; Perry and Kolb, 2003; Perry et al., 2003), isotopic analysis (Dorn and DeNiro, 1985), analysis of fatty acid methyl esters (Schelble et al., 2005), phospholipid fatty acids (Kuhlman et al., 2006a), and extraction of genetic material for phylogenetic insight (Eppard et al., 1996; Perry et al., 2004; Kuhlman et al., 2005; Spilde et al., 2005; Benzerara et al., 2006; Kuhlman et al., 2006a,b; Northup et al., 2010).

In situ studies use light (Francis, 1921; Hunt, 1954; Perfil'ev et al., 1965; Khak-mun, 1966; Peck, 1986), secondary electron (Dorn and Oberlander, 1982; Dorn et al., 1992; Flood et al., 2003; Allen et al., 2004; Dorn, 2007; Northup et al., 2010), back-scattered electron (Dorn and Meek, 1995; Dorn, 1998; Krinsley et al., 2009), and transmission electron (Dorn, 1998; Krinsley, 1998; Probst et al., 2001; Perry and Kolb, 2003) microscopy, often in tandem with X-ray elemental analyses. A general observation persists with *in situ* studies, however, that bacteria are infrequently seen on varnish surfaces located on subaerial desert rock surfaces and even less frequently observed as fossils in cross-sections (Jones, 1991; Dorn and Meek, 1995; Dorn, 1998; Krinsley, 1998; Probst et al., 2002; Perry et al., 2004; Krinsley et al., 2009).

Within this burgeoning literature, increasingly tied to funding the search for life on Mars (Perry and Kolb, 2003, 2004; Kuhlman et al., 2006a; Perry and Lynne, 2006; Kuhlman and McKay, 2007; Perry et al., 2007; Northup et al., 2010), two very clear contradictions have emerged in the past few years. Whereas *in situ* and cultivation studies suggest an important role for microorganisms in the oxidation and fixation of Mn and Fe, bulk sample studies have largely failed to reveal Mn-oxidizing organisms. For example, while Kuhlman et al. (2006b: 1710) explain that it is possible that some organisms might be "able to oxidize iron and/or manganese," they "did not observe organisms known to be involved in metal oxidation."

The second apparent contradiction rests in the shear number of implicated cultivated genera and organics measured in bulk samples. If even a small percentage of the cultivated genera or measured bulk organics somehow play a role in varnish genesis, rates of formation would be orders of magnitude greater than those seen (Dorn, 1998; Liu and Broecker, 2000). If all suspected agents in the published literature help make varnish, then samples from desert rock surfaces should be forming within years to decades and should entomb the types of abundant fossil forms seen in other Mn–Fe deposits (Francis, 1921; Ferris et al., 1987; Konhauser et al., 1994; Chafetz et al., 1998; Kennedy et al., 2003). Such a rapidly-forming sample of rock varnish with entombed Mn-oxidizing fossils has been described at a slag pile

(Dorn and Meek, 1995), but a slag pile differs substantially from conditions found on natural desert rock surfaces; the slag pile has an unusual circumstance of abundant moisture and the paucity of fungal and lichen competitors to bacteria.

We present two possible resolutions to these *prima facie* contradictions.

One resolution is to reject the role of microorganisms in the enhancement of manganese in varnish (Linck, 1901; Engel and Sharp, 1958; Moore and Elvidge, 1982; Smith and Whalley, 1988; Perry et al., 2006). Abiotic formation of varnish requires small pH fluctuations (Krauskopf, 1957) to explain the tremendous enrichment of Mn in varnish. Or, nanoparticles of the iron oxide hematite can catalyze the oxidation of Mn²⁺ forming nanoscale manganese minerals (Hochella et al., 2008).

Although the abiotic processes to explain Mn oxidation proposed decades ago (Krauskopf, 1957; Engel and Sharp, 1958) and more recently (Madden and Hochella, 2005) have not been falsified, the geomorphic distribution of varnish poses at least eleven obstacles reviewed elsewhere (Dorn, 1998: 242–243). Perhaps the largest objection to abiotic enhancement of Mn is the slow temporal scale of varnish accretion – on the order of just a few microns per millennia (Dorn, 1998: 230; Liu and Broecker, 2000). Varnishes that have experienced erosional events – indicated by unconformities – are not used in calculating these rates; thus the measured rates do appear to represent only sequential gain.

If Mn is truly enhanced abiotically, varnish accretion should be much faster. Each year, carbonic acid in rainfall falls on dust that has accumulated on varnished surfaces. The abiotic explanation for varnishing is that carbonic acid wetting leaches Mn out of the dust, to be concentrated in varnish through a slight increase in pH as the rain evaporates. Given known dust deposition rates and concentrations of Mn in the dust, abiotic leaching and precipitation would generate varnishes 10² to 10⁴ times faster than observed (Dorn, 2007: 265). Similarly, there would be no known reason why nanoparticle hematite catalyzing events of Mn-oxidation would limit the rate of varnish accretion to micrometers per millennia. While abiotic varnishes should form far more rapidly than is observed, this is not a disqualification of the hypothesis. Rather, it is an invitation to explain why the proposed abiotic processes should be slowed down several orders of magnitude.

A second resolution to both apparent contradictions rests in changing epistemological perspectives by focusing on timescale and not method. Field, laboratory, bulk and *in situ* research strategies can be reclassified into those methods that analyze organic matter less than a few hundred years old and those that analyze material that could be thousands of years old, or more.

There is very little information published on the residence time of the sorts of bulk (scraped-off powders) organics used to analyze amino acids, fatty acid methyl esters, phospholipids fatty acid, and DNA or RNA analyses. The literature on AMS ¹⁴C dating of varnish is not helpful because of the chemical pretreatments done on all published samples. We have one unpublished measurement on an untreated powdered varnish sample from the Mojave Desert, scraped from the Manix Basin; the powdered varnish yielded a ¹⁴C age of 111.30% (ETH 12881) or essentially post-bomb carbon. Independent insight comes from the high abundance of labile amino acids and the lack of D-alloisoleucine; considering racemization under the extremely high temperatures found on desert rocks, Perry et al. (2003: 436) deduced that a bulk sample would have a bulk age of "possibly less than 200 years old". If these speculative insights on residence time are within a factor of five of reality, then what we have all been doing is analogous to taking "snap shots". The millennial pace of uniformitarianism in rock varnish formation makes it conceivable that every single published cultivation and bulk organic analysis has simply documented adventitious information, not truly relevant to how microbes might form rock varnish.

Failing to find genetic material from Mn-oxidizing microbes in phylogenetic analyses of a single rock sample is also expected – if the analyzed genetic material is truly post-bomb (as suggested by the above radiocarbon age) or less than 200 years old (as suggested by Perry et al., 2003). Furthermore, ongoing oxidation of organic matter and decay of even bacterial sheaths (Dorn, 1998; Krinsley, 1998; Dorn, 2007) combined with evidence for diagenetic alteration of organic matter in a rock varnish environment (Dorn, 1997; Frink and Dorn, 2002; Cohen-Ofri et al., 2006) could make finding fossil DNA problematic. Conversely, if Mn-oxidizing microbes were found in every bulk sample, rates of varnish formation would be much faster than observed in deserts.

Why would an essentially random grab bag sampling strategy (Eppard et al., 1996; Perry et al., 2004; Kuhlman et al., 2005; Spilde et al., 2005; Benzerara et al., 2006; Kuhlman et al., 2006a,b) be expected to yield Mn-oxidizers? The fundamental problem, not yet explored in varnish research, is that no systematic microbial geographic insight exists on the types of micro- and macro-environments where Mn-enhancing bacteria occur. It would take an epistemological shift for microbial ecologists to treat the problem like phytogeographers, employing stratified random sampling schemes of analyzing genetic material from dozens of samples from different environmental contexts to properly assess the microbial hypothesis of Mn-enhancement through genetic analyses.

In a speculative thought exercise, it might be that varnish grows so slowly because paleoenvironmental fluctuations bring the niche of varnish-forming organisms over a rock surface only once every few

centuries or millennia. In this “shifting niche” hypothesis, there might be a particular environmental setting favorable for colonization and for optimization for microbial Mn-enhancement. Although it is unlikely that the microbial niche relates to the surrounding vegetation, Fig. 4A is useful in illustrating the sorts of dramatic changes that can take place in a setting now known to be a harsh arid setting. For the sake of this thought exercise, if the Mn-varnish makers activate only during an assemblage of Utah juniper–sagebrush combined with Halophytic desertscrub (cf. Fig. 4A), then the Mn-rich laminae in Fig. 4C and D would only grow when this “shifting niche” occupied the site. Sampling for DNA, that had oxidized centuries ago, would be fruitless, because the shift in varnish accretion styles can be sudden, as illustrated by a sudden transition from Mn-rich laminae to Mn-poor dust accretion (e.g. Fig. 4B). Other evidence of varnish undergoing a sudden transition rests in the punctuated nature of the Mn-rich microlaminae (e.g. Fig. 4C and D). The point of this speculation is that genetic analyses of grab bag samples, not knowing the temporal longevity of the genetic material and not understanding the spatial context of Mn-enhancing organisms, could be like playing the lottery. This “shifting niche” hypothesis would be testable through a sampling strategy of bulk organics in the surficial layers of varnishes formed in different contemporary environmental contexts.

The methods that do provide data relevant to the millennial timescale of varnish formation in hot deserts are field and *in situ* observations. Finding *in situ* Mn-enhancing bacteria (Fig. 5) only infrequently on desert rock surfaces (Taylor-George et al., 1983; Jones,

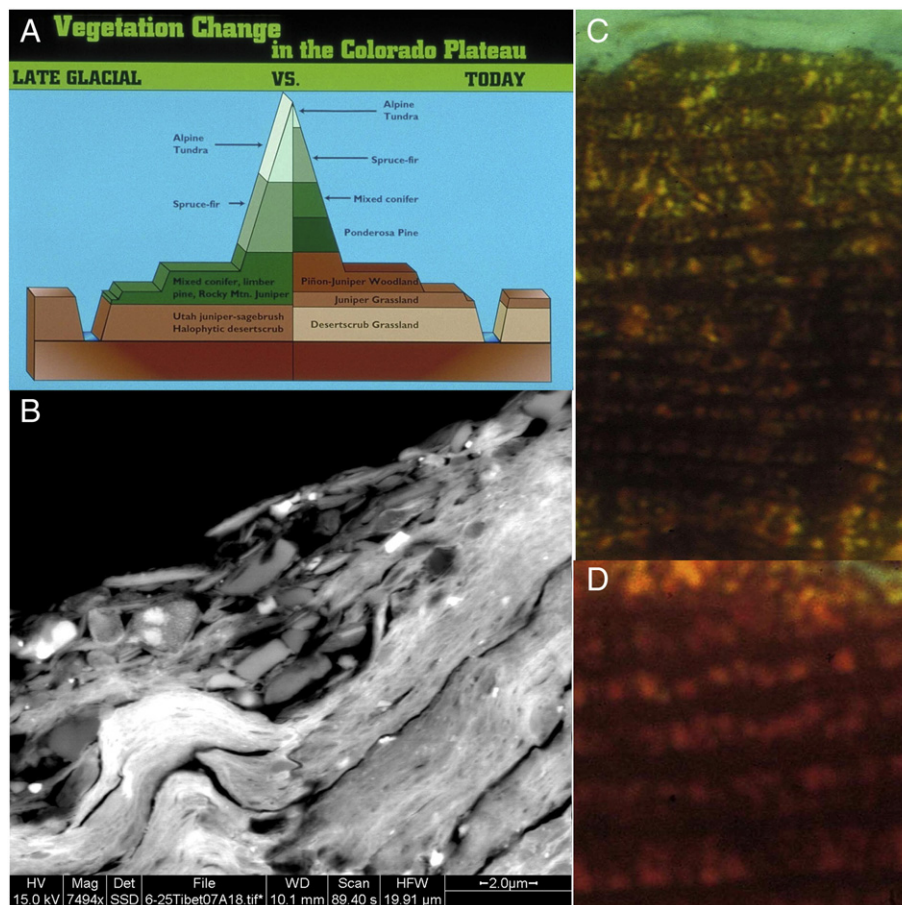


Fig. 4. Thought exercise on interpreting Mn-rich microlaminae. (A). Idealized diagram illustrating general phytogeographic changes from the last glacial maximum to the Holocene at the Grand Canyon, Arizona, courtesy of NOAA (Betancourt, 2001). (B) High resolution back-scattered electron microscope image of varnish from the Ashikule Basin, Tibet, illustrating a sudden transition from Mn-rich varnish to the surficial Mn-poor layer. (C) and (D) show illustrations of varnish microlaminations from petroglyphs engraved along the Snake River, Idaho, where image widths are about 20 μm.

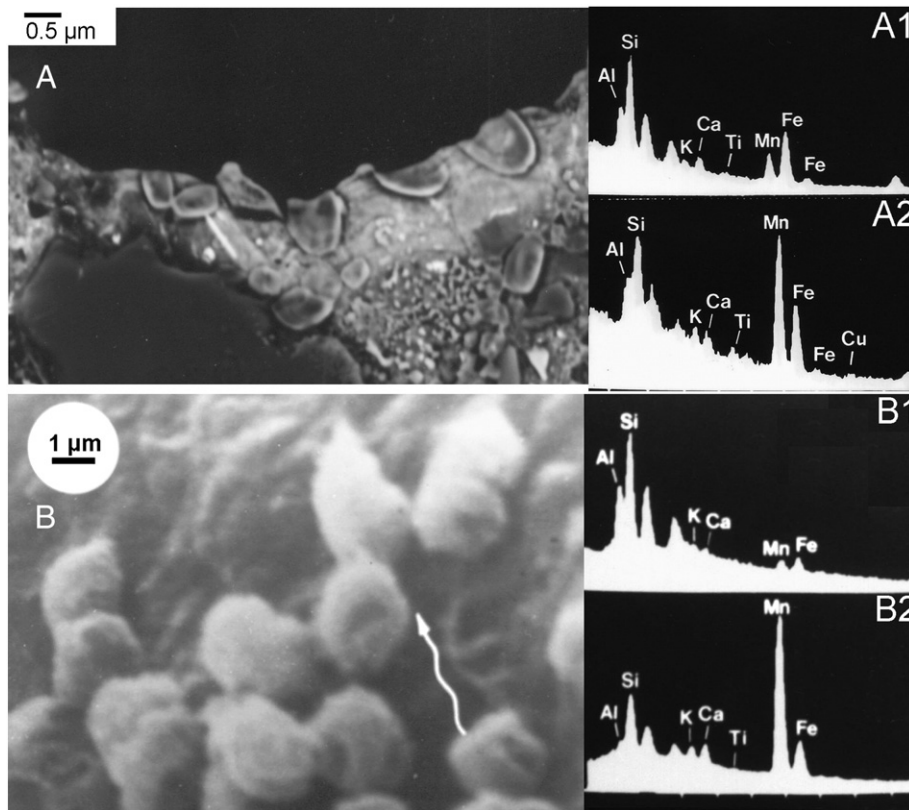


Fig. 5. Examples of infrequent occurrences of *in situ* Mn-enhancement by bacterial-forms in cross-section (A) and on surfaces (B) of subaerial rock varnishes. (A) Sample from Ashikule Basin, Tibet; the Mn-spiked EDS (A2) derives from a ca. 1–2 μm spot on the upper right fossil bacterial form and compares with the defocused beam of just varnish (A1). (B) Sample collected by R. Gerson from Dry Valleys, Ross Desert, Antarctica; EDS on ~1–2- μm spot on cocci-bacterial forms (B2) has much higher abundance of Mn than defocused ~30 μm spot analysis of adjacent varnish material (B1). The arrow in B parallels a possible hyphae from a budding-bacteria form.

1991; Dorn and Meek, 1995; Dorn, 1998; Perry et al., 2004; Krinsley et al., 2009) is an expectation of slow varnish accretion rates. The even less frequent occurrence of bacterial-forms that are encrusted in Mn and Fe in cross-section studies (Dorn and Meek, 1995; Dorn, 1998: 243–245; Krinsley, 1998; Allen et al., 2004) is similarly a reflection of the slow pace of uniformitarianism in rock varnish accretion.

5. Conclusion

We argue that varnish researchers have, during the past two centuries suggested or even clearly asserted that their new data contradict prior findings. Yet, if many of these empiricists had employed a broader epistemological perspective, such *prima facie* contradictions could often be resolved simply by considering the type of varnish collected, the geomorphic context of the collection site, and especially the spatial and temporal scales of varnish processes.

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