



Anthropogenic interactions with rock varnish

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“Anthropogenic interactions with rock varnish”

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KEY POINTS

- Rock varnish is a ubiquitous biogeochemical rock coating that forms as a result of budding bacteria concentrating manganese and iron that then cements clays to rocks surfaces.
- Anthropogenic processes alter the biogeochemistry of rock varnish, which is sensitive to human interactions, for example, though lead contamination, acidification that dissolves the coating, dust loading altering its properties, and wildfire interactions.

ABSTRACT: This chapter focuses on the biogeochemical coating known as rock varnish that forms naturally as a result of interaction between budding bacteria and clay minerals. This chapter interfaces with this book through exploring natural processes that generate this coating and the sensitivity of rock varnish to both natural climatic changes and anthropogenic forcings. High resolution electron microscopy reveals that budding bacteria concentrate both manganese (Mn) and iron (Fe) on cell surfaces. Post-deposition processes mobilize nanoscale Mn and Fe that cements clay minerals to the underlying rock or pre-existing varnish. Although other hypotheses exist to explain varnish formation, this model is the only proposed formation process that has a rate rate-limiting step and does not fall pray to the “varnish rate paradox”. Despite rates of varnish accretion of microns per millennia in warm deserts and microns per century in more mesic settings, anthropogenic processes have altered its biogeochemistry in a variety of ways. Globally, lead fallout has contaminated the surface-most micrometer. Regionally, acid fog and anthropogenic dust generation alters varnish textures. Locally, ash from wildfire combines with graffiti such as chalk to coat varnishes. Humans have also applied “artificial varnish” to minimize the aesthetic impact of road construction in wealthier communities.

PLAIN LANGUAGE SUMMARY: Rock varnish is a paper-thin accretion on rock surfaces. Budding bacteria concentrate manganese and iron on its cells; the manganese and iron then combines with clay minerals in dust to create a firm attachment to rock surfaces. While varnish forms in all land environmental settings from the tropics to Antarctica, rock varnish is most noticeable in warm deserts. Human activities have affected the biogeochemistry of this ubiquitous rock coating in a variety of ways. Prehistorically, humans engraved motifs (petroglyphs) into rock surfaces coated with varnish — thus creating an image that contrasts the lighter-colored engraving with the varnished surface darkened by manganese oxides. Prehistoric actions have also altered rock varnish through creation of Earthen art and such features as stone cairns. Historic lead pollution alters the biogeochemistry of varnish by contaminating the very surface, even in settings as distant from industrial activity as Greenland. Acidification of local environments through industrial and automobile emissions dissolves the manganese-iron from the varnish. Human generation of dust in a region also alters the chemistry of varnish, as does wildfires.

KEYWORDS: acid fog; artificial varnish; dust; landscape geochemistry; lead contamination; wildfire

X.1. Introduction

Prior to the mid-nineteenth century, western thought focused on positive aspects, both religiously and culturally, of the impacts of human activity on Earth's surfaces (Glacken, 1967). Thought began to change with the writings of geographer George Perkins Marsh and naturalist Count Buffon (comte de Buffon, 1749-1804; Marsh, 1864). These approaches to the study of the destructive effects of human activities initiated the modern sustainability movement (Lowenthal, 2000). In envisioning this book, Dontsova et al. (2018) present a level of detail and evidence for the pervasiveness of human impact unthinkable in the time of George Perkins Marsh — teasing out anthropogenic from natural drivers of biogeochemical change (Dontsova et al., 2018).

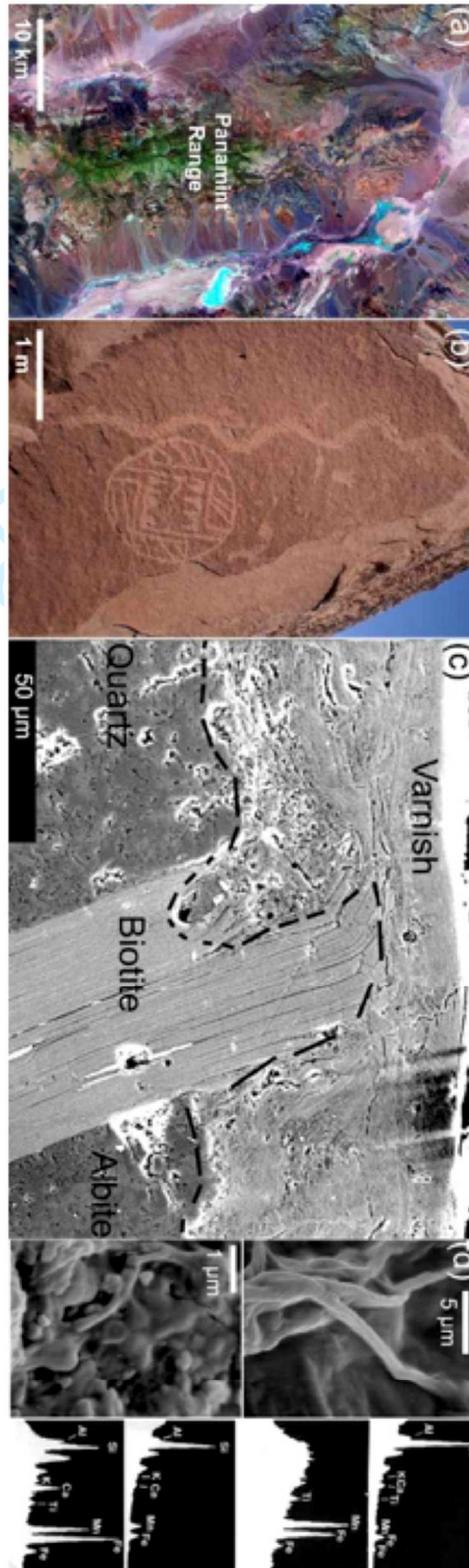
The chapters of this book analyze biogeochemical changes from three broad perspectives: (i) natural forcings such as mineral and rock decay; (ii) climate change that potentially mixes anthropogenic and natural impacts on; and (iii) anthropogenic forcings. This chapter interfaces with all three perspectives by reviewing natural forcings that lead to the accretion of the ubiquitous biogeographical rock coating known as rock varnish (and sometimes also termed desert varnish), and then how rock varnish responds to both natural climatic changes and anthropogenic processes.

The dark ferromanganese-rich and clay accretion of rock varnish is often termed desert varnish because it is most noticeable in warm arid regions. However, Krumbein and Jens (1981) and Dorn and Oberlander (1982) emphasized that rock varnish is a better term because of the presence of this same coating in all terrestrial environments. Recent examples of varnish studies in non-deserts include settings in southeast Asia (Casanova-Municchia et al., 2016), southern Belgium (Goossens et al.,

2015), caves in Spain (Lozano and Rossi, 2012), a German Gothic cathedral (Macholdt et al., 2017), and different settings in China (Xu et al., 2018).

Rock varnish greatly alters the appearance of rock surfaces at all different scales, even though it is typically less than 100 μm thick (**Fig. X.1**). Its constituents do not derive from the underlying rock (Potter and Rossman, 1977; Krumbein and Jens, 1981; Dorn, 1998), but instead derive from external sources such as dust deposited on rock surfaces. Rock varnish typically grows at rates of microns per thousand years in arid environments (Liu and Broecker, 2000), although faster growth rates do occur in more mesic settings (Dorn and Meek, 1995; Krinsley et al., 2017). These very slow rates of accretion deposit millennial-scale microlaminations that are recognized as a paleoclimatic indicator and dating technique (Liu, 2017; Liu et al., 2013; Liu and Broecker, 2013). With such slow rates of accretion, however, rock varnish is not generally recognized as an indicator of anthropogenic activity.

This chapter presents evidence that rock varnish that forms in both warm desert and wetter settings should receive more recognition as a biogeochemical indicator of anthropogenic interactions. This chapter starts with a summary of current knowledge on the processes by which rock varnish accretes on rock surfaces. The next section then explores how, prehistorically, humans used varnished surfaces as natural blackboards on which to engrave rock art – sometimes leaving behind iron-rich paint and quartz mechanically driven into engraved surfaces. Historically, humanity's imprint on rock varnish processes rest at global scales where the accretion of lead and other heavy metals contaminate the surface-most layer of rock varnish, even in such distant locations as Greenland. Regional impacts include anthropogenic acid fog dissolving varnish and increases in atmospheric dust loading inundating varnishes with particle fragments. More local impacts include ash from wildfires accreting onto nearby rock surfaces and the creation of “artificial varnish” to try to disguise the impact of development in deserts.



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Fig. X.1 Rock varnish viewed at different scales. (a) Alluvial fans debouching from

the Panamint Range into Death Valley on the east and the Panamint Valley on the west are visibly darkened with varying amounts of rock varnish. Thanks to NASA for the Landsat 7 image (<https://earthobservatory.nasa.gov/IOTD/view.php?id=6470>). (b) Petroglyph carved into a joint face partly coated with rock varnish from Petrified Forest National Park. (c) Secondary electron image of rock varnish coating rocks of the Orinoco River, the first site for the scholarly study of rock varnish (von Humboldt, 1812). (d) Bacteria sheaths concentrating Mn-Fe rich material in rock varnish from Tibet (Krinsley et al., 2009), as indicated by energy dispersive spectra of bacteria hyphae as compared with spectra of the adjacent varnish.

X.2. Landscape geochemistry of rock varnish

Clay minerals dominate the composition of rock varnish (Dorn and Oberlander, 1982; Krinsley et al., 1995; Potter and Rossman, 1977), comprising up to two-thirds of a typical rock varnish found in warm deserts. Although over forty other minor and trace elements also occur in rock varnish (Bard et al., 1978; Dorn, 1998; Dorn et al., 1990; Engel and Sharp, 1958; Fleisher et al., 1999; Macholdt et al., 2015; Nowinski et al., 2010), the key to varnish formation rests in the oxyhydroxides of manganese and iron (Hooke et al., 1969; McKeown and Post, 2001; Potter and Rossman, 1979) that typically range from 15-40% by weight and are the agents that cementing clay minerals together and to the underlying rock surface (Dorn and Oberlander, 1982; Krinsley, 1998; Krinsley et al., 2013; Potter, 1979). Table 1 presents variations in the elemental chemistry of bulk samples of scraped rock varnish from different global settings.

Table X.1.

Examples of elemental variation exhibited in bulk chemical analyses of rock varnishes found in desert regions. Samples are analyzed by particle induced X-ray excitation (Dorn et al., 1990). Abbreviations bld is below limit of detection and na is not analyzed.

SITE:	Trail Fan, Death Valley	Manix Lake, Mojave Desert	Makanaka Till, Hawaii	Sinai Peninsula, Egypt	Petroglyph South Australia	Ingenio, Peru Desert	Ayers Rock, Australia
POSITION:	Former Rock Fracture	> 1m Above Soil	With Silica Skin	>1m Above Soil	> 1 m Above Soil	At Soil Surface	From Rock Fracture
Na	bld	1.1	0.62	0.28	0.17	na	na
Mg	0.14	3.44	1.98	1.5	1.21	2.11	1.58
Al	23.74	25.77	21.13	22.94	22.81	20.45	28.77
Si	39.09	32.35	29.77	32.81	33.34	45.88	35.69
P	0.49	1.15	0.69	bld	0.53	0.53	bld
S	0.7	0.3	0.2	bld	bld	1.13	bld
K	3.45	2.11	3.3	2.42	2.79	2.91	2.11
Ca	4.87	1.35	4.89	2.91	2.18	6.22	1.45
Ti	1.52	0.84	0.73	0.68	0.65	0.85	1.19
Mn	10.87	12.47	13.6	11.97	21.7	4.94	11.91
Fe	13.47	18.09	21.13	22.94	13.26	12.03	16.57

Ni	0.13	bld	bld	bld	bld	bld	bld
Cu	0.12	0.22	0.33	0.25	0.44	0.04	bld
Zn	0.27	0.3	0.49	0.42	0.44	0.16	bld
Rb	bld	0.25	bld	bld	bld	bld	bld
Sr	bld	0.21	bld	0.42	bld	0.11	bld
Zr	0.29	0.22	bld	bld	bld	bld	bld
Ba	0.85	0.19	0.16	0.18	0.14	2.42	0.73
Pb	bld	0.74	0.98	0.27	0.34	0.22	bld

Landscape geochemistry (Fortescue, 1980; Perel'man, 1966) is an environmental geochemistry paradigm focused on explaining spatial geochemical patterns found in low-temperature weathering environments. From a landscape geochemistry perspective, the different constituents of rock varnish accrete because specific physical, biological, and geochemical barriers exist on rock surfaces (Perel'man, 1986).

The clay minerals and other small bits of aeolian particles initially attach to varnish (Aulinas et al., 2015; Dorn et al., 2013) through van der Waals forces (Fig. X.2). These particles are then loosely cemented by nanoscale deposits of silica (Langworthy et al., 2010), carbonate, Mn and Fe (Dorn et al., 2013; Krinsley et al., 2009). Clay minerals are then fixed to the underlying rock (Dorn, 1998; Dorn et al., 2012b) and to other rock varnish (Krinsley et al., 2013) by Mn-Fe oxyhydroxides.

Budding bacteria are the key agents that concentrate both Mn and Fe (Dorn and Oberlander, 1982; Krinsley et al., 2017). Budding bacteria, for example the genera *Pedomicrobium* (Dorn and Oberlander, 1982), encrust Mn and Fe oxides around their cells and hyphae (Fig. X.2; X.3). The budding process enables these bacteria to be buried underneath the accumulation of varnish and still reproduce by hyphae extension. After cells are encrusted with Mn and Fe, ongoing diagenesis breaks apart these cell encrustations into nanoscale granules (Dorn, 1998; Krinsley, 1998) that are then remobilized and reprecipitated as nanoscale Mn-Fe (Krinsley et al., 2017) amongst the mixed-layer clays (Fig. X.2) in a process first explained by Potter (1979, 174-175):

"Deposition of the manganese and iron oxides within the clay matrix might then cement the clay layer...the hexagonal arrangement of the oxygen in either the tetrahedral or octahedral layers of the clay minerals could form a suitable template for crystallization of the layered structures of birnessite."

However, varnish is not stable at the nanoscale; McKeown and Post (2001: 712) explained that ongoing disequilibria exists even after the varnish formed:

"[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".

Thus, while budding bacteria originally concentrate the Mn-Fe, it is the geochemical dissolution at the nanoscale and subsequent reprecipitation of oxyhydroxides in clays that results in varnish formation. It is important to stress, however, that shifts at the nanoscale do not create instability in the laminations seen at the micron scale that are stable for tens of millennia (Liu, 2017; Liu et al., 2013; Liu and Broecker,

2013) — much like cars moving around inside a parking lot do not change the lot itself.

Budding bacteria comprise only a small component of the microbial community that has been found associated with rock varnish through culturing techniques (Dorn and Oberlander, 1982; Krumbein and Jens, 1981; Northup et al., 2010; Palmer et al., 1985; Perry et al., 2004; Taylor-George et al., 1983) and phylogenetic insight (Benzerara et al., 2006; Eppard et al., 1996; Esposito et al., 2015; Kuhlman et al., 2005; Kuhlman et al., 2006a; Kuhlman et al., 2006b; Kuhlman et al., 2008). In general, these studies find a broad diversity of eukaryotic and bacterial taxa, most of which do not actively participate in manganese or iron concentration through oxidation. However, the authors of these studies admit that sampling thus far has been analyzing varnish materials from just a few sampling sites. In addition, other sorts of organic analyses reveal that the nature of the organic matter in analyzed varnish samples are consistent with a bacterial origin (Malherbe et al., 2017) and that the microbial community of varnish is similar to adjacent soils in that prokaryotic and fungal communities exist with gram-positive bacteria found more often (Schelble et al., 2005). In brief, varnish is home to a diverse microbial community, most of which is not directly involved in Mn-Fe concentration or varnish formation.

The budding bacteria (Fig. X.3) hypothesis (Dorn and Oberlander, 1982; Krinsley et al., 2017) to explain the great enrichment of Mn and also Fe in rock varnish has a number of competing explanations that can be grouped into several broad categories. Some favor enrichment through purely abiotic processes that involve alternating reducing and oxidizing environments (Engel and Sharp, 1958; Goldsmith et al., 2014; Soleilhavoup, 2011). Another group of hypotheses favors organisms different than budding bacteria that can concentrate Mn and Fe (Krumbein and Jens, 1981; Northup et al., 2010; Palmer et al., 1985; Taylor-George et al., 1983). Still others potentially draw connections to growing phylogenetic insight about the organisms growing on and in varnish (Benzerara et al., 2006; Eppard et al., 1996; Esposito et al., 2015; Kuhlman et al., 2005; Kuhlman et al., 2006a; Kuhlman et al., 2006b; Kuhlman et al., 2008). The problem with these competing explanations is that they all lack a rate-limiting step and fall prey to the “varnish rate paradox”.

Physical Barrier: van der Waals force promotes dust accumulation, providing raw ingredients of clays

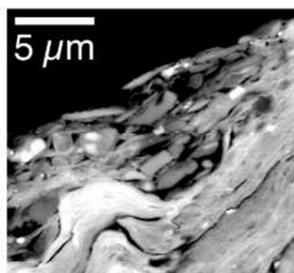
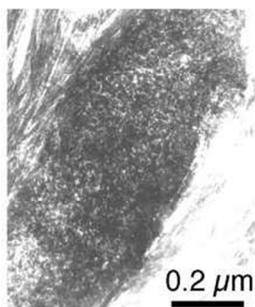
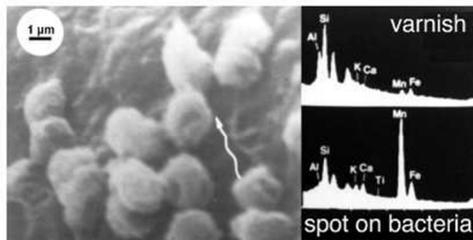


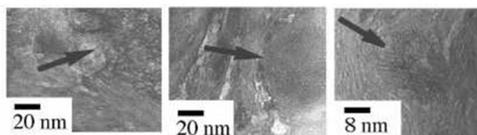
Fig. X.2 Rock varnish accretion requires a series of different types of barriers to transport of the various constituents (Dorn 1998).



Biological Barrier: Mn and Fe fixation in bacteria sheaths

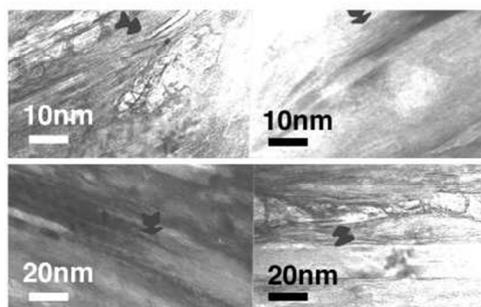


Dissolution from cell wall (granular fragments)



&

Physiochemical Barrier: Fixation in clay matrix cementing mixed-layered clays



The varnish rate paradox, presented previously (Dorn, 2007; Dorn and Krinsley, 2011; Krinsley et al., 2017), is that there are so many different ways proposed to explain Mn (and Fe) enrichment in varnish — yet warm desert locations studied by the various researchers display rates of varnishing of microns per millennia (Dorn, 1998; Liu and Broecker, 2000). Non-desert sites display much faster rates of varnishing and often contain *in situ* evidence of budding bacteria (e.g. Dorn and Meek, 2005; Krinsley et al., 2017). Although the process of bacterial adsorption and oxidation can be quite fast (Namgung et al., 2018; Vázquez-Ortega and Fein, 2017), budding bacteria are only rarely observed *in situ* in warm desert varnishes. Still, Dorn and Krinsley (2011) emphasized that only budding bacteria have been observed *in situ* concentrating Mn and Fe, while other organisms have never been seen actively enhancing Mn or Fe in varnish samples.

In contrast to the occasional growth of budding bacteria, abiotic processes would generate varnishes 100x to 10,000x faster than observed (Dorn and Krinsley,

2011; Krinsley et al., 2017). The reason for faster formation through abiotic enrichment is that there is no rate-limiting step. Theoretically, Mn and Fe concentration relies on leaching of the divalent cations from dust sources during acidic wetting events, followed by increases in pH to oxidize the Mn and Fe. Given that dust deposition and wetting events occur tens of thousands of times over a millennia, if small pH-Eh shifts actually generated varnish as proposed (Engel and Sharp, 1958; Goldsmith et al., 2014; Soleilhavoup, 2011), varnishes should be meters thick and not microns thick as found naturally.

Similarly, if all the various organisms growing in and on varnish (Palmer et al., 1985; Eppard et al., 1986; Dragovich, 1993; Benzezara et al., 2006; Kuhlman et al., 2006a, 2006b, 2008; Northup et al., 2010; Lozano and Rossi, 2012; Esposito, 2015; Kutovaya et al., 2015; Paulino-Lima et al., 2016; Malherbe et al., 2017; Brewer and Fierer, 2018; Gleeson et al., 2018; Lang-Yona et al., 2018) contributed to varnish formation, rates of accretion would be orders of magnitude higher than observed for the warm desert sites studied (Dorn, 2007; Krinsley et al., 2017). The only hypothesis that explains Mn and Fe concentration, as well as the slow rate of varnish growth in warm deserts, and also some faster growth rates in non-desert environments (e.g. Dorn and Meek, 1995; Spilde et al., 2013), involves the rare event of the growth of budding bacteria (Fig. X.3) and associated concentration of Mn and Fe (Krinsley et al., 2017).

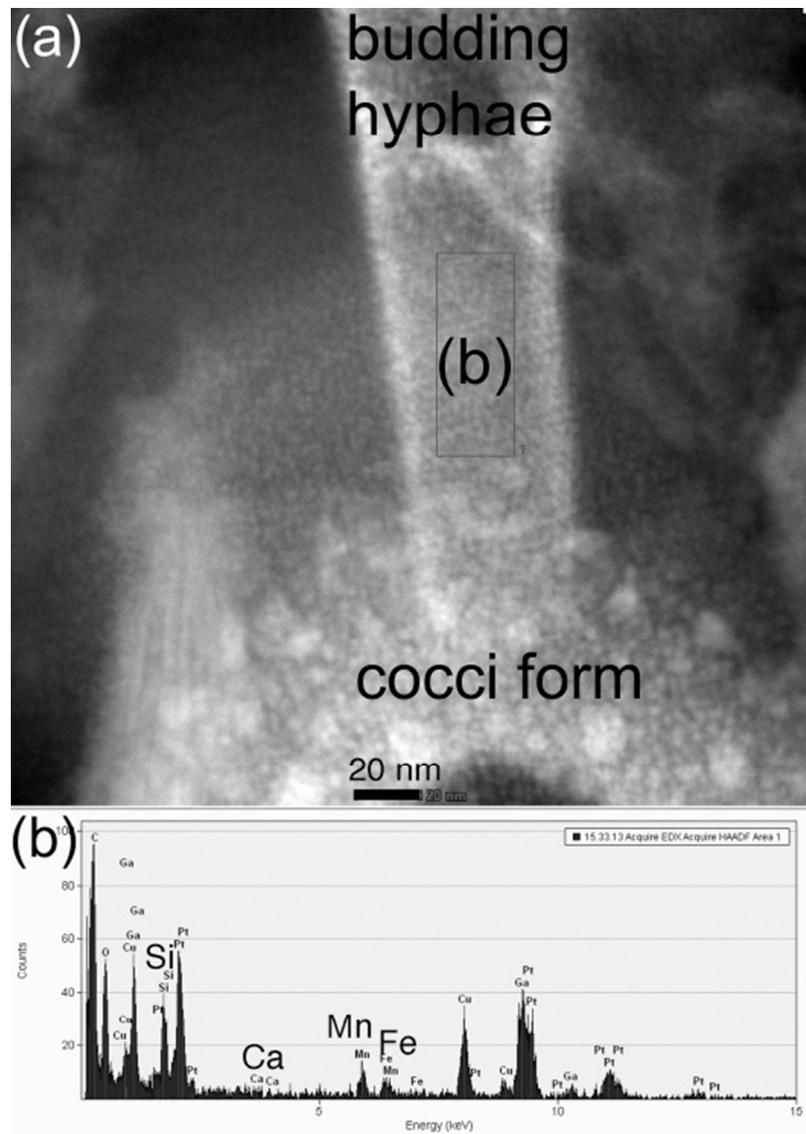


Fig. X.3. High resolution perspective on fixation of Mn and Fe. (a) Electron microscope image of budding bacteria concentrating Mn and Fe (Krinsley et al., 2017), where a budding hyphae emerges from a cocci bacterial form. (b) location in image (a) matching the energy dispersive spectra showing the concentration of Mn and Fe with Si and small amounts of Ca. The other peaks are artifacts associated with sample preparation.

The landscape geochemistry of rock varnish is not only one of accretionary processes that fix constituents on rock surfaces. Rock varnish is also dissolved naturally by acid-secreting organisms such as lichens (Dragovich, 1987) and microcolonial fungi (Dragovich, 1993). The organic acids dissolve the Mn-Fe, thus destroying the cement that binds the varnish together (Fig. X.4). In summary, the landscape geochemistry of rock varnish is a complex dance among processes that fix constituents to rock surfaces and those that release coating components.

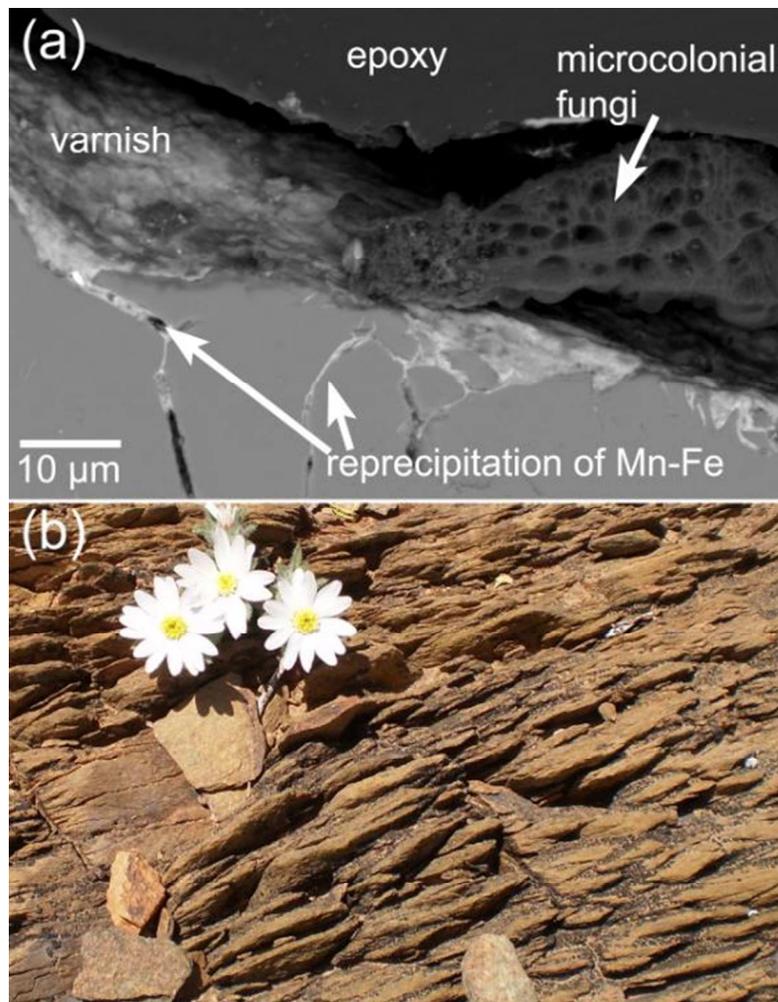


Fig. X.4. Biofilms grow on rock surfaces where sufficient moisture exists (Viles, 2011). Such biofilms in the Sonoran Desert of central Arizona typically consist of fungi and lichens. (a) Microcolonial fungi secretes organic acids that then dissolve the Mn and Fe in varnish (Dragovich, 1993). In the case of this cross-section view using backscattered electrons some of the Mn and Fe have been reprecipitated in rock fractures. (b) Field site near Black Canyon City, where flower widths of 2 cm provide scale.

X.3 Prehistoric Anthropogenic Interactions

Rock engravings (or petroglyphs) represent the rare circumstance where this biogeochemical deposit has actually received widespread attention for its anthropogenic interactions. The act of engraving art into a rock face coated by dark Mn-Fe-rich varnish is commonly discussed in scholarship (Black et al., 2017; Whitley, 2001), in teaching materials about archaeology (Whitley and Loendorf, 1994), and in popular culture describing various rock art sites (<https://www.nps.gov/pefo/learn/historyculture/newspaper-rock.htm>) where ancient peoples have carved motifs (Fig. X.5)



Fig. X.5. Newspaper Rock at Petrified Forest National Park exemplifies how rock varnish provides a 'blackboard' for prehistoric rock engravings that range in age from terminal Pleistocene to the twentieth century (Dorn, 2006).

The prehistoric artists did not only engrave motifs into rock varnish, but also applied painting materials. Fig. X.6 presents an example from Buffalo Eddy, Washington, where ocre — identified as a strong iron energy dispersive X-ray signal — was applied to a pattern of dots. The varnish microlamination pattern that formed on top of the paint material has a pattern consistent with varnish layering unit Wet Holocene Unit 4 that has a calibrated calendar age of about 2800 yr BP (Liu and Broecker, 2007).

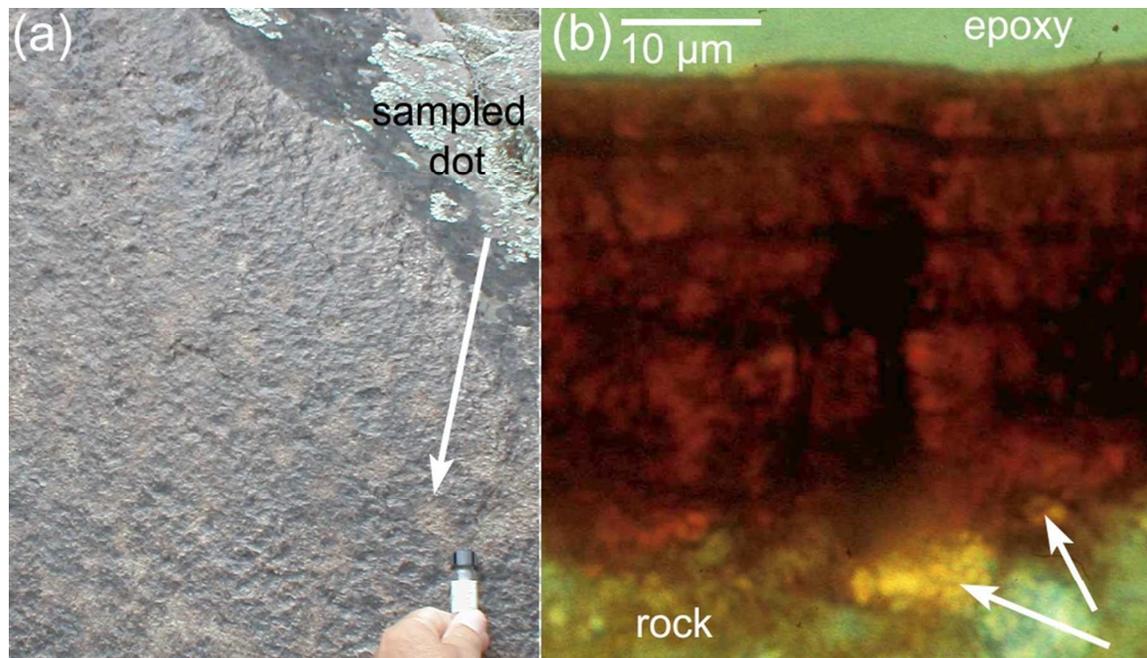


Fig. X.6. An engraving consisting of a pattern of dots (image a), at Buffalo Eddy, Washington, USA, was subjected to painting (Merrell and Dorn, 2009). Iron-rich materials, perhaps goethite, was painted into the dots. (b) Then, rock varnish formed on top of the paint material, as seen in a light microscope ultrathin cross-section of varnish. Arrows in (b) identify the iron-rich materials as confirmed by energy dispersive X-ray analyses.

Luminescence occurs when quartz minerals are mechanically fractured. Quartz also exhibits luminescence when it is rubbed. Dr. David Whitley and colleagues have compiled evidence that quartz was used in the making of many petroglyphs. In particular, basalt flows that generally lack free quartz provide an appropriate way to study whether quartz was used in engraving rock art. The basalt flows of the Coso Range and basalt flows in the Mojave Desert, both in Eastern California, reveal shards of quartz embedded into engravings (Whitley, 2000; Whitley, 2001; Whitley et al., 1999). The flows hosting the Conejo Mine petroglyphs (e.g. Fig. X.7) do not contain free quartz. The archaeological interpretation is that the shamans making the art likely knew of the luminescence and perhaps engraved the art at night (Whitley et al., 1999).

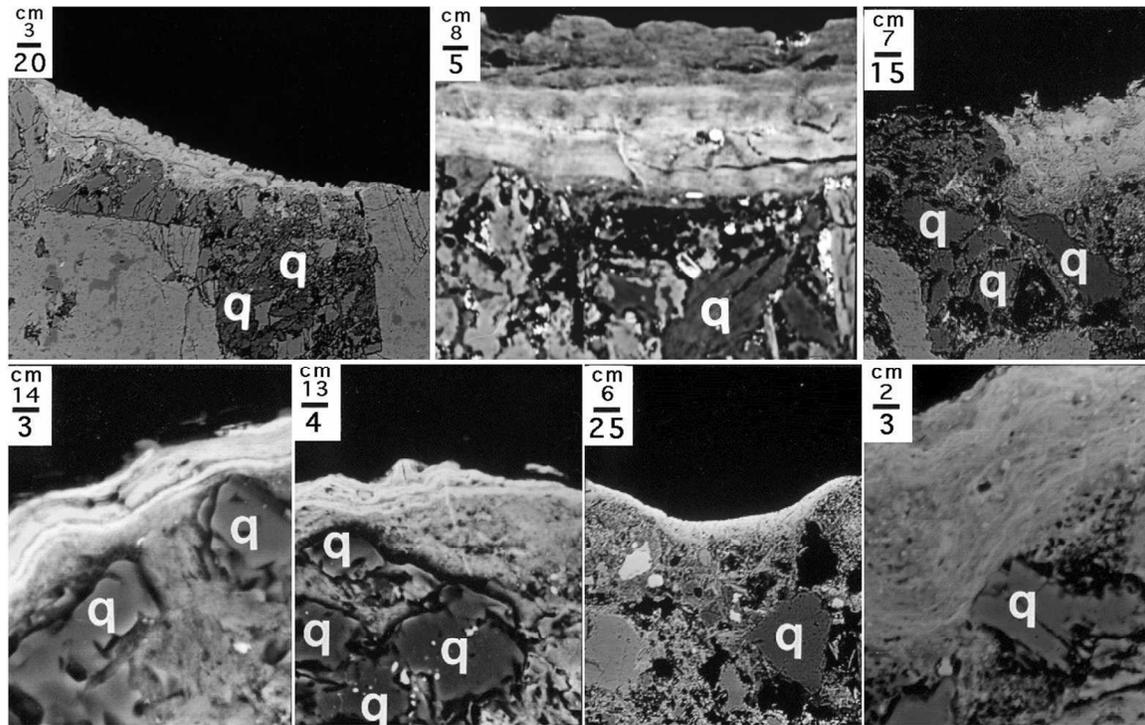


Fig. X.7. The Conejo Mine petroglyph site in the Coso Range, eastern California, consists of a basalt flow that lacks free quartz. Backscattered electron micrographs of cross-sections of rock varnish formed on top of engravings regularly reveal the presence of quartz — identified by the letter q. The numbers CM3, CM8, CM7, CM14, CM13, CM 6 and CM2 refer to specific engravings sampled (Whitley, 2000; Whitley, 2001; Whitley et al., 1999).

Prehistoric humans undertook considerable effort to modify stones on Earth's surface. Such modifications are sometimes called earthen art (Frink and Dorn, 2001; von Werlhof, 1989). Earthen art such as the Nasca geoglyphs of Peru and southwestern North America are some of the most well studied (Clarkson, 1994; Dorn et al., 2001). However, earthen art can be found all over the deserts of the world in the form of rock cairns (Fig. X.8a). The rocks that were assembled to make a cairn in the Panamint Valley of eastern California had an original arrangement of rock coatings (Fig. X.8b), most typically dark rock varnish on top of a boulder, a thin shiny black ground-line band, iron film underneath the boulder, and perhaps laminar calcrete if the boulder was originally embedded into the Bk (carbonate) soil horizon. When the boulder was moved to build a cairn, sometimes, the orientation of the rock coatings changed (Fig. X.8c). This change provides the opportunity to utilize dating techniques, for example, radiocarbon dating carbonate formed over rock varnish. This carbonate only started to form after the rock was flipped and embedded into the ground (Cervený et al., 2006).

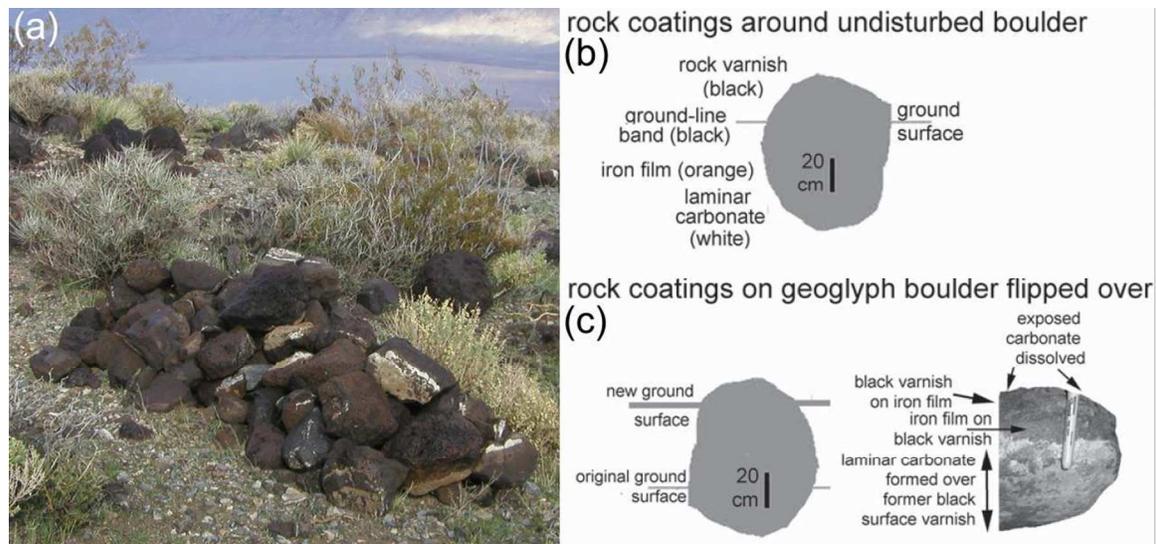


Fig. X.8. Rock cairn from the Panamint Valley, eastern California (Cervený et al., 2006). The boulders used to build this cairn came from a desert pavement with considerable antiquity (Seong et al., 2016). Some of the boulders were flipped on their side and embedded deeply in the ground. These boulders formed laminar carbonate on top of rock varnish. Thus, the original sequence of rock coatings in image b was altered to image c. The laminar carbonate only started to form after the cairn was constructed, thus a radiocarbon age for the laminar carbonate provides a minimum age for the cairn.

In summary, prehistoric humans interacted with and altered rock coatings such as rock varnish in a variety of different ways. Although the most common example involves carving motifs into heavily varnished rock surfaces, a careful inspection of both rock and earthen art reveals that people painted art, mechanically abraded art with quartz that exhibits luminescence, and moved boulders and rocks to create earthen art.

X.4 Historic Biogeochemical Interactions with Rock Varnish

X.4.1. Artificial varnish

“Imitation is the sincerest form of flattery that mediocrity can pay to greatness.”
Oscar Wilde

Urban development in deserts leave behind visual scars when bedrock is disturbed to create features such as roadcuts. The aesthetic problem rests in the contrast between naturally dark varnish and the much brighter hues of freshly-exposed rock. Fig. X.9a illustrates colluvium coated with rock varnish where and freshly broken rock surfaces stand out prominently.

Wealthy subdivisions in the Phoenix metropolitan area have experimented with the application of “artificial varnish” — a process whereby sodium hydroxide is first sprayed onto places like exposed road cuts, followed by the application of a mixture of divalent Mn and Fe in solution. Upon contact with the alkaline sodium hydroxide, the Mn and Fe oxidizes and the rock surfaces are thus coated with an artificial varnish (Elvidge and Moore, 1980). Fig. X.9c displays a road cut covered with artificial varnish, where only the uppermost bit of soil is light in color. A key difference between true rock varnish (e.g. Fig. X.9b) and artificial varnish (e.g. Fig. X.9d) is the lack of clays. The result is that the artificial varnish applied over two decades ago is undergoing disaggregation into granules that detach and degrade the artificial varnish (Fig. X.9d).

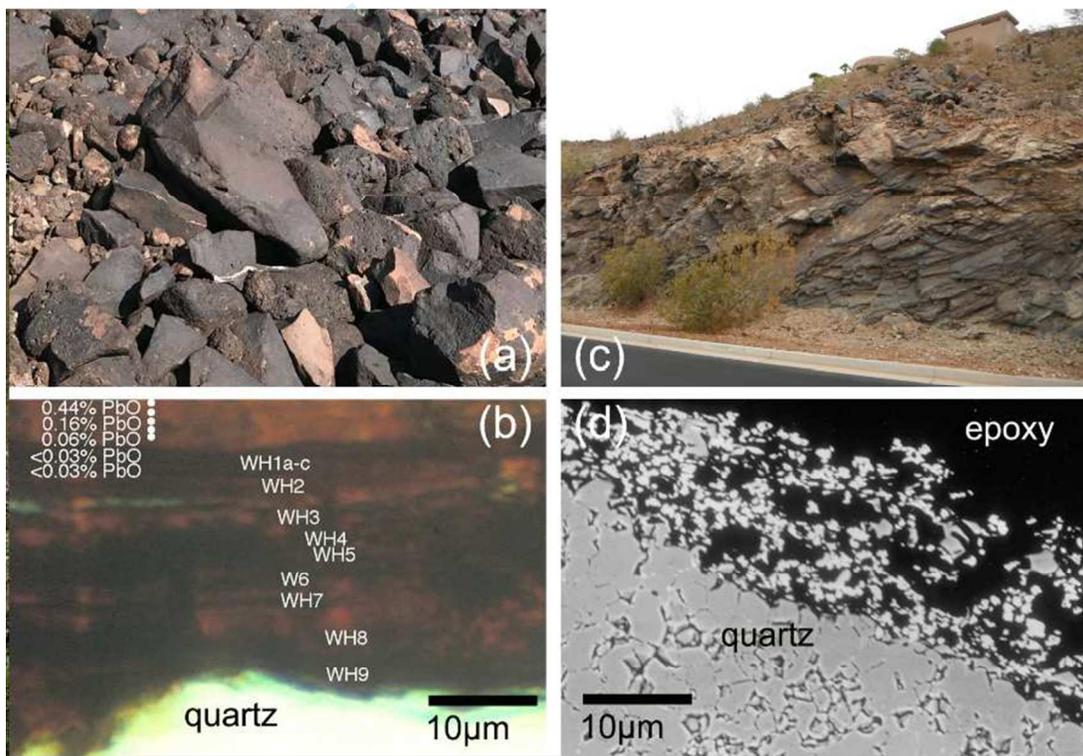


Fig. X.9. Rock varnish as the dominant natural rock coating in metropolitan Phoenix. (A) Colluvial boulder field at Shaw Butte darkened by rock varnish. The occasional orange iron film indicates rocks spalled by the dirt cracking physical weathering process. (B) Microlaminations form discrete black, orange, and yellow layers in rock varnish thin sections. Electron microprobe analyses reveal a spike in lead in the uppermost micron of this rock varnish from the Phoenix area. Background levels occur once the layer of the varnish is beneath the 20th century. The layer Wet Holocene Unit 1 (WH1) ceased forming about 1850, and its lead concentrations are below the limit of detection at < 0.03% PbO. (C) Urbanization tends to create scars across rock faces, but developers in an affluent Phoenix neighborhood applied “artificial varnish” (Elvidge and Moore, 1980) to minimize the aesthetic impact of this road cut. (D) Back-scattered electron microscope image of artificial varnish from image C that is experiencing ongoing dissolution, generating a granule-like appearance.

X.4.2. Lead contamination of varnish

The first study of lead in relation to rock varnish occurred with respect to the Earthen figure (or geolyph) called the Bouse Fisherman, a human holding a spear with a quartz tip. The spear is aimed at a wavy line with fish symbols below the wavy line. A field trip lead by the Arizona Geological Survey visited this motif (Spencer and Pearthree, 2015).

Working with the Bureau of Land Management, lead concentrations were measured in the micron-thick varnish that had accreted on the stones that were exposed to make the Bouse Fisherman. This varnish was greatly enriched in lead, analyzed with a 300 second counting time with a wavelength dispersive electron microprobe yielding limits of detection at about 0.03% PbO (Dorn 1998). In contrast, the natural varnish had a very different situation explained as follows:

“Lead accumulates in rock varnishes and dust films on desert surfaces. Electron microprobe profiles reveal that lead is a contaminant in the uppermost surfaces of rock varnishes, but these concentrations drop to background levels below the very surface of natural rock coatings that have formed since lead additives were introduced into gasoline in 1922.” (Dorn 1998: 139)

Figure X.9b exemplifies what is normally encountered when rock varnishes are analyzed. In this figure, lead measurements are superimposed on a color thin section showing varnish microlaminations; note that the lead contamination occurs only after the Wet Holocene Unit 1, which is a microlamination pattern that formed during the Little Ice Age.

Thus, Dorn (1998) found that the Bouse Fisherman is not prehistoric. It was made in the twentieth century, perhaps for fun or perhaps to become a tourist attraction, consistent with the use of twentieth century symbols for water and fish. Since then, lead profiles have been used to authenticate prehistoric petroglyphs (Dorn, 2006; Merrell and Dorn, 2009) as well as to indicate that a regionally famous Marcos de Niza engraving is not real, but 20th century in origin (Dorn et al., 2012a).

The basic observation that lead and other anthropogenic pollutants are enriched in the surface most layer of varnish now has extensive replication (Fleisher et al., 1999; Goldsmith et al., 2014; Hoar et al., 2011; Hodge et al., 2005; Nowinski, 2009; Nowinski et al., 2013; Sims et al., 2017; Spilde et al., 2013). The iron or manganese in varnish scavenge lead from the surrounding environment (Adams et al., 2009; Dong et al., 2002; Grangeon et al., 2017; Hassellöv and von der Kammer, 2006; van Genuchten and Peña, 2016). Twentieth-century industrial activities spread lead and other elemental pollutant around the globe, even in areas distant from major lead-pollution sources (Andersen, 1994; Getty et al., 1999). Fig. X.10a is an epiglacial deposit of boulders near the margin of the Greenland Ice cap. Fig. X.10b superimposes electron microprobe measurements of lead on a back-scattered electron microscope image of rock varnish on the identified boulder in Fig. X.10a. Even in such remote locations as Greenland, rock varnish can record an anthropogenic lead signal.

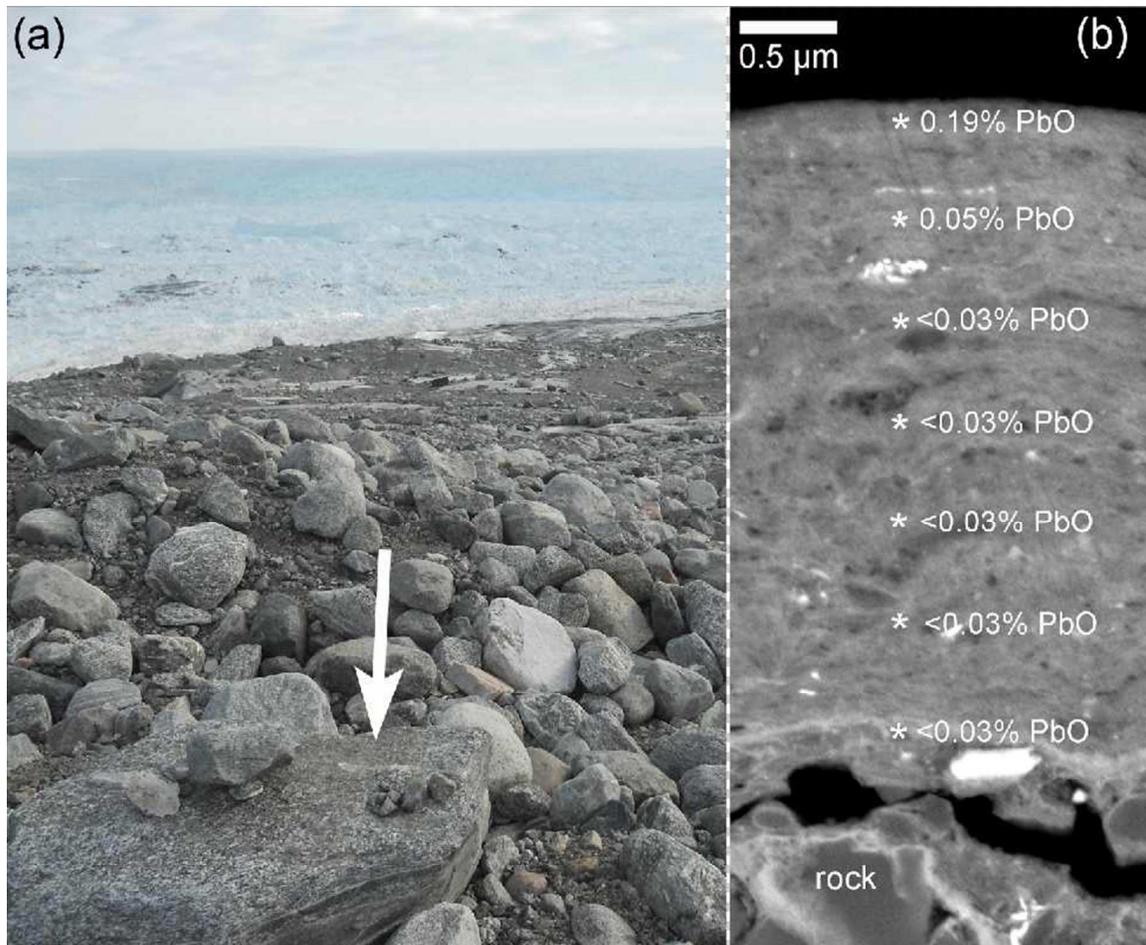


Fig X.10. Epiglacial till of the Greenland glacier contaminated by lead. (a) Greenland outlet glacier study site on a medial moraine, identifying the boulder where rock varnish accreted and has been contaminated by lead. (b) BSE images of a cross-section of rock varnishes where the surface most layer is contaminated with lead (Dorn, 1998). Each electron microprobe measurement point is about 0.5 μm apart, and this means that there exists spatial overlap in the focused beam analyses. Less than 0.03% lead is background, below the limit of detection.

X.4.3. Effects of acidification on varnish

Industrial activity near rock art in the Burrup Peninsula of Western Australia has increased the acidity of atmospheric fallout, exposing rock surfaces to pH values just above 4. Prior to industrialization, the pH values of rock surfaces was near neutral (Black et al., 2017). The substantial decrease in pH leads to reduction of Fe (III) and Mn (IV) to mobile divalent forms. This changes the color of rock and petroglyph surfaces and hence endangers the priceless rock engravings.

Acidity from urban activities in the Los Angeles area led to the development of acid fog in the region (Brewer et al., 1983; Waldman et al., 1982). Fig. X.11. compares a sample of varnish-coated sandstone in the Santa Monica Mountains in

1941 in what is now Tuna Canyon Park less than a kilometer from the Pacific Ocean (Fig.X.11a) and sample collected from the same site in 1983 (Fig. X.11b). The 1941 sample shows the typical laminar appearance of rock varnish. In 1983, however, no laminar varnish was found. Instead, the texture of varnish shows evidence of considerable leaching (Dorn and Krinsley, 1991) in the form of increased porous zones and redistribution of Mn-Fe in the form of stringers deposited along the walls of fractures. One explanation for the substantial change in texture in just four decades could be acid fog increasing the mobility of Mn-Fe.

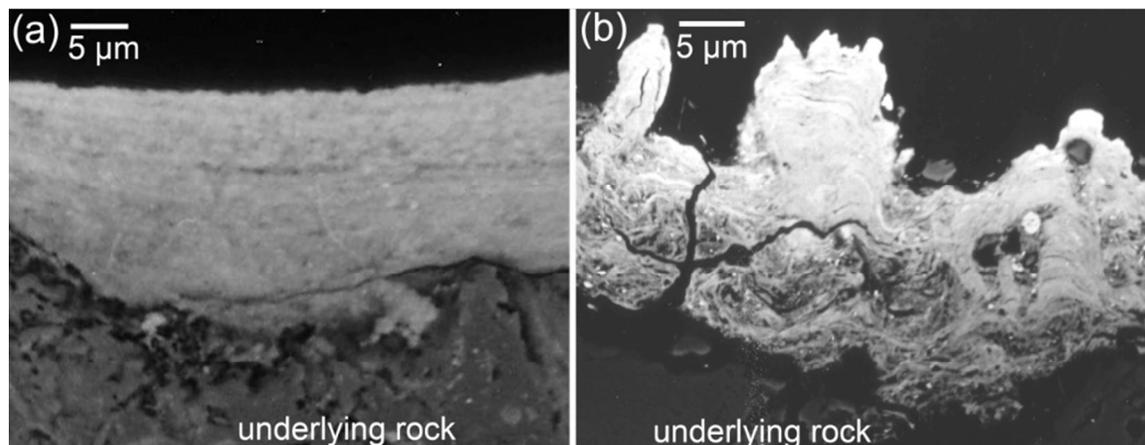


Fig. X.11. Comparison of rock varnish collected near the Pacific Ocean in Los Angeles that was impacted by acid fog. (a) BSE showing a representative image of the laminar texture observed from a sample collected by Joseph Spencer in 1941. (b) The author collected samples from the same site in 1982 and did not find any laminar textures. Instead, the irregular surface, evidence of reprecipitation of Mn-Fe on fracture walls, and zones of leaching could reflect the impact of acid fog.

X.4.4. Dust loading onto varnish

Rock varnish naturally shows considerable variation in its texture as a result of the abundance of aeolian dust. Some varnishes show a finely layered texture without the incorporation of angular pieces of dust (e.g. Figs. X1c and X.11a), but rock varnishes collected from particularly dusty locations do show considerable evidence of angular particles of dust being incorporated into varnish (Aulinas et al., 2015; Dorn et al., 2013).

Anthropogenic activities are known to increase the abundance of dust in many settings (Baddock et al., 2013; Brazel, 1989; Goudie, 2014), with Owens (Dry) Lake as an example. Diversion of water to Los Angeles lead to Owens (Dry) Lake becoming the largest single source of particulate matter under 10 μm in the USA (District, 2013). Severe drought in California exacerbates the dust problem in the region (Borlina and Rennó, 2017).

An example of the impact of anthropogenic dust loading in the region can be found even in the high alpine setting of the nearby Palisades Glacier of the Sierra Nevada, California. Boulders immediately adjacent to the margin of the Palisades Glacier accumulated dust material whose source could be from Owens (Dry) Lake. A

reason why anthropogenic dust from Owens (Dry) Lake is the suspected cause is the presence of chlorine (sum spectrum in Fig. X.12b). Chlorine would not be expected if the source of dust was local, but ongoing additions of chlorine, and then removal by leaching from snowmelt, would be consistent if at least some of the dust had a source related to Owens (Dry) Lake.

The dust is cemented by silica glaze rather than manganiferous rock varnish (Fig. X.12). Silica glaze is a coating composed primarily of amorphous silica, but sometimes mixed with aluminum and iron (Dorn, 1998). Its formation is abiotic and results from nanoscale deposition of silica spheroids (Langworthy et al., 2010). Silica glaze often interdigitates with other rock coatings such as varnish (Dorn, 1998).

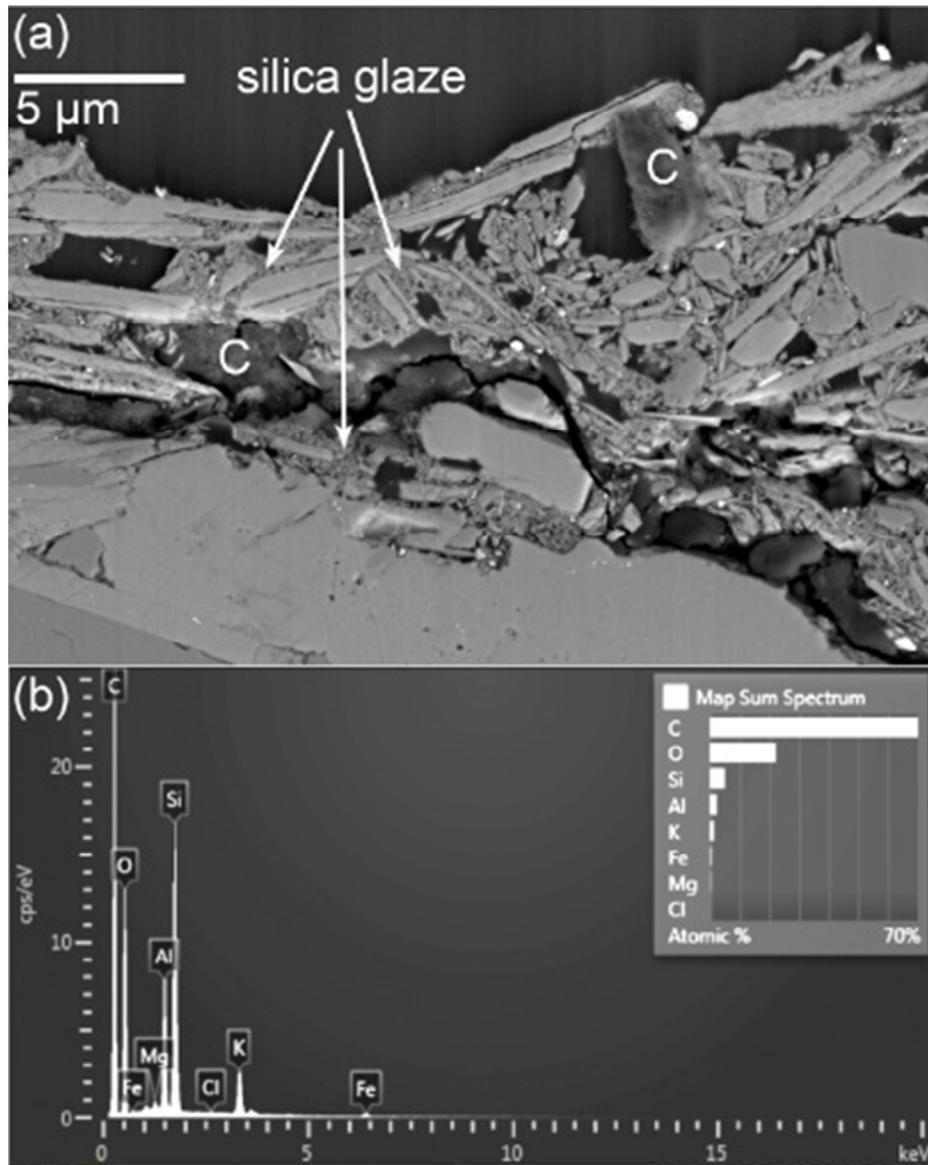


Fig. X.12 Silica glaze is the cement for dust fall on a glacial boulder next to the Palisades Glacier, Sierra Nevada, California. (a) BSE image of dust inorganic mineral

and organic (C, carbon) particles. (b) Several EDS analyses of this and similar cross sections were combined and the spectra is a sum of all of the EDS data gathered for the coating. The Cl in the sum spectrum is a signal consistent with the source of the dust being from Owens Dry Lake, even though snowmelt would gradually leach Cl over time in this environmental setting. The strong C signal reflects the carbon coating and organic materials; the other elements derive from the dust particles and inorganic minerals the compose much of the dust.

X.4.5. Wildfire interactions with varnish

Wildfires, both natural and human caused, result in millimeter and centimeter-scale spalling of rock surfaces, thus removing rock varnish (Dorn, 2003). However, human activities have accelerated the incidence of wildfires in dryland settings such as the western USA (Abatzoglou and Williams, 2016). A minimally explored arena of research involves the interactions of rock coatings and wildfire ash (Tratebas et al., 2004). Fig. X.13 illustrates how chalking of petroglyphs has combined with ash from wildfire to make a paste that adheres to and coats the underlying natural rock varnish. This one pilot study indicates interactions between human-induced wildfires and rock varnish, however, and there are undoubtedly far more interactions than those observed by Tratebas et al. (2004).

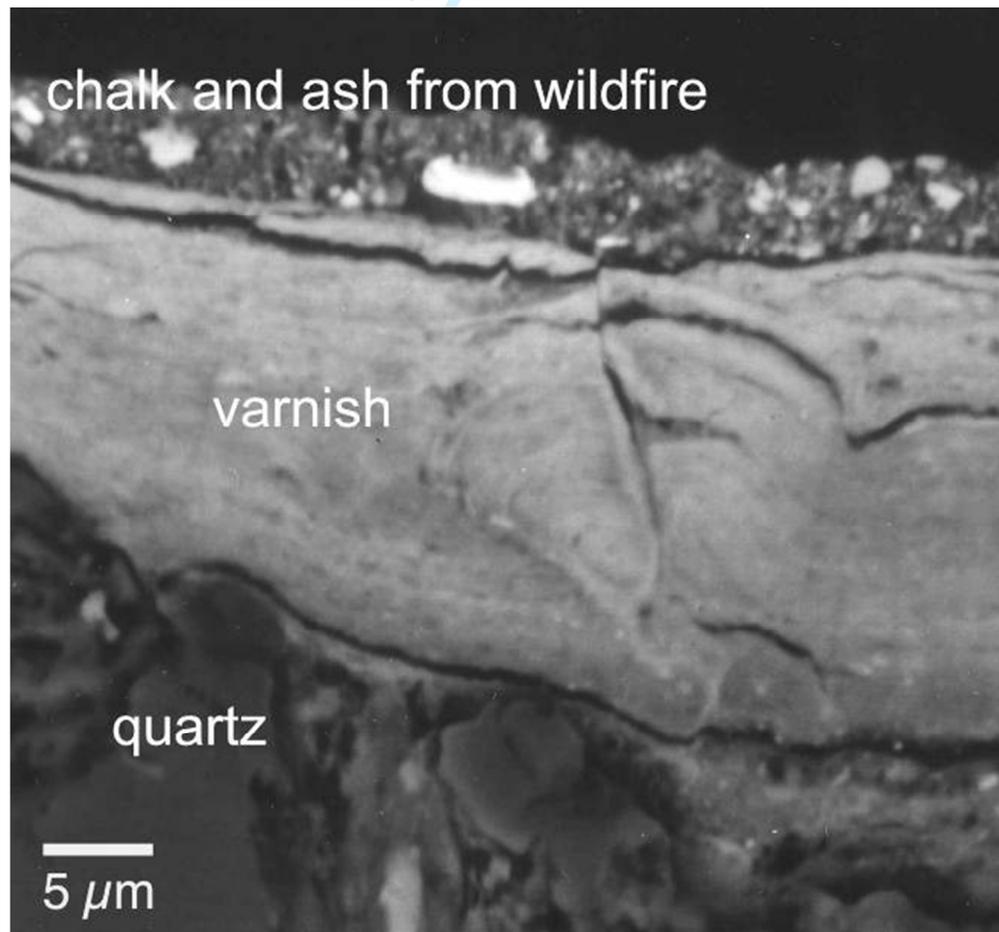


Fig. X.13. BSE image of petroglyph that was chalked by amateur archaeologists in hopes of improving a photograph of the motif at Whoop-up Canyon, Wyoming (Tretabas et al., 2004). Then, a wildfire influenced the area, and the chalk mixed with soot from a wildfire. The combination of chalk and ash adhered to the underlying rock varnish for a period of at least 1.5 years when the sample was collected.

X.5 Summary

This chapter concerns the natural, slow growing rock coating known as rock varnish. Rock varnish (sometimes called desert varnish in warm arid settings) is typically less than 50 micrometers thick, but it can completely darken rock surfaces changing even the lightest colored rock black. The key to understanding its formation rests in the process by which iron and especially manganese is greatly concentrated in this rock coating — well over 50 times concentrations in the underlying rock, dust or nearby soil.

There are a number of competing explanations for how the manganese (and iron) concentration occurs. Abiotic explanations involving small pH-Eh fluctuations and a plethora of different organisms such as bacteria and fungi can explain Mn concentration found in varnish. However, all extant explanations except one do not involve a rate-limiting step. If any of the proposed abiotic explanations actually made varnish, it would form in deserts at rates orders of magnitude faster than the observed microns per millennia rates. If all of the various biotic concentration mechanisms were in play, formation rates would be even faster. The only process that explains the Mn (and Fe) concentration and also slow rate of formation involves the occasional growth of budding bacteria. Also, budding bacteria are the only proposed agent of varnish formation with direct observational support of observed *in situ* concentration of Mn (and Fe).

The focus of this chapter rests in exploring interactions between natural rock varnish and human modification of the environment. Prehistorically, humans used rock surfaces darkened by varnish as 'blackboards' on which to engrave motifs called petroglyphs. Humans also altered stones and boulders to create Earthen art, and in the process modified rock varnish in such a way as to change its relative position, and as a consequence allow its dating by radiometric and varnish microlamination methods.

The biogeochemistry and structure of rock varnish has been modified by human activities in a number of different ways. At the global scale, atmospheric lead pollution (as well as other heavy metals) has contaminated the surface-most micrometer of varnish, even in such remote areas as Greenland. At the regional scale, modification of the earth to create dry lake beds has created massive dust loadings that have altered the structure of rock coating formation in general in the surrounding region. Also at the regional scale, acidification of the environment in the Los Angeles area of California and the Burrup Peninsula in Australia has dissolved Mn and Fe from the varnish and altered its structure; a ripe area for future biogeochemical research involves the alteration of rock varnish in other settings

acidified by anthropogenic activities. More locally, ash from wildfire has combined with anthropogenic graffiti such as chalk on rock surfaces to alter rock coatings. A final example of human activities involves the attempt by wealthier suburban housing developments to mimic natural rock varnish by coating road scars with artificial varnish, still composed of Mn and Fe, but lacking clay minerals and hence lacking long term stability.

Key publications

- Dorn, R.I., 2013. Rock coatings. In: Pope, G.A. (Ed.), *Treatise on Geomorphology*, vol. 4. Academic Press, San Diego, pp. 70-97.
[*Introduction to the great variety of natural rock coatings*]
- Krinsley, D.H., Dorn, R.I., DiGregorio, B.E., Razink, J., Fisher, R., 2017. Mn-Fe enhancing budding bacteria in century-old rock varnish, Erie Canal, New York. *Journal of Geology*, **125**, 317-336.
[*Presents latest key evidence about the formation of rock varnish*]
- Liu, T., 2018. VML Dating Lab. <http://www.vmldating.com/>, **last accessed June 20**.
[*Greatest website about rock varnish and the nature of its layering patterns*]
- Schindler, M., Dorn, R.I., 2017. Rock and mineral coatings: Records of climate change, pollution, and life. *Elements*, **13** (3). GeoScienceWorld, McLean, VA.
[*Special issue of Elements devoted to rock coatings*]
- Spilde, M.N., Melim, L.A., Northrup, D.E., Boston, P.J., 2013. Anthropogenic lead as a tracer for rock varnish growth: implications for rates of formation. *Geology*, **41**, 263-266.
[*One of the most thorough analyses of the geochemical imprint of human pollution on rock varnish*]

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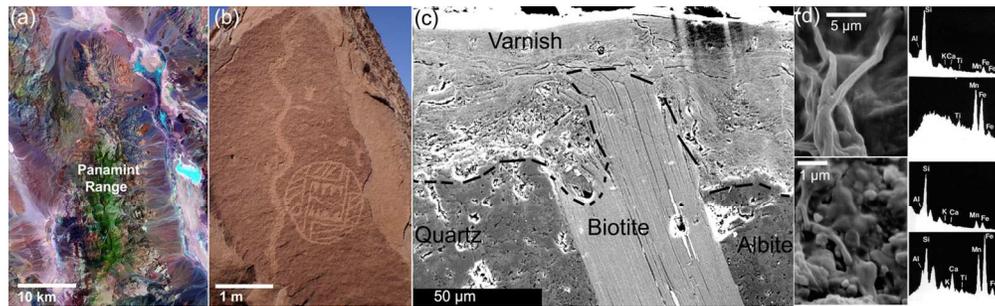
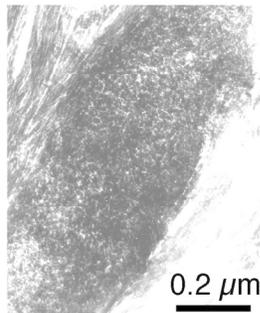
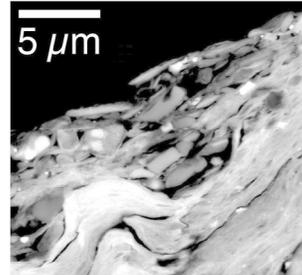


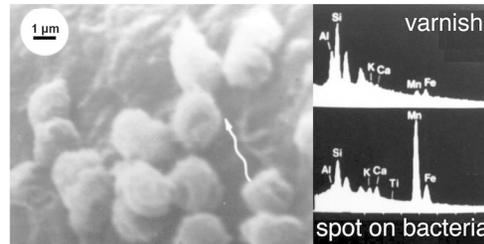
Fig. X.1 Rock varnish viewed at different scales. (a) Alluvial fans debouching from the Panamint Range into Death Valley on the east and the Panamint Valley on the west are visibly darkened with varying amounts of rock varnish. Thanks to NASA for the Landsat 7 image (<https://earthobservatory.nasa.gov/IOTD/view.php?id=6470>). (b) Petroglyph carved into a joint face partly coated with rock varnish from Petrified Forest National Park. (c) Secondary electron image of rock varnish coating rocks of the Orinoco River, the first site for the scholarly study of rock varnish (von Humboldt, 1812). (d) Bacteria sheaths concentrating Mn-Fe rich material in rock varnish from Tibet (Krinsley et al., 2009), as indicated by energy dispersive spectra of bacteria hyphae as compared with spectra of the adjacent varnish.

127x38mm (300 x 300 DPI)

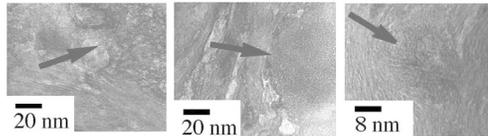
Physical Barrier: van der Waals force promotes dust accumulation, providing raw ingredients of clays



Biological Barrier: Mn and Fe fixation in bacteria sheaths



Dissolution from cell wall (granular fragments)



&

Physiochemical Barrier: Fixation in clay matrix cementing mixed-layered clays

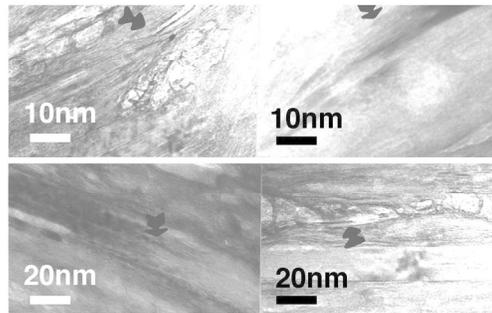


Fig. X.2 Rock varnish accretion requires a series of different types of barriers to transport of the various constituents.

152x231mm (300 x 300 DPI)

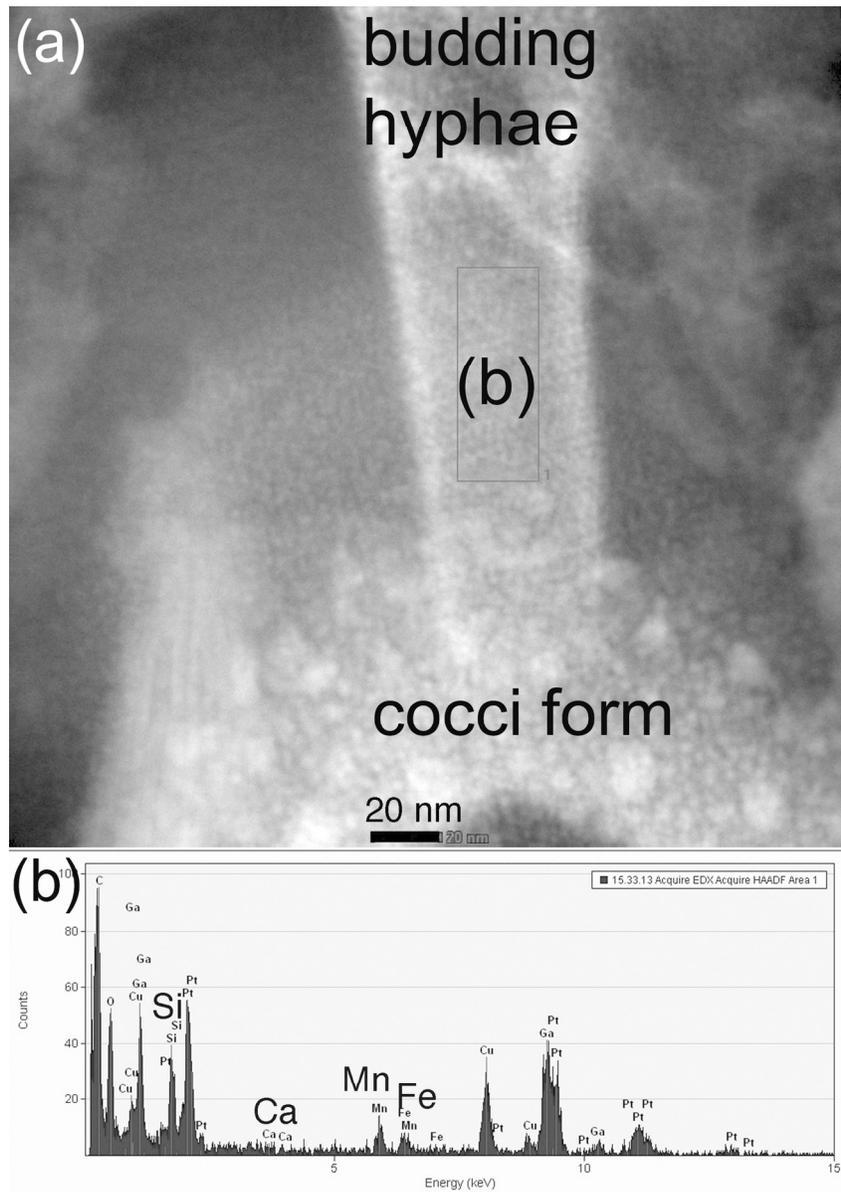


Fig. X.3. High resolution perspective on fixation of Mn and Fe. (a) Electron microscope image of budding bacteria concentrating Mn and Fe (Krinsley et al., 2017), where a budding hyphae emerges from a cocci bacterial form. (b) location in image (a) matching the energy dispersive spectra showing the enhancement of Mn and Fe with Si and small amounts of Ca. The other peaks are artifacts associated with sample preparation.

127x180mm (300 x 300 DPI)

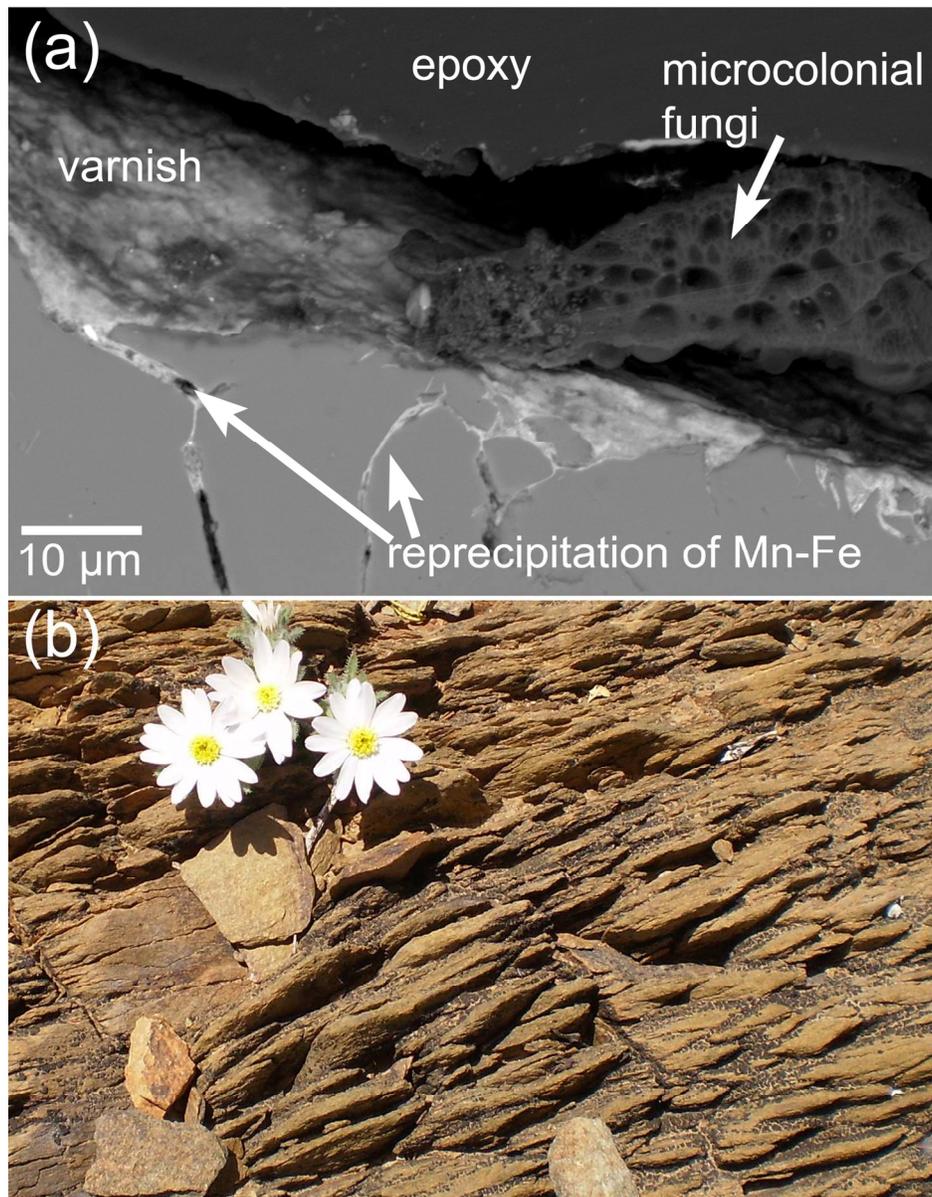


Fig. X.4.

Biofilms grow on rock surfaces where sufficient moisture exists (Viles, 2011). Such biofilms in the Sonoran Desert of central Arizona typically consist of fungi and lichens. (a) Microcolonial fungi secretes organic acids that then dissolve the Mn and Fe in varnish. In the case of this cross-section view using backscattered electrons some of the Mn and Fe have been reprecipitated in rock fractures. (b) Field site near Black Canyon City, where flower widths of 2 cm provide scale.

130x168mm (300 x 300 DPI)



Fig. X.5. Newspaper Rock at Petrified Forest National Park exemplifies how rock varnish provides a 'blackboard' for prehistoric rock engravings that range in age from terminal Pleistocene to the twentieth century (Dorn, 2006).

127x95mm (300 x 300 DPI)

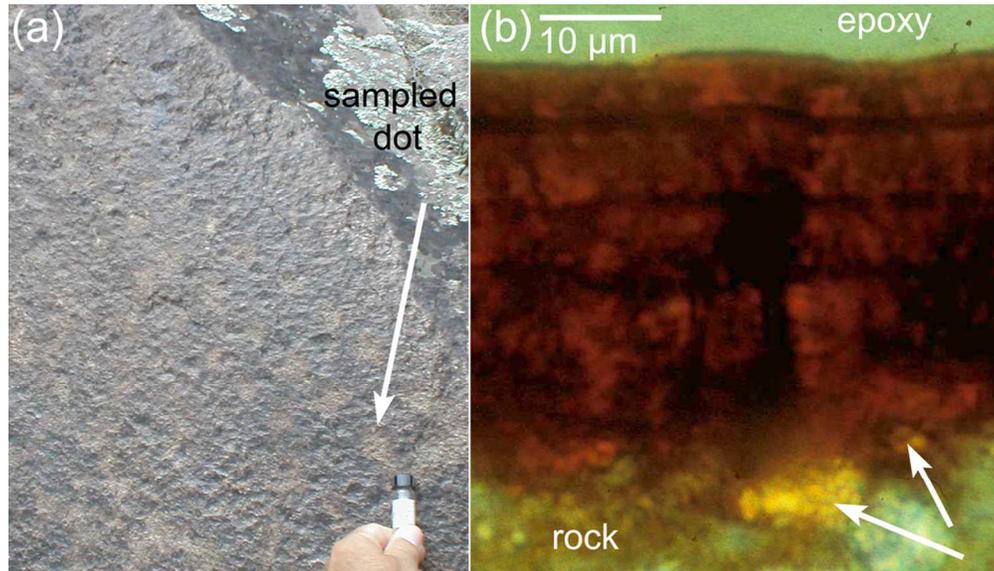


Fig. X.6. An engraving consisting of a pattern of dots (image a), at Buffalo Eddy, Washington, USA, was subjected to painting. Iron-rich materials, perhaps goethite, was painted into the dots. (b) Then, rock varnish formed on top of the paint material, as seen in a light microscope ultrathin cross-section of varnish. Arrows in (b) identify the iron-rich materials as confirmed by energy dispersive X-ray analyses.

101x58mm (300 x 300 DPI)

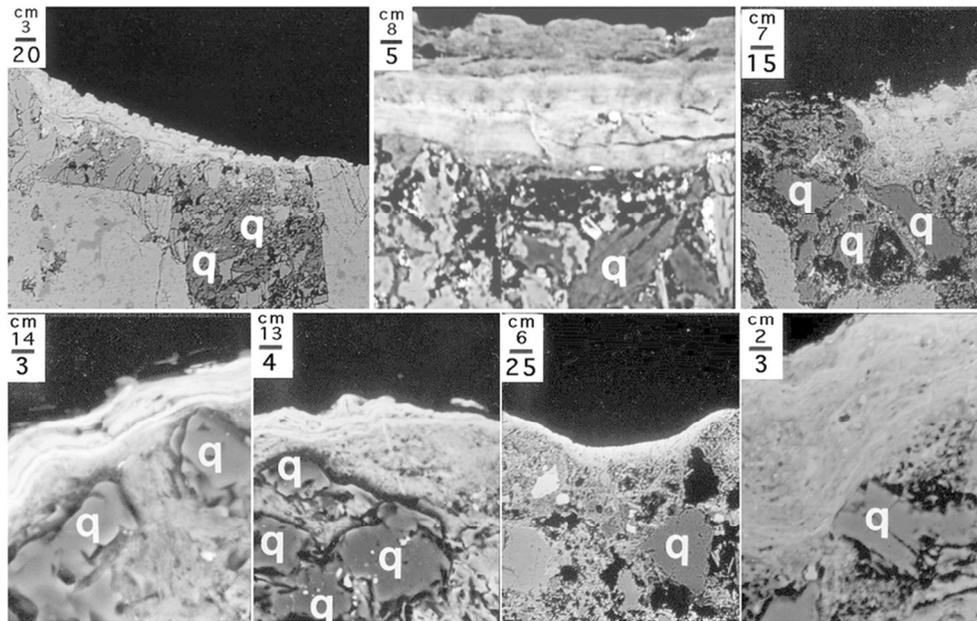


Fig. X.7. The Conejo Mine petroglyph site in the Coso Range, eastern California, consists of a basalt flow that lacks free quartz. Backscattered electron micrographs of cross-sections of rock varnish formed on top of engravings regularly reveal the presence of quartz — identified by the letter q. The numbers CM3, CM8, CM7, CM14, CM13, CM 6 and CM2 refer to specific engravings sampled (Whitley, 2000; Whitley, 2001; Whitley et al., 1999).

79x50mm (300 x 300 DPI)

Only

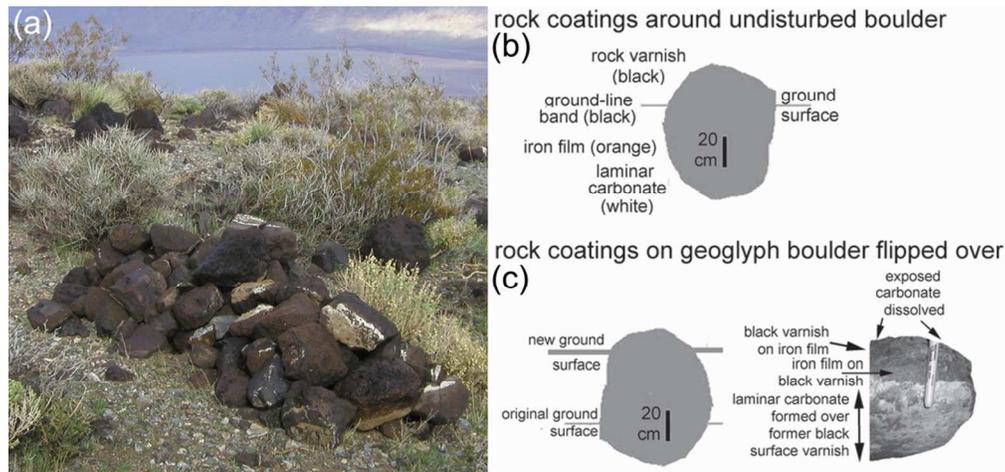


Fig. X.8. Rock cairn from the Panamint Valley, eastern California (Cerveny et al., 2006). The boulders used to build this cairn came from a desert pavement with considerable antiquity (Seong et al., 2016). Some of the boulders were flipped on their side and embedded deeply in the ground. These boulders formed laminar carbonate on top of rock varnish. Thus, the original sequence of rock coatings in image b was altered to image c. The laminar carbonate only started to form after the cairn was constructed, thus a radiocarbon age for the laminar carbonate provides a minimum age for the cairn.

101x47mm (300 x 300 DPI)

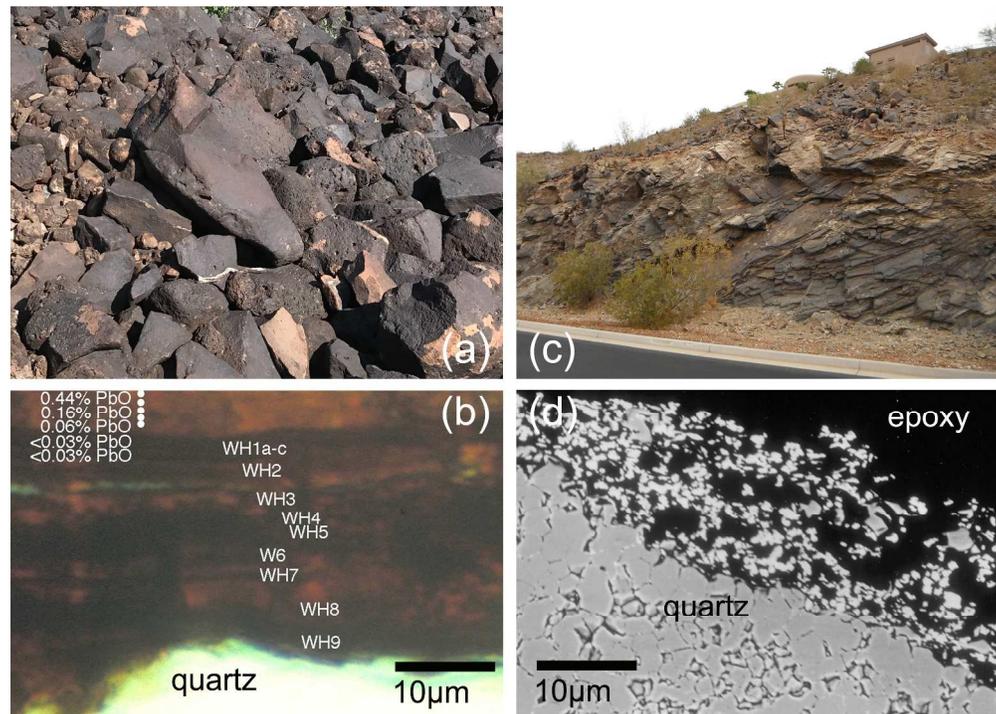


Fig. X.9. Rock varnish as the dominant natural rock coating in metropolitan Phoenix. (A) Colluvial boulder field at Shaw Butte darkened by rock varnish. The occasional orange iron film indicates rocks spalled by the dirt cracking process (Figure 13.3). (B) Microlaminations form discrete black, orange, and yellow layers in rock varnish thin sections. Electron microprobe analyses reveal a spike in lead in the uppermost micron of this rock varnish from the Phoenix area. Background levels occur once the layer of the varnish is beneath the 20th century. The layer WH1 ceased forming about 1850, and its lead concentrations are below the limit of detection at < 0.03% PbO. (C) Urbanization tends to create scars across rock faces, but developers in an affluent Phoenix neighborhood applied “artificial varnish” (Elvidge and Moore, 1980) to minimize the aesthetic impact of this road cut. (D) Back-scattered electron microscope image of artificial varnish from image C that is experiencing ongoing dissolution, generating a granule-like appearance.

1182x845mm (72 x 72 DPI)

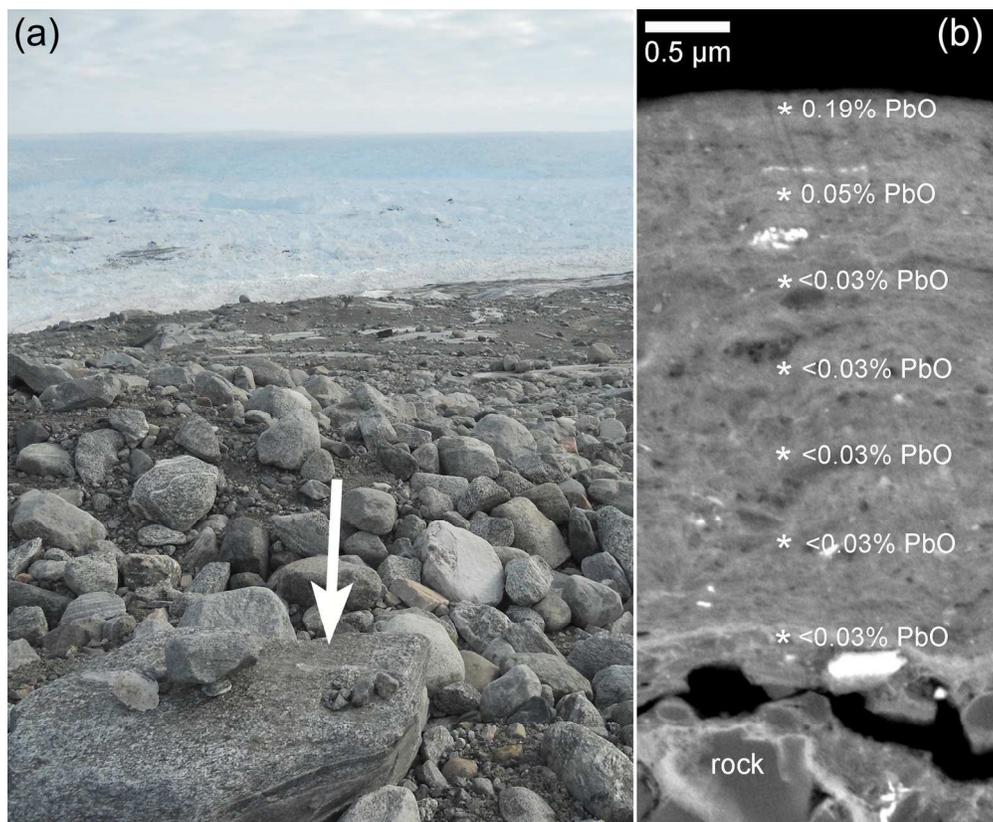


Fig X.10. Epiglacial till of the Greenland glacier contaminated by lead. (a) Greenland outlet glacier study site on a medial moraine, identifying the boulder where rock varnish accreted and has been contaminated by lead. (b) BSE images of a cross-section of rock varnishes where the surface most layer is contaminated with lead. Each electron micorprobe measurement point is about 0.5 μm apart, and this means that there exists spatial overlap in the focused beam analyses. Less than 0.03% lead is background, below the limit of detection.

152x125mm (300 x 300 DPI)

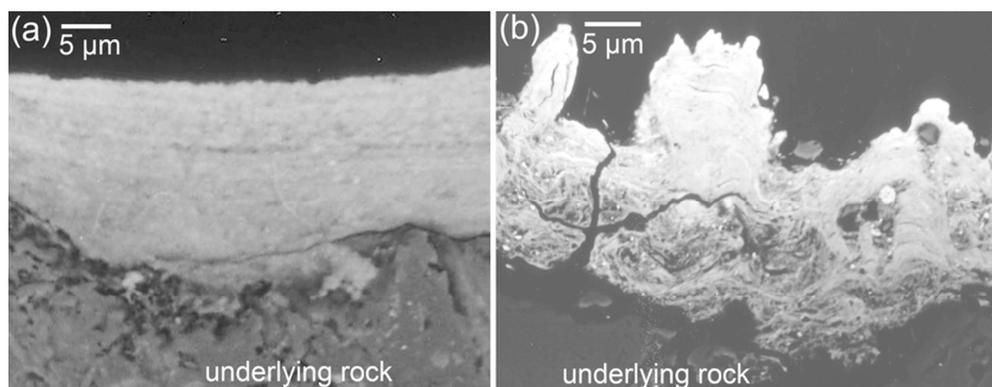


Fig. X.11. Comparison of rock varnish collected near the Pacific Ocean in Los Angeles that was impacted by acid fog. (a) BSE showing a representative image of the laminar texture observed from a sample collected by Joseph Spencer in 1941. (b) The author collected samples from the same site in 1982 and did not find any laminar textures. Instead, the irregular surface, evidence of reprecipitation of Mn-Fe on fracture walls, and zones of leaching could reflect the impact of acid fog.

83x32mm (300 x 300 DPI)

Review Only

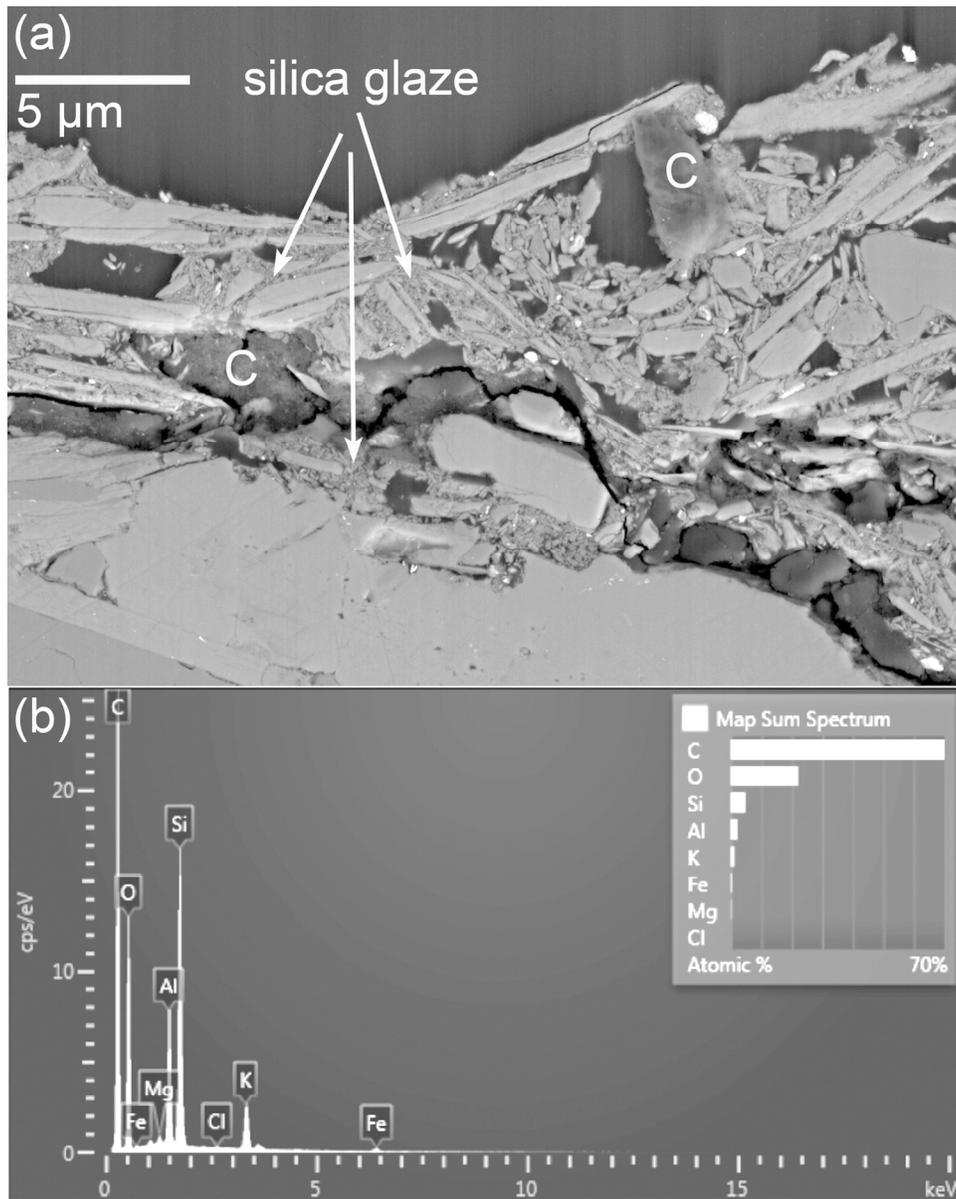


Fig. X.12 Silica glaze is the cement for dust fall on a glacial boulder next to the Palisades Glacier, Sierra Nevada, California. (a) BSE image of dust inorganic mineral and organic (C, carbon) particles. (b) Several EDS analyses of this and similar cross sections were combined and the spectra is a sum of all of the EDS data gathered for the coating. The Cl in the sum spectrum is a signal consistent with the source of the dust being from Owens Dry Lake, even though snowmelt would gradually leach Cl over time in this environmental setting. The strong C signal reflects the carbon coating and organic materials; the other elements derive from the dust particles and inorganic minerals the compose much of the dust.

126x158mm (300 x 300 DPI)

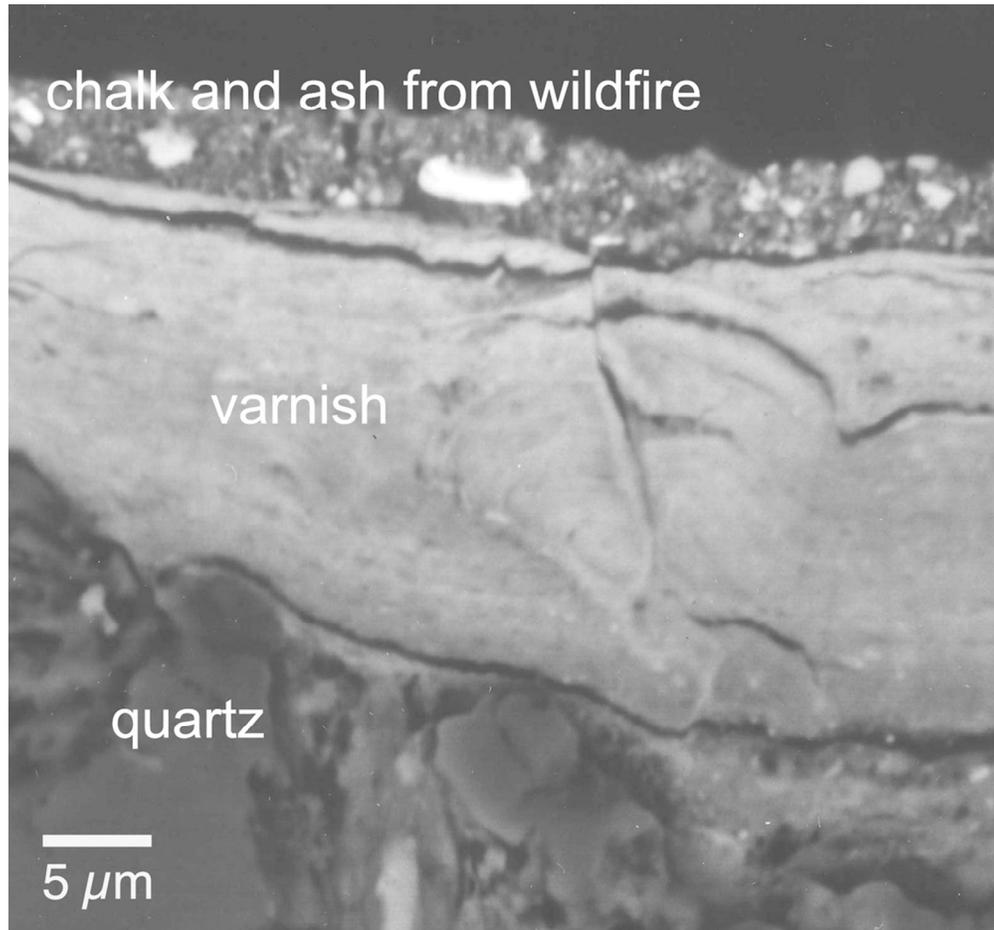


Fig. X.13. BSE image of petroglyph that was chalked by amateur archaeologists in hopes of improving a photograph of the motif at Whoop-up Canyon, Wyoming (Tretabas et al., 2004). Then, a wildfire influenced the area, and the chalk mixed with soot from a wildfire. The combination of chalk and ash adhered to the underlying rock varnish for a period of at least 1.5 years when the sample was collected.

101x94mm (300 x 300 DPI)