



Rock varnish revisited

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Abstract

Investigators seeking to solve the mystery of rock varnish formation have yet to embrace hypothesis testing. Thus, this paper presents nine tests that assess the validity of the eight hypotheses proposed over the last four decades to explain varnish formation. An almost singular focus on manganese (Mn)-enrichment by many in varnish research may have led to six of the eight hypotheses failing to explain iron (Fe)-enrichment, as well as why clay minerals dominate the composition of rock varnish. Many varnish researchers displayed a sampling bias by collecting samples only from hot and dry deserts; thus, it should be of no surprise that four hypotheses failed a test of explaining varnishes in different climates; five hypotheses failed to explain varnishes in subsurface locations; and seven hypotheses failed to explain differences in varnish growth rates in hot deserts versus wetter locations. In the end, seven of eight proposed hypotheses to explain varnish formation failed more than five tests, any one of which would falsify the hypothesis. Only one hypothesis “passed” all nine tests.

Keywords

Budding bacteria, diagenesis, microbial, nanoscale, rock coating, scholarship

Introduction

The history of science is replete with alternative hypotheses to explain patterns of empirical observations (Cleland, 2001; Elliott and Brook, 2007; Nordstrom, 2012). Tests of these hypotheses sometimes facilitate refinement of a hypothesis and sometimes undermine a hypothesis altogether (Koslowski, 1996; Poincaré, 2001). While some have argued against the use of hypothesis testing in scientific research (England, 1991), it is most unusual for a field of science to eschew hypothesis testing.

This journal published “rock varnish” four decades ago (Dorn and Oberlander, 1982) as a synthesis of past scholarship, a summary of its basic characteristics, combined with advocating the importance of microorganisms in the formation of rock varnish.

In the four decades that followed, an expansion of interest resulted in the application of new methods, generating new insights and new ideas on how varnish forms. This growth in empirical knowledge, however, lacked a concomitant development in normal scientific research: hypothesis testing. The purpose of this paper rests in establishing specific tests and then applying these tests on hypotheses of rock varnish formation.

Before these tests can be explained, however, it is important to first overview the nature of rock varnish

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in the next section. Then, I present the nine tests of hypotheses of rock varnish formation. Methods and research results are then incorporated into the section that presents new data used in testing the polygenetic model of varnish formation. The fifth part of this paper subjects other hypotheses to the nine tests. A discussion section then pulls together some common themes in research exploring the origins of rock varnish.

What is rock varnish?

Rock varnish consists of over half clay minerals, about a third Mn and Fe oxides, as well as minor and trace elements that deposits as a paper-thin accretion on an underlying rock. This definition remains basically unchanged from [Potter and Rossman \(1977\)](#) and has been adopted widely: ([Andreae et al., 2023](#); [Aulinas et al., 2015](#); [Chaddha et al., 2021, 2022, 2024](#); [Dietzel et al., 2004](#); [Dorn and Oberlander, 1982](#); [Dragovich, 1988](#); [Drake et al., 1993](#); [Elshabrawy and Ali, 2021](#); [Esposito et al., 2019](#); [Forster et al., 2021](#); [Glazovski, 1985](#); [Harrington, 1987](#); [Hodge et al., 2005](#); [Hungate et al., 1987](#); [Jahn and Maneck, 1991](#); [Jones, 1991](#); [Krinsley, 1998](#); [Krinsley et al., 2013](#); [Krumbein and Jens, 1981](#); [Kuhlman and Abrecht, 2008](#); [Kuhlman et al., 2006](#); [Lingappa et al., 2021a](#); [Liu et al., 2021](#); [Martinez-Pabello et al., 2021a, 2021b](#); [McKeown and Post, 2001](#); [Nagy et al., 1991](#); [Northup et al., 2010](#); [Otter et al., 2020](#); [Pineda et al., 1988](#); [Reneau et al., 1992](#); [Spilde et al., 2007, 2013](#); [Wang et al., 2011](#); [Wayne et al., 2004](#); [Whalley et al., 1990](#); [Xu et al., 2019](#); [Zerboni et al., 2022](#); [Zhang et al., 2012](#); [Zhou et al., 2000](#)).

[Figure 1](#) illustrates the clay-Mn-Fe-rich definition of rock varnish, using equipment that is typically available at universities around the world. The ultrathin section in [Figure 1\(A\)](#) shows black (Mn-rich), orange (Mn-low), and yellow (Mn-absent) microlaminations ([Perry and Adams, 1978](#)). [Figure 1\(A\)](#) also illustrates the importance of trace/minor elements, where asterisks indicate the location of electron microprobe measurements of PbO. The upper few microns have a strong lead spike ([Figure 1\(A\)](#)) from 20th century pollution ([Dorn, 1998](#); [Spilde et al., 2013](#)).

[Figure 1\(B\)](#) and [1\(C\)](#) present different sorts of electron micrographs showing the clay-Mn-Fe-rich nature of rock varnish. A back-scattered electron (BSE) image, from Kitt Peak, Arizona, shows the sheet-like nature of clay minerals causing a layered texture ([Figure 1\(B\)](#)). [Figure 1\(C\)](#) includes three different types of imagery of rock varnish from the tropical Kaho'olawe Island Hawai'i. First, the secondary image ([Figure 1\(C2\)](#)) illustrates a botryoidal morphology on top of layered texture. Then, this sample was polished for the BSE image ([Figure 1\(C1\)](#)) that also shows a botryoidal texture on layered varnish. Botryoidal textures develop in wetter climates where Mn-Fe accumulates around discrete nucleation clusters ([Dorn, 1986](#)). The layering imposed by clays can be seen at the highest magnifications ([Figure 1\(C3\)](#)). This type of imagery, along with chemical analyses, reflect the dominance of clay minerals, abundant Mn-Fe oxides, and a mix of minor and trace elements.

Rock varnish is not limited to any particular climate region, or to any particular environmental setting, even though varnish is most noticeable on subaerial rocky surfaces in warm deserts—hence its older name of “desert varnish.” Rock varnish is not limited to: (i) particular textures such nanoscale layering imposed by the dominance of clay minerals ([Krinsley et al., 1995](#)); (ii) samples that have microlaminations or those that do not ([Liu and Broecker, 2013](#); [Liu et al., 2013](#)); (iii) very slow growing varnish that forms at rates of microns per millennia ([Dorn, 1998](#); [Liu and Broecker, 2000](#)) or faster-accumulating varnishes ([Dorn and Meek, 1995](#); [Spilde et al., 2013](#)); (iv) varnishes that contain variations in minor or trace elements such as barium ([Dorn et al., 1990](#)), lead ([Dorn, 1998](#); [Hoar et al., 2011](#); [Otter et al., 2020](#); [Sims et al., 2022](#); [Spilde et al., 2013](#)), and others ([Thiagarajan and Lee, 2004](#)); (v) varnishes with particular suites of organic matter ([Chaddha et al., 2023](#); [Nagy et al., 1991](#)); or (vi) varnishes with ancient organic matter than can become entombed in an under varnish ([Cremaschi et al., 2014](#); [Wang et al., 2023](#); [Zerboni and Cremaschi, 2007](#)).

Mn-mineralogy is not part of this definition, because ongoing diagenesis at the nanoscale transforms Mn-oxides, as interlayer cations exchange with slight

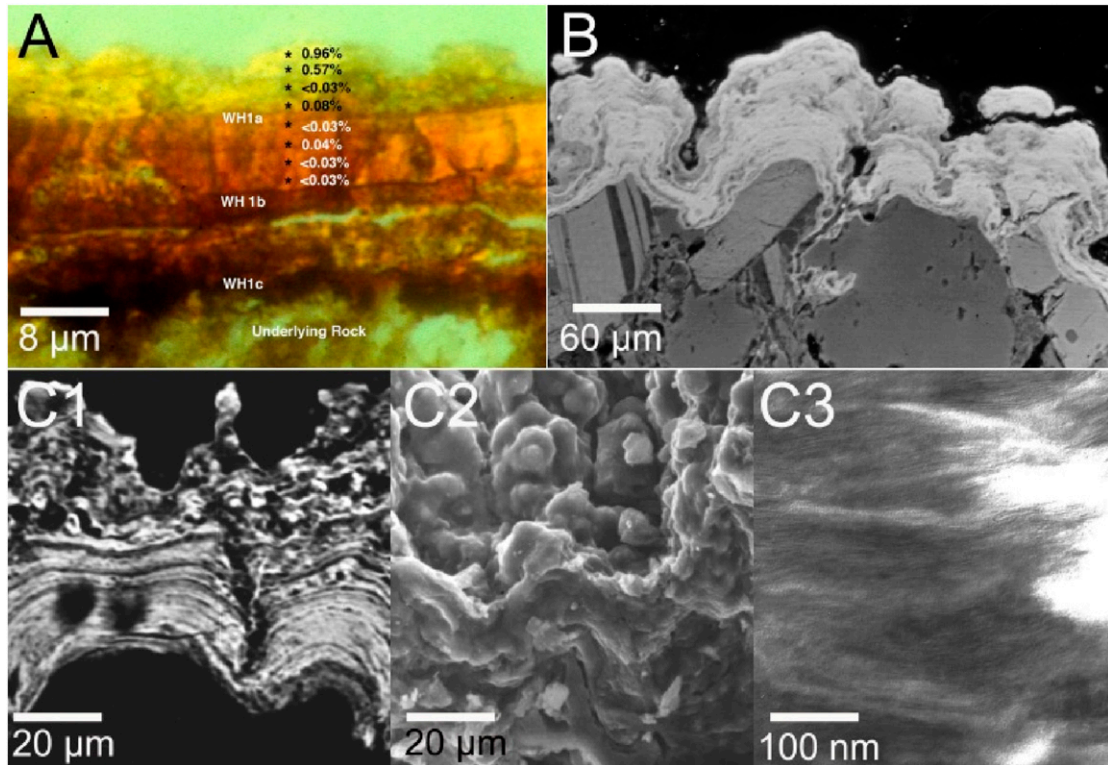


Figure 1. Different microscope views of rock varnish in cross-section. A: Optical ultrathin section from the Sonoran Desert, Arizona, where electron microprobe data reveal the upper 4 microns to be contaminated with more than ½ percent lead from Phoenix area, Arizona, air pollution. B: Semi-arid varnish resting on quartz and feldspar of Kitt Peak, Arizona. C1-C2-C3: Back-scattered electron, secondary electron and high resolution transmission microscopy images of rock varnish from Kaho’olawe, Hawai’i. For interpretation of the references to colours in this figure legend, refer to the online version of this article.

changes in chemistry shifts mineralogy between todorokite or birnessite-like phases at the nanoscale (McKeown and Post, 2001). This definition does not exclude varnishes with an abundance of mineral detritus (Aulinas et al., 2015; Dorn et al., 2013), nor does it exclude varnishes that have undergone a lot of internal dissolution and internal reprecipitation of varnish constituents (Krinsley et al., 1990). While its coloration tends to be dark because of the dominance of Mn-oxides as a whole, considerable color variations occur (Dorn and Oberlander, 1982).

This definition, however, does exclude rock coatings like heavy metal skins and case hardening that can be rich in Mn and Fe (Dorn, 1998, 2022). A

variety of heavy metal skins form rock coatings (Dorn, 1998, 2022) that do not include a significant clay component, such as thin Mn-skins (Carpenter and Hayes, 1978; Eren et al., 2014; Gatuingt et al., 2021; Sharps et al., 2020; Tani et al., 2003) and thicker ferromanganese accumulations (Dorn, 1998; Spinks and Uvarova, 2019). Case hardening involves the reprecipitation of the remobilized rock coatings, including rock varnish constituents, inside the porous weathering rind of a rock (Conca and Rossman, 1982; Dorn et al., 2012a, 2017). Hence, case hardening is not a rock coating, but rather externally-sourced materials infused into the decayed outer weathering rind of a rock.

Key tests to adjudicate proposed hypotheses of rock varnish formation

Revisiting the physical geography of rock varnish (Dorn and Oberlander, 1982) should review advances in scholarship over the last 40 years. This review's length, however, is equivalent to a separate paper. This detailed analysis of prior scholarship is, therefore, presented in [Supplemental File 1](#). The organization of this scholarship review in [Supplemental File 1](#) focuses on prior research as the empirical foundation of the nine tests of hypothesis to explain rock varnish formation.

These nine tests are formulated as questions here. Does the proposed hypothesis explain:

- (i) the great enrichment in Mn compared with potential source materials?
- (ii) the substantial enrichment in Fe above potential source materials?
- (iii) the abundance of clay minerals?
- (iv) the nature of the contact between varnish and the underlying rock surface?
- (v) varnish occurrence on subaerial surfaces in all different climate regions?
- (vi) varnish occurrence in settings that have not been exposed to sunlight?
- (vii) the paucity of microfossils within varnish? [applies to biotic hypotheses only]
- (viii) ongoing diagenesis of varnish at the nanoscale?
- (ix) variable rates of accretion in various environmental settings?

Testing the polygenetic hypothesis of varnish formation involving budding bacteria

The polygenetic model

The polygenetic model of varnish formation (Figure 2) combines three types of abiotic processes with budding bacteria as the main agent of Mn and Fe enhancement (Dorn, 1998, 2007, 2009, 2019; Krinsley et al., 2013, 2017). The polygenetic model starts with an abiotic step that allows raw varnish ingredients to attach to surfaces, such as van der

Walls force or the presence of cations that can flocculate clays.

Then, budding bacteria grow and enhance and fix Mn and Fe in cellular casts or sheaths. A variety of budding bacterial forms have been noted in association with rock varnish including *Pedomicrobium* spp. (Braun et al., 2009; Dorn and Oberlander, 1981b; Taylor-George et al., 1983), *Hyphomicrobium* spp. (Palmer et al., 1985), and *Metallogenium* (Bolotina, 1976b; Dorn and Oberlander, 1981a) (whose DNA suggests it may be associated with *Gallionella* in some acidic contexts (Walsh and Mitchell, 1973).

The third step is abiotic and involves nanoscale diagenesis that breaks down Mn-Fe cell casts into smaller granular pieces. The fourth step is also abiotic that involves nanoscale movement of Mn-Fe granules into clay minerals, cementing those clays to varnish. Each of these steps will be detailed with in situ evidence in subsequent testing of this hypothesis in the results section.

Methods

The entire focus of the methods used here is to employ a “gold standard” for research on rock varnish formation: in situ electron microscope observations of the process in action. This requires “seeing the process” (imaging) that is carrying out the Mn-Fe-enhancement and documenting that enhancement by energy dispersive spectroscopy (EDS). This gold standard is the same for all proposed hypotheses: “seeing the process is believing” turns an interesting idea into something more than theoretical modeling or speculation.

The gold standard of evidence requires: (i) imaging the Mn-Fe-enhancement in all of the various environmental settings where varnish occurs; (ii) in situ chemistry of the enhancement via EDS; (iii) imaging and obtaining EDS chemistry on the breakdown of Mn-Fe fragments small enough to interact with clay minerals; and (iv) documenting the insertion of these Mn-Fe-rich fragments into clay minerals.

Research for the first “rock varnish” paper in this journal focused on determining if this gold standard of evidence could be met. This assessment required

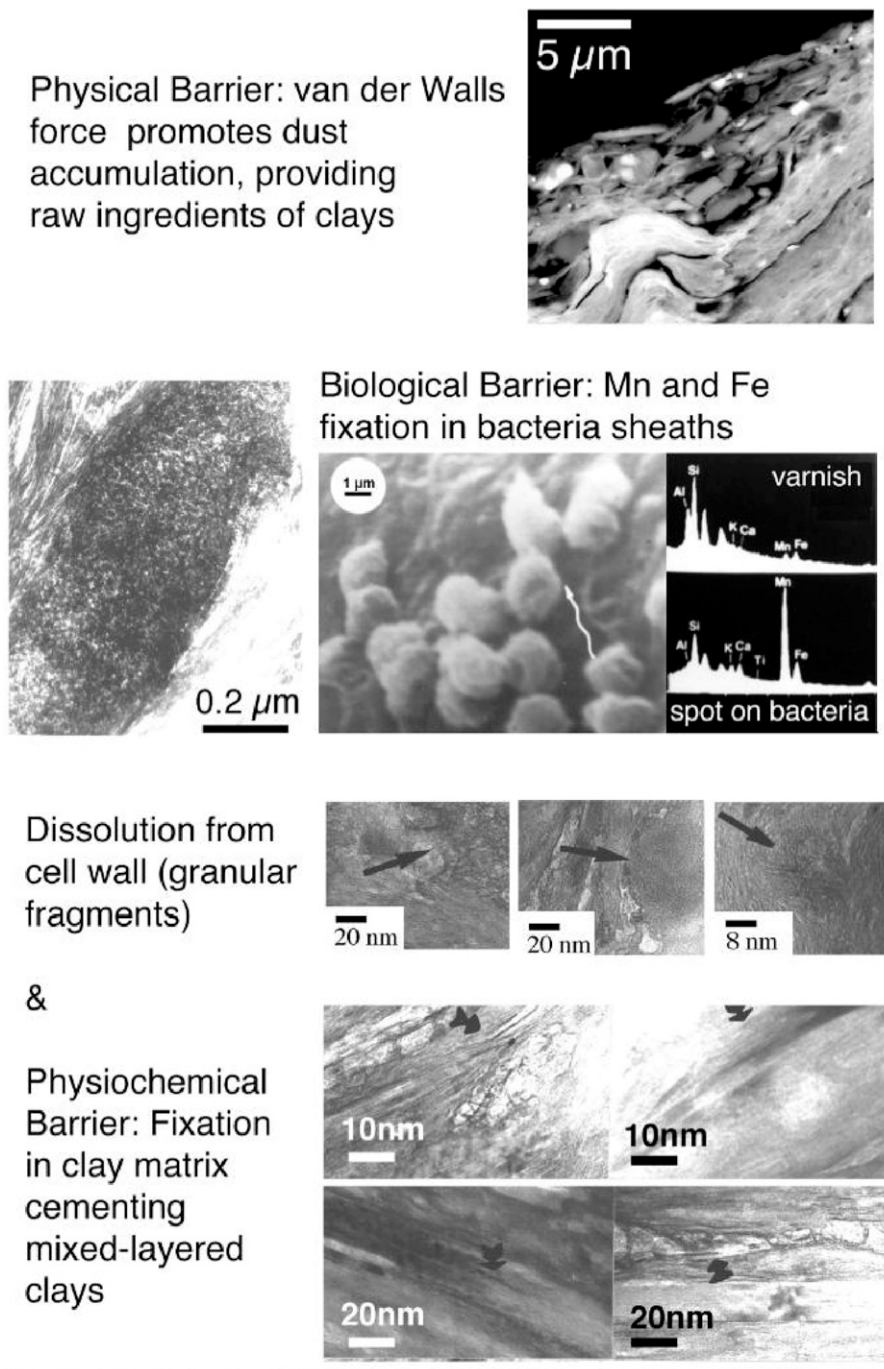


Figure 2. The polygenetic hypothesis starts with an abiotic step that attaches raw varnish ingredients to surfaces. Then, budding bacteria enhance and fix Mn and Fe in their sheaths. The third and fourth abiotic steps involve nanoscale diagenesis that breaks down Mn-Fe sheaths into smaller granular pieces, then then migrate into and cements the Mn-Fe-clays into varnish.

examining varnish surfaces for areas of Mn-Fe-enrichment compared to adjacent varnish (Dorn, 1998; Dorn et al., 1992; Dorn and Oberlander, 1981a, 1981b, 1982). Since varnish accumulates slowly in hot deserts, this sort of in situ evidence should not be a common observation. Consider Dorn and Oberlander's (Figure 3 in the 1982 rock varnish article) secondary image of a cluster of Negev Desert *Metallogenium*-like bacteria enhancing Mn and Fe. That image required secondary electron examination of 40,000,000 μm^2 of varnish surface to find such a cluster. Such an infrequent occurrence of budding bacteria makes sense given slow rates of varnish accretion in this hot and dry region (Liu et al., 2013).

The overall approach used here is the same as Dorn and Oberlander (1982): search a varnish surface for budding bacteria enhancing Mn-Fe with secondary electrons and EDS, and then carry out a careful electron microscope study in that area of the sample. However, the scanning transmission electron microscopes (STEM) used for this paper have much higher resolutions for imagery and EDS. A revolution in varnish sample preparation also occurred with the focused ion beam (FIB) that allows sectioning of varnish with much greater precision and reliability (Krinsley et al., 2013). A variety of electron microscopes were used over time as newer technologies became available.

Results

The results reported in this section are new and do not duplicate data from other publications about budding bacteria and the polygenetic model (Dorn, 2007; Krinsley et al., 2013, 2017). Two figures, however, involve the re-analysis of older samples with newer technology: the Negev Desert (Dorn and Oberlander, 1982) sample discussed in methods 4.2; and a sample collected by R. Gerson from the Bungar Oasis, Antarctica (Dorn et al., 1992) discussed later.

The remainder of the new imagery derive from sites selected to explore the different falsification tests, particularly the need to analyze samples from the different environmental settings where rock varnish is known to occur (see Supplemental File 1).

Each of the references linked to these sites provides details about the following sampling sites: the Sonoran Desert (Dorn, 2023), Hanaupah Canyon alluvial fan in Death Valley (Hooke and Dorn, 1992), from a Nazca Peru pukio (underground wet canal) ceiling (Clarkson and Dorn, 1991), from a morainal boulder on a Greenland outlet glacier, from the Gokyo Valley in the Khumbu region of Nepal, and from a granitic rock fracture 6 m deep from a road cut in central Arizona (Dorn and Whitley, 2023).

The results here are organized along the lines of the nine falsification tests of the polygenetic model of varnish formation with budding bacteria. Failure of any one test means that the hypothesis is falsified based on current understanding.

Does the proposed mechanism explain the enrichment in Mn compared with potential source materials? Figure 3 updates the original Dorn and Oberlander (1982) Negev Desert example using more modern STEM. This re-evaluation shows gold standard evidence of varnish formation in sufficient detail to identify several key processes:

- (i) as hyphae are slowly buried in varnish, buds emerge from those hyphae at the surface (Figure 3(A) and (B)) and are able to escape from the oxide coating, as in other budding bacteria research (Ehrlich, 1999; Gebers and Beese, 1998);
- (ii) hyphae and buds are actively enhancing Mn and Fe in casts (cf. EDS X1, X5, X6, X7 in Figure 3)—as in other studies where Mn-Fe accumulates on cell surfaces (Frankel and Bazylinski, 2003; Larsen et al., 1999; Tebo et al., 1997) with varying forms (Jurgensen et al., 2004; Klaveness, 1999; Miyajima, 1992) such as Mn-oxides forming branching filaments as in Figure 3(A) and (C) (Ghiorse and Hirsch, 1979);
- (iii) the casts of budding bacteria hyphae (Figure 3(E)) and buds (Figure 3(B) and (C)) have granular textures; biogenetic Mn around cells often consist of granular nanoparticles (Villalobos et al., 2003, 2005) and this is the case for budding bacteria casts seen on and in rock varnish. and

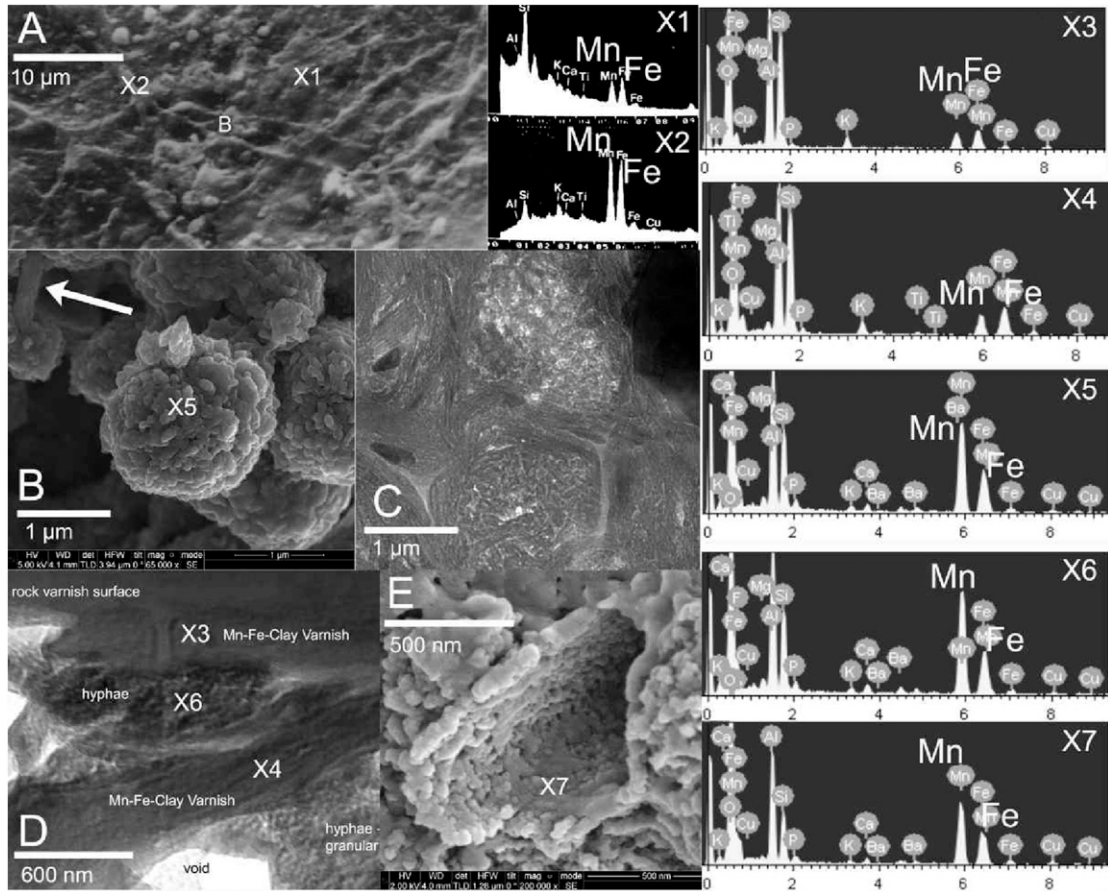


Figure 3. Negev Desert pavement varnish with budding bacteria enhancing Mn and Fe. A. Low-resolution secondary image of a Metallogenium-like form with multiple hyphae and multiple buds. X1 and X2 match EDS spectra for typical varnish (X1) and a hyphae cluster (X2). B. Location B (in image A) identifies an area with bacteria buds, and EDS X5 shows enrichment in Mn and some Fe. C. Scanning transmission electron microscope (STEM) image of the bacteria buds in image B showing the granular texture of cell casts and hyphae between the buds. D. Arrow in image B identifies location of this STEM cross-section. The reason for presenting this complicated image is to show how granular bits of Mn derived from bacterial hyphae (EDS X6) migrate into adjacent clays. In contrast to the strong Mn-Fe peaks in the hyphae (EDS X6), adjacent areas show how clays are enriched in Mn-Fe as the granular bits of bacterial cast undergo nanoscale diagenesis slowly migrating into clay structure. This results in typical varnish EDS spectra of X3 and X4. E. Secondary image of cross-section of budding hyphae, again showing the granular texture of Mn-Fe-rich casts (see EDS X7).

- (iv) the granular bits of Mn-Fe material break apart and migrate into adjacent clay minerals to produce Mn-Fe-clay varnish (Figure 3(D)).

Other new results show budding bacteria actively enhancing Mn follow, but those are contextualized by other falsification tests.

Does the proposed mechanism(s) explain the enrichment in Fe compared with potential source materials, albeit not as much as Mn? Budding bacteria are known for enriching both Fe and Mn in situ (Hirsch, 1974; Moore, 1981) in a variety of terrestrial weathering environments (Aristovskaya, 1975; Aristovskaya and Hirsch, 1974; Bolotina, 1976b; Braun et al., 2009; Crerar et al., 1980; Walsh and Mitchell,

1973). Note that in EDS showing Fe-enhancement, there is overlap of the Mn-K_b and Fe K_a peaks, meaning some Mn adds to the height of the main Fe K_a peak.

Figure 4 illustrates both Fe- and Mn-enhancement in the context of an orange varnish microlamination (VML). Orange microlaminations are not greatly enriched in Mn, hence their orange color reflecting the dominance of Fe minerals as a coloring agent (Liu and Broecker, 2013; Liu et al., 2013). As is often the case with budding hyphae, there are micron-scale zones with strong Mn peaks (Figure 4(F)) and zones with strong Fe peaks (Figure 4(E)) (Krinsley et al., 2013, 2017). However, within the orange layer, Fe is more abundant and is more commonly enhanced by budding bacteria (e.g., Figure 4(D)).

The importance of finding both Mn- and Fe-enrichment in situ associated with budding bacteria on and within rock varnish cannot be overstated here. All but one of the other hypotheses, summarized in section V and detailed in Supplemental File 2, failed to explain Fe-enrichment.

In contrast, evidence of Fe enhancement shown in this section by budding bacteria can also be seen the following papers (along with Mn-enhancement): Figures 7–9 in (Dorn and Krinsley, 2019); Figures 4(A)–11 in (Krinsley et al., 2017); Figures 7 and 9 in (Krinsley et al., 2013); Figures 9 and 21 in (Dorn et al., 2013); Figure 5 in (Dorn and Krinsley, 2011); Figure 5 in (Krinsley et al., 2009); Figure 1 in (Dorn et al., 1992); plate 3 in (Dorn and Dragovich, 1990); Figure 3 in (Dorn and Oberlander, 1982); and Figure 1 in (Dorn and Oberlander, 1981a).

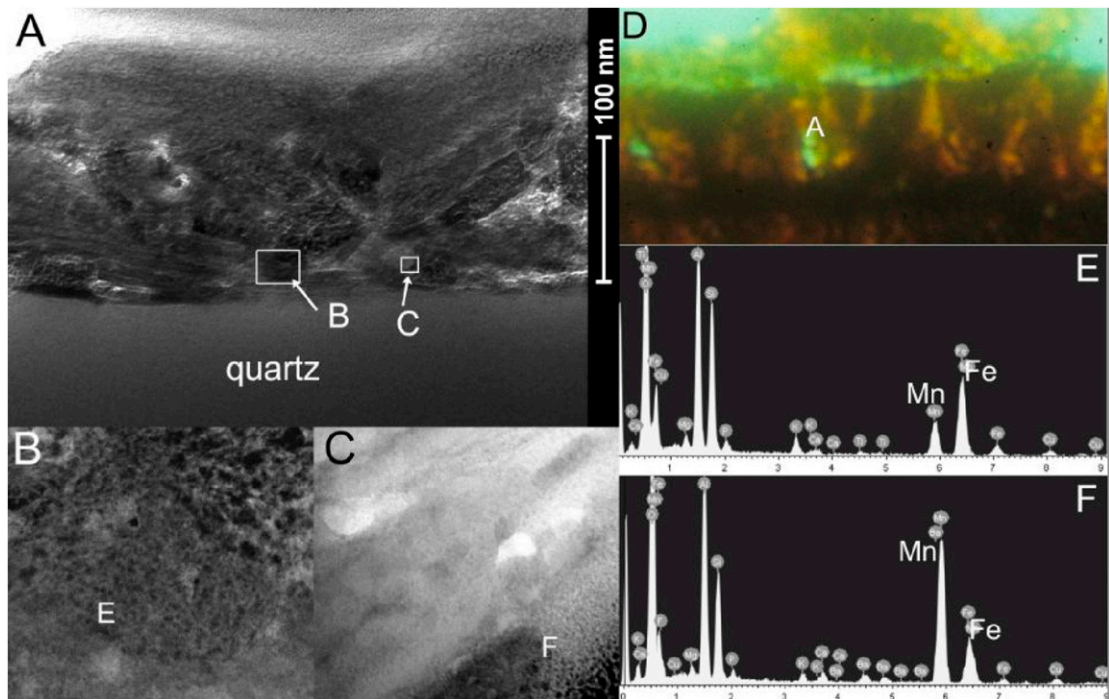


Figure 4. Fe-enrichment via budding bacteria in an orange varnish microlamination, on a fairy chimney in the Sonoran Desert (Dorn, 2023). A. STEM cross-section from the location of the small A in image D. The STEM cross-section in A shows clay minerals on top of the granular texture of the cast of a hyphae, on top of a detrital quartz grain. Boxes B and C correspond with close-ups of granular area of iron-rich (Box B, EDS E) and Mn-rich (Box C EDS F). D. The color ultrathin section is 100 microns across, where the letter A identifies the location of the STEM image A. For interpretation of the references to colours in this figure legend, refer to the online version of this article.

Does the proposed mechanism explain the abundance of clay minerals? Explaining the dominance of clay minerals in varnish is the third falsification test. Prior research showed Mn-Fe fragments of budding bacterial casts migrating into clay mineral structures (Dorn, 1998, 2007), and this process is illustrated here in Figures 3(D), 5 and 6. It is not a coincidence that smectite and illite (and interlayered clays) are able to fix large amounts of Mn (Reddy and Perkins, 1976).

The abundance of dust in a hot-dry desert is not the reason for the dominance of clays in varnish (Potter, 1979). Supplemental File 1 provides confirming evidence from non-desert sites that the cause of clay mineral abundance cannot be from loading a rock surface with dust. For example, Figure 5 exemplifies an environment without abundant dust: the ceiling of underground pre-historic canal that still supports water transport (Clarkson and Dorn, 1991). In this moist setting, like other wet locations in prior scholarship (e.g., Krinsley et al., 2017), budding hyphae enhance Fe-Mn; then, the cast decays (Figure 5(B)); Mn-Fe fragments then break off and migrate into adjacent clays in Figure 5(A).

Death Valley, California, has become a classic collection location for rock varnish research (Hooke et al., 1969; Hunt, 1961; Liu and Broecker, 2008, 2013; Macholdt et al., 2017; Potter, 1979). Thus, Figure 6 presents another example of how budding bacteria cement clays into varnish, at the classic varnish site (Hooke and Dorn, 1992). Even though dust is abundant, the limiting factor on varnish accretion is the availability of Mn-Fe granular particles to break off from a bacterial sheath and migrate into clays (Figure 6) that started out as mixed-layered illite-smectite (Robert and Tessier, 1992). Scanning transmission electron microscope images like Figure 6 show these clays, with irregular feathering characteristic produced by Mn-Fe granules, and how the Mn-Fe cements the clays into varnish.

Does the proposed mechanism explain the nature of the contact between varnish and the underlying rock surface? To meet this test, an experiment assessed varnish colonization of a bare rock surface by budding bacteria. The simple experiment involved

four steps. First, *Pedomicrobium* spp. was cultured from the same site as Figure 3 in the Sonoran Desert using methods detailed elsewhere (Dorn and Oberlander, 1981a). Second, the cultured Mn-Fe-encrusted *Pedomicrobium* spp. was placed on a sterilized rock chip of quartz and left out on a South Mountain, Phoenix, desert pavement site, where details on this site are presented elsewhere (Jeong et al., 2018). Third, the rock chip was then left to interact with the natural Sonoran Desert pavement environment for 5 years and recollected. Fourth, STEM examination of the rock chip revealed that clay minerals had deposited on top of bacterial casts (Figure 7(A)). Energy dispersive spectroscopy analyses of this cast reveal it to be mostly Mn-rich (Figure 7(C)), but with areas of Fe-rich granules. The clay minerals that had deposited on top of the cast had been infused with both Mn and Fe (Figure 7(B)). This experiment simply illustrates that it is feasible that varnishing could start directly on top of the underlying rock through the actions of budding bacteria interacting with the natural environment.

Does the proposed mechanism explain varnish occurrence on subaerial surfaces in all different climate regions? Budding bacteria enhance Mn and Fe in a wide variety of settings where varnish accretes, including cave deposits (Northrup et al., 2003), humid rock exposures (Krinsley et al., 2017), locations with flowing water (Larsen et al., 1999), in soil settings (Aristovskaya, 1963, 1975; Aristovskaya and Hirsch, 1974; Bolotina, 1976b), and a wide variety of other terrestrial weathering environments (Braun et al., 2009; Ehrlich, 1999; Hirsch, 1974; Hirsch et al., 1995; Moore, 1981). Microbial oxidation rates of oxidation from Mn(II) to Mn(IV) can be quite rapid in these moist, near-neutral to slightly acidic conditions (Spiro et al., 2010; Tebo et al., 2004, 2005; Tebo and He, 1998).

Meeting this test would require gold standard imagery such as budding hyphae emerging from cocci forms on an Antarctic varnish sample (Dorn et al., 1992); a semi-arid locale in Tibet that shows *Metallogenium*-like forms enhancing both Mn and Fe (Dorn, 2019); and the Erie Canal in upstate New York that hosts budding bacteria involved in

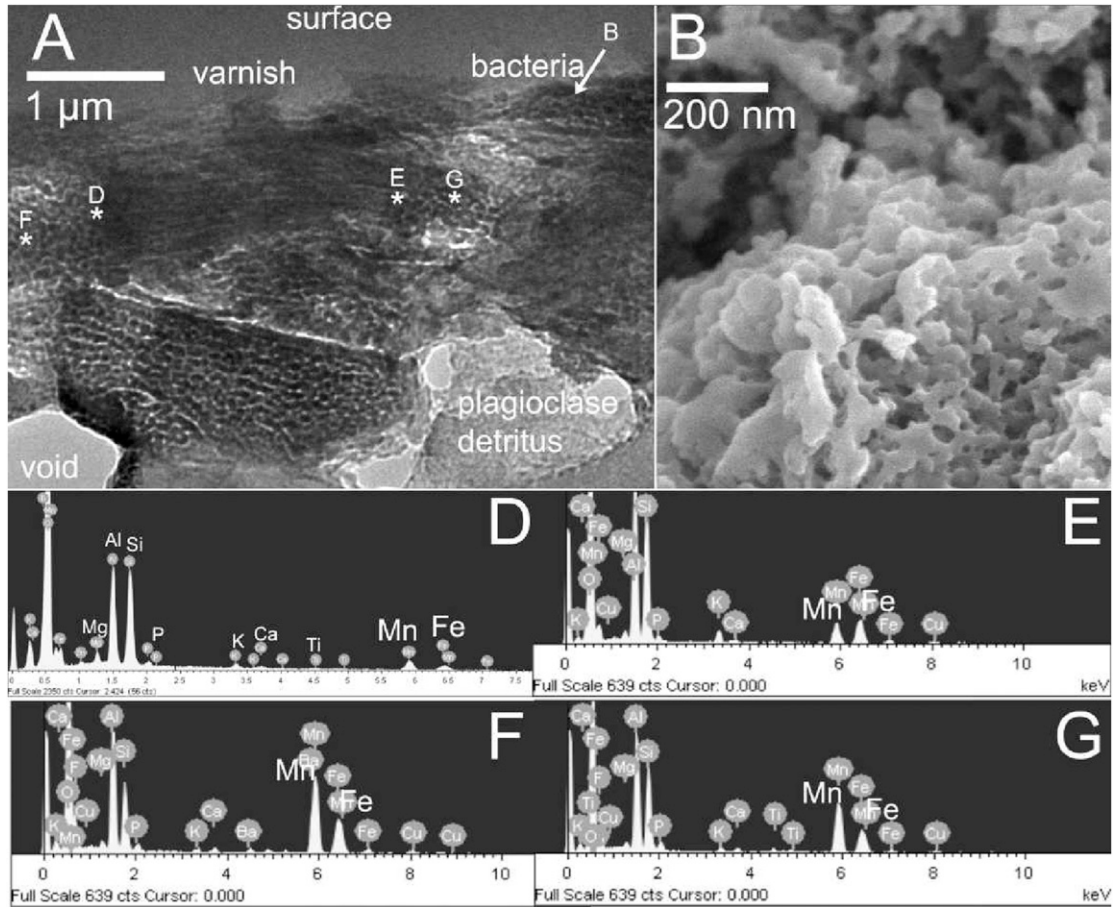


Figure 5. Pocket of rock varnish collected from a Nazca, Peru pukio (underground canal) ceiling (Clarkson and Dorn, 1991). Image A is STEM cross-section of the incipient varnish while image B is a secondary electron image of location B (arrow) identified in Image A. Image B also shows the dissolution of a bacterial cast into small granular bits of Mn. Image A shows nanoscale migration into a clay fragment between the letters G and F that are locations of the corresponding EDS spectra showing Mn (and some Fe) enhancement. The granules at G and F migrate into the clays, inserting Mn and Fe and generating EDS spectra typical of rock varnish (EDS D and E).

Mn-Fe-rich varnish formation (Krinsley et al., 2017). This section presents additional in situ analyses showing the role of budding bacteria and the polygenetic model in non-desert subaerial settings.

A low-resolution Antarctic figure (Dorn et al., 1992) is regularly cited as evidence of Mn-rich varnish in Antarctica. The original image is repeated as Figure 8(A) and (B), where a wavy arrow identifies hyphae emerging from a bud greatly

enriched in Mn. An update of this figure reveals a granular texture for the bud (letter E in Figure 8(C)) that is Mn-Fe-rich (Figure 8(E)). A granular-textured hypha connects to the bud and runs along the top of Figure 8(C). The material underneath the budding bacteria is a typical texture of particles (sometimes called pods) of clay minerals that are in the process of being cemented into a varnish. The clay particle identified by the letter D in image C has already experienced some

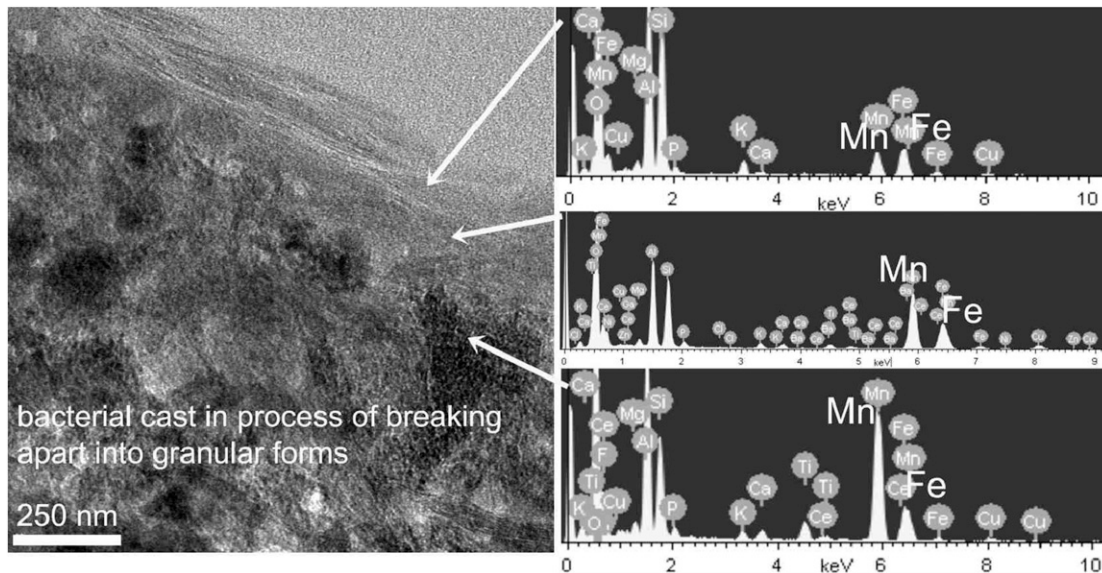


Figure 6. STEM image a rock varnish collected from Hanaupah Canyon alluvial fan, Death Valley (Hooke and Dorn, 1992), where a budding hyphae cast is being coated by a few nanometers of new varnish. The cast has a typical granular texture, and a particularly dense cluster of granules is greatly enriched in Mn (lowest EDS spectra). The middle arrow shows a Mn-rich EDS spectra for varnish. Further from the bacteria sheath, with fewer granules inserted into the clays, the upper EDS spectra shows more Fe than Mn inserted into clay minerals.

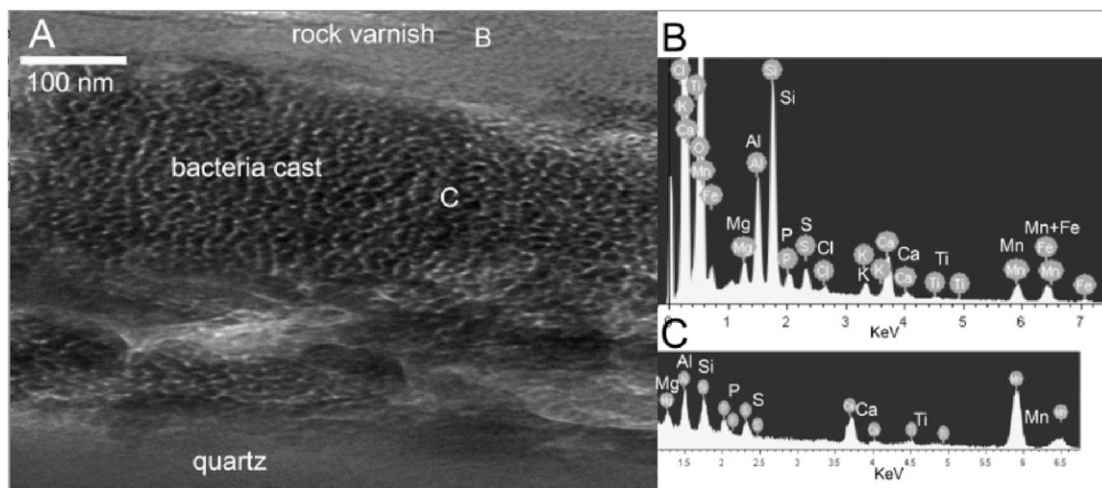


Figure 7. A. Cultured *Pedomicrobium* spp. hyphae placed on a rock surface, then interacting with naturally deposited clay minerals. Note how the granularly-textured Mn-rich sheath (EDS image C) is breaking apart and migrating into the clays at location B (that also identifies the EDS image B).

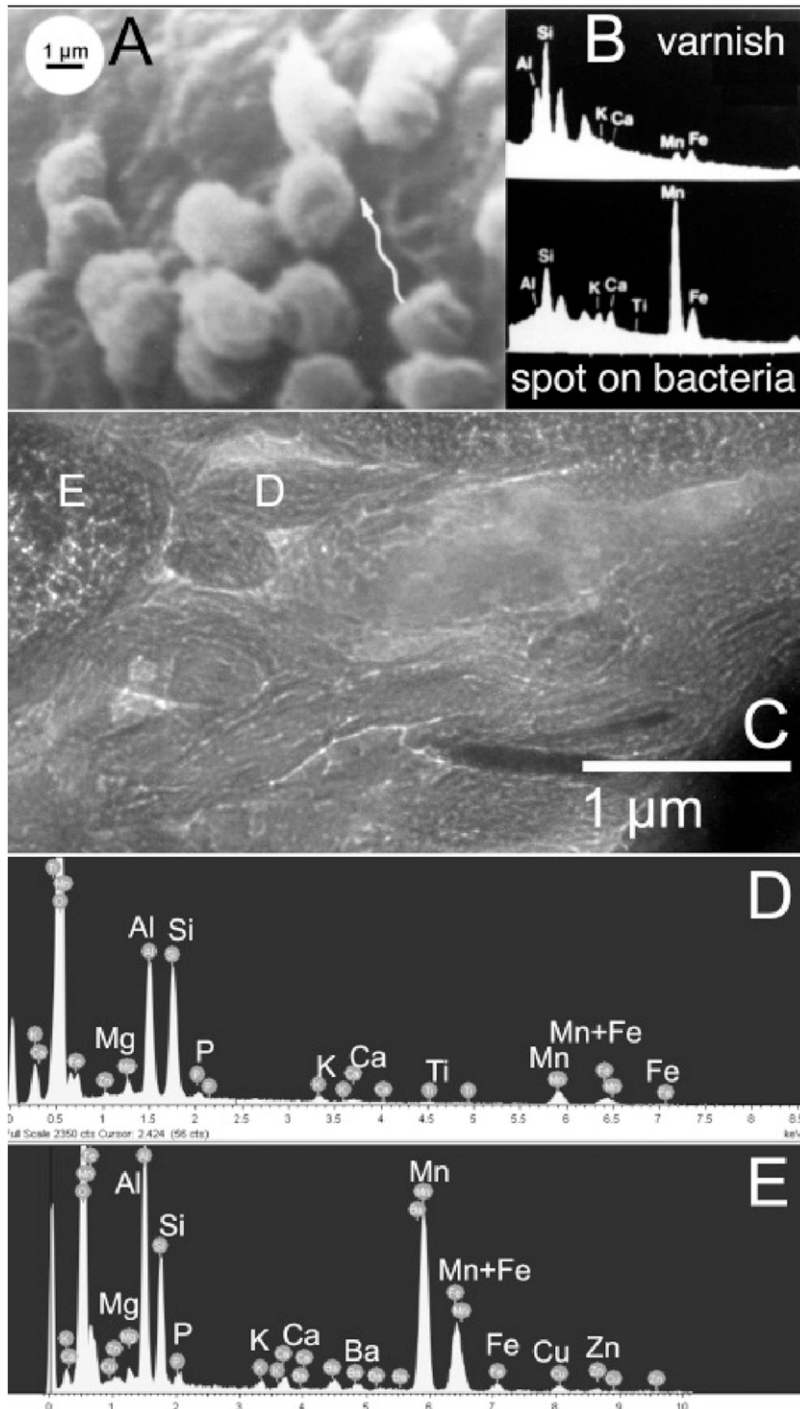


Figure 8. Budding bacteria on Mn-rich varnish collected by R. Gerson from the Bungar Oasis, Antarctica. A and B: Original figure (Dorn et al., 1992) at a low-resolution. C: Transmission electron microscopy just underneath the surface of the bud and hyphae arrow in image A. Letter E is a bud with a granular texture. Letter D is a clay mineral particle, as are the other structures underneath D. Letters D and E in image C correspond with EDS analyses D and E.

cementation with granules of Mn and Fe (EDS in Figure 8(D)), even though it is just underneath the surface.

Another example of budding bacteria developing varnish outside of a warm desert comes from morainal boulders of outlet glaciers of the Greenland ice cap. Others have noted that varnish in Greenland can cover entire rock surfaces (Washburn, 1969), but only pockets of rock varnish occurred on these recently deposited gneissic morainal boulders (Figure 9(A)). These varnishes are typically 2 to 40 μm thick (e.g., Figure 9(B)). One of depressions about 5 mm wide showed the process of active budding (Figure 9(C)). The material inside the budding forms had EDS spectra of only carbon and oxygen (Figure 9(D)) indicating organic matter. Only the outer surface was Mn-Fe-rich (Figure 9(E)) with needle-fiber textures (Figure 9(C)).

Alpine regions have a long history of observations of rock varnish (Chaddha et al., 2023; Dorn, 1995; Dorn et al., 1991; Elliott-Fisk, 1987; Klute and Krasser, 1940; Larson and Dorn, 2012; Wang et al., 2023; Zahn, 1929). Figure 10 exemplifies an incipient varnish in the classic alpine region of the Khumbu in Nepal. The Gokyo Valley in the Khumbu region of Nepal contains a debris flow that was 12 years old at the time of sampling (X in Figure 10(A)) with varnish forming in submillimeter depressions, like Figure 10(B).

This speed of varnishing is similar to observations by others in cold, wet alpine environments (Höllerman, 1963; Klute and Krasser, 1940). The smooth surface of an albite mineral was unvarnished (Figure 10(B), EDS 1), but an adjacent depression hosted varnish and spherical forms having an EDS spectrum similar to rock varnish (Figure 10(B), EDS 2) with a granular texture (Figure 10(C)).

Does the proposed mechanism explain varnish occurrence in settings that have not been exposed to sunlight? Rock varnishes form in subsurface positions such as on the sides of rock fractures (Dorn and Oberlander, 1982; Douglas, 1987; Eren et al., 2014; Hunt, 1972; Weaver, 1978), under glaciers (Surdam et al., 1989; Whalley et al., 1990), on the ceilings of

subterranean pukio (Clarkson and Dorn, 1991), on ancient Egyptian walls (Elshabrawy and Ali, 2021), on rocks in soils (Bolotina, 1976a; Ha-mung, 1968; Huang et al., 2011; Khak-mun, 1966; Li et al., 2017; Xu et al., 2018), and in caves (Boston et al., 2008; Northrup et al., 2003). Concomitantly, budding bacteria have been observed in most of these settings actively enhancing Mn, Fe or both (Aristovskaya, 1975; Aristovskaya and Hirsch, 1974; Braun et al., 2009; Ehrlich, 1999; Keim et al., 2015; Lozano and Rossi, 2012).

Figure 5 illustrates budding bacteria both enhancing Mn-Fe and cementing clays in location never exposed to sunlight. Figure 11 is the sort of HRTEM image that is commonly encountered in subsurface settings, with several small fragments of a budding cast. These zones of granular material continue to shed Mn-Fe-rich granules into clay minerals. This particular example comes a foliated granitic rock fracture 6 m deep from a road cut in central Arizona (Dorn and Whitley, 2023). The varnished fracture walls were followed 0.5 m into the road cut to ensure the varnish formed in the subsurface.

Does the proposed mechanism explain the paucity of microfossils within varnish? Dave Krinsley and I searched for well-preserved microbial fossils in varnish layers. Although we did find some (Dorn and Krinsley, 1991; Krinsley, 1998; Krinsley and Dorn, 1991; Krinsley et al., 1990, 2009, 2017; Krinsley and Rusk, 2000), fully intact microbial fossils are rare. Thus, microbial hypotheses must also explain this paucity of microbial fossils.

Figures 3–8 and Figure 11 illustrates why the budding bacteria-polygenetic hypothesis meets this test. Over time, the granular casts of budding bacteria decay, and eventually, the most common appearance of a microfossil is seen in Figure 11: a few granular fragments of cell casts. Thus, the infrequent occurrence of preserved microfossils is an inherent part of varnish formation via budding bacteria and the polygenetic hypothesis.

Does the proposed mechanism explain ongoing diagenesis of previously accreted varnish at the nanoscale? Post-depositional modification of rock

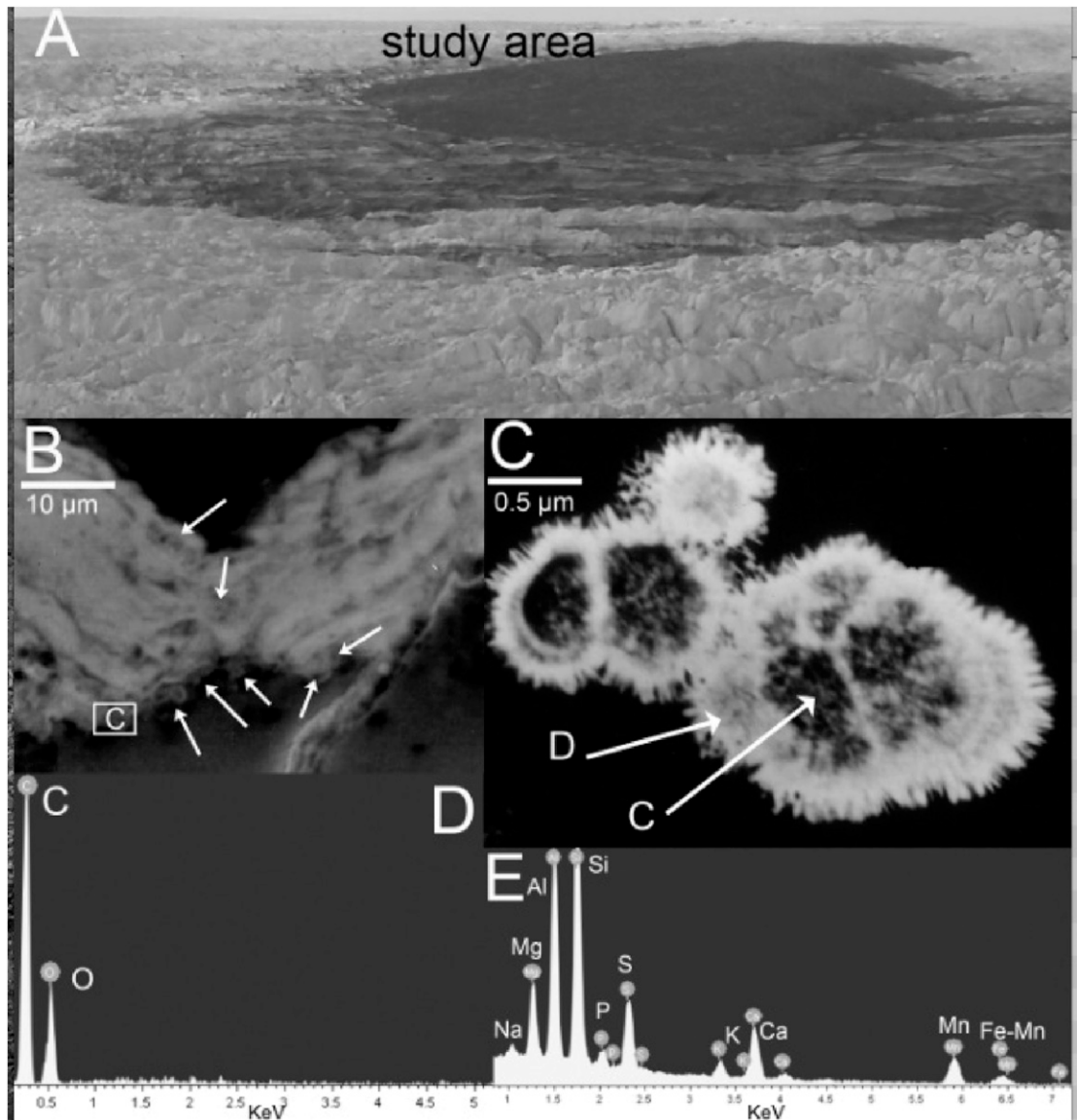


Figure 9. Morainal boulder on a Greenland outlet glacier hosted millimeter-scale pockets of rock varnish. A: Oblique aerial view (63.5540, -50.5833). B: Back-scattered electron (BSE) image of a polished cross-section. Arrows identify round cocci-shaped forms, some of which are not Mn-Fe-rich (and are dark). The box identified by letter C is the location of a close-up BSE image that shows the process of budding. The internal portions of these new buds are just carbon and oxygen (EDS image C). The outer portions have an EDS spectrum that is enriched in Mn and Fe (EDS image D).

varnish occurs at different scales. No matter the process that concentrates Mn and Fe, a cluster of oxides would then need to break apart into small enough fragments to incorporate into illite,

montmorillonite and mixed-layered clays. This type of nanoscale diagenesis, observed in [Figures 3–8](#), is an attribute of the budding bacteria-polygenetic hypothesis.

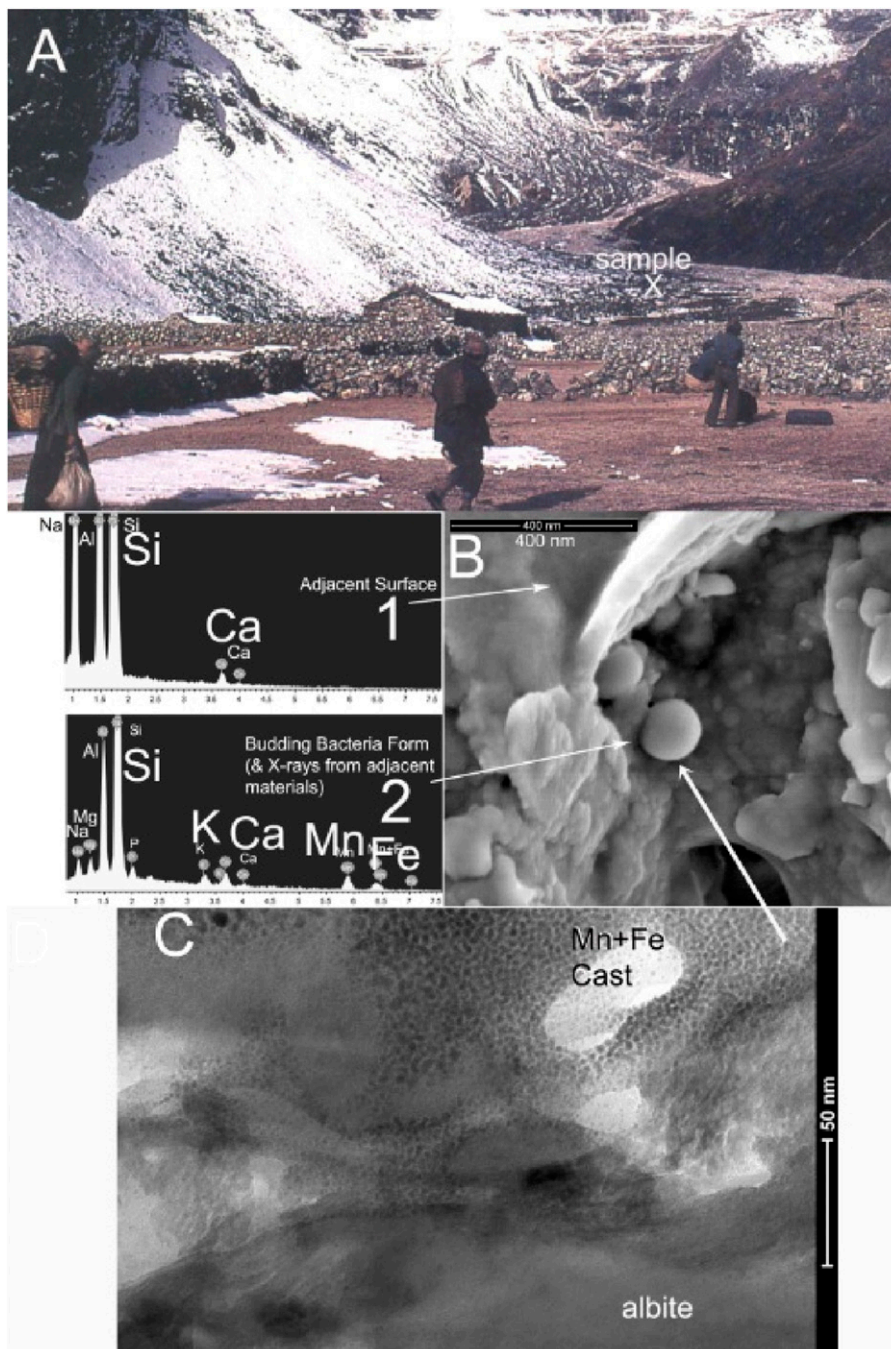


Figure 10. A 12-year-old debris flow in the Gokyo Valley area (see sample X in Image A), Khumbu region of Nepal, shows the development of rock varnish in submillimeter-size depressions (Image B). Cocci-shaped spheroid, possibly budding cells encrusted in Mn-Fe and desiccated, have a granular texture (Image C) and EDS chemistry (#2 in Image B) of rock varnish. For interpretation of the references to colours in this figure legend, refer to the online version of this article.

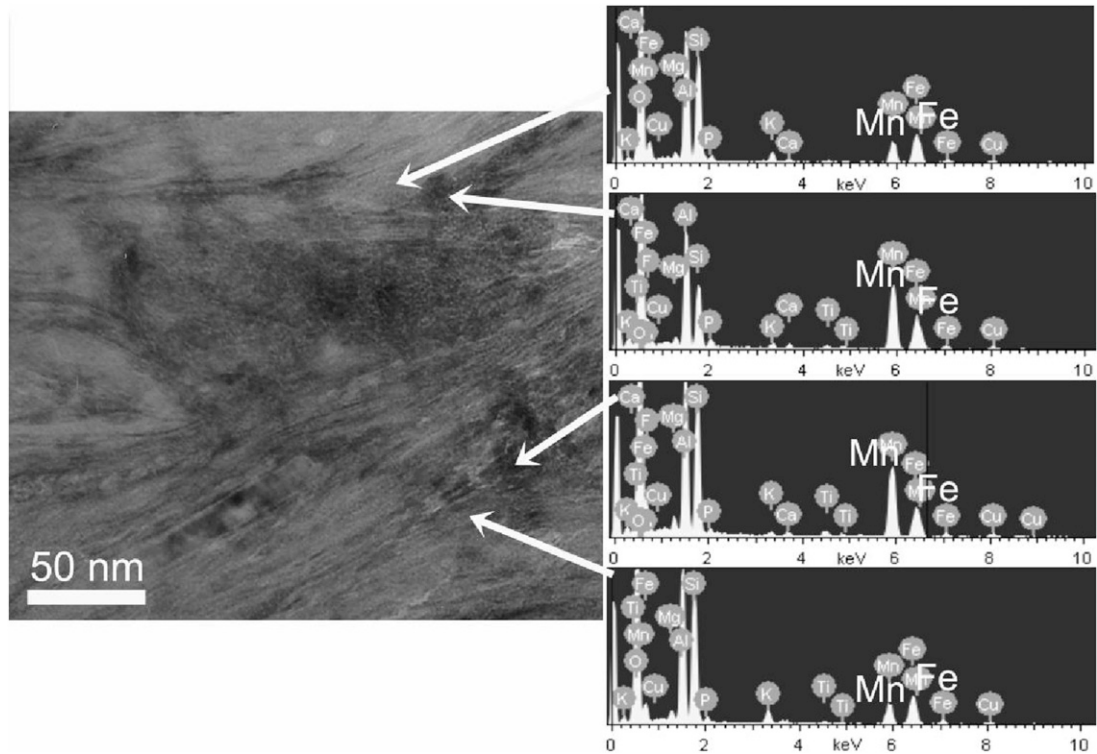


Figure 11. STEM image of varnish 6 m deep in a rock fracture, illustrating a commonly observed texture of granular bits of bacterial fragments enriched in Mn and Fe. The two middle EDS spectra were acquired from granular fragments. Next to these fragments are areas where the spacing of the original mixed-layered illite-smectite (Robert and Tessier, 1992) have been altered into ragged edges due to the insertion of both Mn-rich and Fe-enriched granules (upper and lower most EDS spectra).

Another nanoscale process involves patterns of trace and rare elements in varnish (Bard, 1979; Engel and Sharp, 1958; Fleisher et al., 1999; Hodge et al., 2005; Lakin et al., 1963; Otter et al., 2020; Sims et al., 2022; Thiagarajan and Lee, 2004; Wayne et al., 2006; Xu et al., 2019).

Some suggest that trace and rare element found in varnish indicate a role for aqueous processes (Fleisher et al., 1999; Otter et al., 2020; Thiagarajan and Lee, 2004; Xu et al., 2019). Aqueous deposition is fully compatible with budding bacteria enhancement of Mn-Fe in a polygenetic model where varnish formation requires aqueous nanoscale movement of Mn-Fe granules into clays (Figures 3–8, and 11). Other studies also show trace and REE scavenging capabilities for biogenic Mn-oxides (Nelson and

Lion, 2003; Tebo et al., 2004; Villalobos et al., 2005). Thus, trace element enrichment as a part of nanoscale varnish diagenesis is compatible with the polygenetic model of varnish formation, either in the abiotic steps or microbially enhancement step, or both.

Does the proposed mechanism explain variable rates of accretion in various desert and non-desert settings?. Supplemental File 1 reviews scholarship on rates of varnish formation. Hot deserts accumulate varnish at microns per millennia (Dorn, 1998; Liu and Broecker, 2000). Much wetter environments can accrete varnish as fast as 422 $\mu\text{m}/\text{millennia}$ (Dorn and Meek, 1995; Krinsley et al., 2017; Spilde et al., 2013). Mesic microclimates in deserts occur on the shaded north-sides of boulders. Such settings

experience much less evapotranspiration, and such settings experience rates of varnishing between 12 and 50 $\mu\text{m}/\text{millennia}$ (Dorn, 2014). The question here is whether data for budding bacteria are consistent with this test of explaining rates of accretion.

Table 1 provides empirical insight into rates of varnishing for sites studied in this part of this paper. The ergodic assumption is that space substitutes for time, with the implication that slow rates of varnish accumulation in hot deserts correspond with infrequently observed in situ enhancement of Mn-Fe in Table 1. In contrast, faster growing varnishes in wetter regions host more budding bacteria per square micron of varnish surface area (Table 1). While more research is needed on how the abundance of budding bacteria scales with moisture and other environmental variables, currently available data reveal that budding bacteria's abundance is controlled in part by moisture availability and roughly matches known rates of varnish accretion in different environmental settings.

Testing other hypotheses to explain rock varnish formation

Varnish scholars have advocated a wide variety of hypotheses to explain how rock varnish forms over the past four decades. These hypotheses were subject to the falsification tests explained in the third section of this paper and detailed in Supplemental File 1. A

full analysis of the testing is the length of a separate paper and is presented in Supplemental File 2. This section is just a synopsis of Supplemental File 2, starting with a brief summary of each hypothesis in, followed by more detailed explanations of one or more of the failed tests of each hypothesis.

Hypotheses to explain rock varnish formation

Microbial community. An extensive microbial community exists on and within rock varnish, with inference that microbial processes play a role in varnish formation. See Supplemental File 2 for citations on this hypothesis.

Culturing Mn-Fe organisms. A variety of Mn-Fe-concentrating microorganisms have been cultured from rock varnish. See Supplemental File 2 for citations on this hypothesis.

Silica binding hypothesis. Slow dissolution of silica and its subsequent gelling, condensation, and induration, provides a likely mechanism for the formation of desert varnish and silica glazes (Perry et al., 2006).

From the rock. A role for the underlying rock as a source of varnish ingredients continues in modern scholarship (Lebedeva et al., 2019; Muncichia et al., 2016; Raymond et al., 1988; Soleilhavou, 1986; Thiagarajan and Lee, 2004).

Table 1. Surface area of rock varnish hosting at least 1 colony/patch of budding bacteria.

Figure, Location	Setting	Surface μm^2 examined ^a	Climate	Number clusters ^b
3. Negev Desert	Subaerial desert pavement	40,000,000	Hot desert	1
4. Sonoran Desert	Subaerial, bedrock	36,000,000	Hot desert	1
5. Peru	Underground water canal	8000	Cool, moist	6
6. Death Valley, CA	Subaerial desert pavement	67,000,000	Hot desert	1
7. Sonoran Desert	Planted colony <i>Pedomicrobium</i>	4000	Not relevant	1
8. Antarctica	Subaerial Bungar Oasis	16,000,000	Cold desert	1
9. Greenland	Subaerial moraine bolder	9000	Cold, wet	4
10. Khumbu Nepal	Subaerial debris flow	12,000	Cold, wet	3
11. Central Arizona	Subsurface rock fracture	120,000	Warm, dry	1

^asurface area examined with secondary electrons and energy dispersive spectroscopy (EDS).

^bnumber of clusters of budding bacteria observed.

Photo-oxidation of manganese. Certain minerals in varnish such as birnessite and hematite promote Mn(II) oxidation in 1–5 μm “tunnels” in existing varnish (Xu et al., 2019).

Cyanobacteria. Cyanobacteria growing on sunlit rocks sequester manganese in their cells. (Lingappa et al., 2021b).

Fluctuations in acidity. This abiotic process was proposed over 65 years ago (Engel and Sharp, 1958) and starts with a shift to slightly acidic wetting conditions that leaches Mn from its source material, followed by oxidation to Mn(IV) that then fixes Mn in varnish after water evaporation or an increase in pH (Goldsmith et al., 2014; Otter et al., 2020; Thiagarajan and Lee, 2004).

Hypothesis testing reveals fatal flaws

None of the hypotheses summarized above, briefly evaluated below and analyzed in detail in Supplemental File 2 passed all nine tests. The microbial community hypothesis did not pass any of the nine tests. Culturing Mn-Fe organisms passed the greatest number of tests, 4 of 9. Full details are provided in Supplemental File 2. Table 2 summarizes the results of the hypothesis testing detailed in Supplemental File 2. This section exemplifies a few failed tests of these hypothesis to explain the origin of rock varnish.

Microbial community. A long tradition in varnish research infers that just the presence of organisms and organic material on or in varnish might form varnish. This speculation, for example, is exemplified by Lang-Yona et al. (2018: 269) who did not find evidence for “direct enzymatic involvement in varnish formation”; still, they suggest that “an indirect influence of the detected microorganisms could not be excluded (Lang-Yona et al., 2018).” In summary, the microbial community hypothesis fails tests to explain Fe-enrichment, the abundance of clays, the presence of varnish in different climates and in settings lacking exposure to light, and the role of nano-scale diagenesis.

Culturing Mn-Fe organisms. Existing research on culturing microorganisms from varnish able to oxidize and enhance Mn-Fe is currently falsified by five of the nine tests. Proponent scholars do not present information pertaining to: explaining the abundance of clay mineral in varnish; explaining the nature of the varnish-rock contact; explaining the paucity of microfossils within varnish; explaining ongoing nanoscale diagenesis; or explaining variable rates of varnish accretion.

Silica binding hypothesis. This hypothesis does not discuss Mn-enrichment. Furthermore, no aspect of the proposed process explains Fe-enrichment in varnish. The third test links the proposed process of varnish formation to the dominance of clay minerals. The silica binding model depends on the interpretation that clay minerals are not a dominant part of rock varnish (Perry et al., 2006)—an interpretation that is contradicted by prior scholarship (Potter, 1979; Potter and Rossman, 1977, 1979) establishing clay minerals as the dominant component: (Chaddha et al., 2021, 2022; Diaz et al., 2002; Dietzel et al., 2008; Dorn et al., 2012b; Dorn and Krinsley, 2019; Dorn and Oberlander, 1982; Drake et al., 1993; Duerden et al., 1986; Fang et al., 2023; Haberland, 1975; Israel et al., 1997; Johnson et al., 2002; Krinsley, 1998; Krinsley et al., 1995, 2012; Liu and Broecker, 2007; Martinez-Pabello et al., 2022; Probst et al., 2002; Sarmast et al., 2017; Spilde et al., 2007).

From the rock. A role for the underlying rock as a source of varnish ingredients, however, still continues in more modern scholarship (Lebedeva et al., 2019; Municchia et al., 2016; Raymond et al., 1988; Soleilhavoup, 1986; Thiagarajan and Lee, 2004). These papers offer only speculation as to how the rock might play a role in Mn-enhancement, avoid consideration of Fe-enhancement. The hypothesis only meets tests of occurring in different climate regions and on surfaces not exposed to sunlight. The other seven tests falsify the continuing notion that the underlying rock somehow plays a role in varnish formation.

Photo-oxidation of manganese. Nothing in the proposed photo-oxidative hypothesis explains Fe-enrichment

Table 2. Summary of falsification testing results for the various hypotheses analyzed in [Supplemental File 2](#). “No” indicates that currently available evidence on a test falsifies the hypothesis. Yes indicates currently available evidence on the test is consistent with the hypothesis. U (for uncertain) is that currently available evidence provides uncertain support in that test of a hypothesis.

Tested hypothesis	Mn-rich	Fe-rich	Clay abundance	Rock contact	Different climates	No light	Few microfossils	Nanoscale diagenesis	Variable rates
Microbial biome	No	No	No	U	No	No	U	No	No
Cultured Mn oxidizers	Yes	Yes	No	No	Yes	Yes	No	No	No
Silica binding	No	No	No	Yes	No	No	U	No	No
Underlying rock	No	No	No	No	Yes	Yes	No	No	No
Photo-catalysis	Yes	No	No	Yes	No	No	Yes	No	No
Cyanobacteria	Yes	No	No	U	U	No	No	No	No
Abiotic acidity fluctuations	U	No	U	U	No	No	Yes	No	No

or the abundance of clays in varnish. In fact, [Xu et al. \(2019: 55\)](#) assert that the light-responsive semi-conducting minerals (birnessite, hematite, goethite, rutile, anatase) are “the major components of rock varnish.” This assertion is not consistent with their own microprobe data showing fairly typical oxide weight percentages for clay-bearing Si-Al-Mg. This assertion is also not consistent with their ICP-MS bulk analyses showing the clay-bearing Si-Al-Mg percentages of 60%–80%. [Xu et al. \(2019\)](#) acknowledge their hypothesis does not meet the tests of varnishes formed in different climates and in settings with no light.

The photo-oxidative hypothesis also does not explain how Mn incorporates into clays to form varnish.

Cyanobacteria. [Lingappa et al.’s \(2021a\)](#) Cyanobacteria hypothesis fails to meet the tests of explaining substantial enrichment of Fe in varnish, or of explaining the abundance of clay minerals in varnish. [Lingappa et al.’s \(2021a\)](#) Cyanobacteria hypothesis starts with the observation that they grow on “sunlit rocks.” Thus, this hypothesis fails the test of explaining rock varnishes in subsurface positions such as on the sides of rock fractures ([Dorn and Oberlander, 1982](#); [Douglas, 1987](#); [Eren et al., 2014](#); [Hunt, 1972](#); [Weaver, 1978](#)), under glaciers ([Surdam et al., 1989](#); [Whalley et al., 1990](#)), on the

walls of subterranean pukios ([Clarkson and Dorn, 1991](#)), on ancient Egyptian walls ([Elshabrawy and Ali, 2021](#)), on rock surfaces in soils ([Bolotina, 1976a](#); [Ha-mung, 1968](#); [Huang et al., 2011](#); [Khakmun, 1966](#); [Li et al., 2017](#); [Xu et al., 2018](#)), and in caves ([Boston et al., 2008](#); [Northrup et al., 2003](#)).

Fluctuations in acidity. Nothing in the acidity fluctuation hypothesis explains Fe-enhancement. Abiotic acid fluctuations will not work on subaerial surfaces in the many humid regions, or in the many subaerial rock surfaces in all regions that experience geochemical conditions too acidic to oxidize Mn(II) ([Dorn, 1990](#)). Humid settings receive an abundance of naturally acidic precipitation, without any alkaline dust to oxidize Mn. These wetter subaerial settings also have the challenge of acid-secreting fungi ([Fabero-Longo et al., 2011](#); [Gadd, 2007, 2017](#)), lichens ([Aghamiri and Schwartzman, 2002](#); [Armstrong and Bradwell, 2010](#)), and other epilithic organisms ([Viles, 2011, 2013](#)).

The extensive scholarship on rock varnish cited above with regards to Cyanobacteria includes rocks found subsurface positions in soils, subterranean Egyptian tombs, subterranean prehistoric canals, fractures in bedrock of different types and other subsurface settings. Nothing in scholarship explains how slight acidity fluctuations might explain varnishes in these subsurface settings.

Even the presumed strength of this hypothesis, explaining Mn-enrichment, still remains speculative after 65 years of little besides theoretical arguments and geochemical modeling for support. No proponents of acidity fluctuations have shown in situ evidence of the proposed process operating. In fact, no research has yet presented direct evidence that this process operates on rock varnish. A field experiment to assess the reality of this hypothesis has not yet been conducted by proponents; such an experiment detailed in [Supplemental File 2](#) failed to provide empirical evidence of Mn-enhancement by the acidity fluctuation hypothesis.

Discussion

Two mental frameworks appear to have had a substantial influence on varnish researchers. First, most have focused on a process to explain the great enrichment in Mn in varnish, often to the exclusion of other issues. Second, many researchers have focused sample collection entirely in warm or hot deserts, often to the exclusion of varnishes formed in other environmental settings.

This discussion section first explores how these mental frameworks may have led to failed hypothesis testing. Then, I discuss rock varnish classification, a mostly ignored topic that could emerge in importance as researchers deal with the implication of failed hypothesis testing.

An emphasis on Mn

Rock varnish scholarship has long tried to explain its great abundance of manganese, starting with [Von Humboldt \(1812\)](#), and continuing with French ([Boussingault, 1882](#)), British ([Lucas, 1905](#)), German ([Walther, 1912](#)), and American ([White, 1924](#)) scholars. Rock varnish has only three major ingredients: clay minerals, Mn-oxides, and Fe-oxides. Six of eight hypotheses tested here failed to explain the enhancement of Fe as a major component of rock varnish. Six of eight hypotheses also failed to explain how a preferred process of varnish formation would lead to clay minerals being the dominant component of rock varnish. It is difficult to envision why researchers working on the origins of rock varnish

would ignore two of its three major ingredients—that is unless their mental framework had an overarching focus on just manganese.

A focus on deserts

A climatic transect involves making observations of how something changes with wetter conditions, cooler conditions, or both. Geochemical research regularly employs climate transects ([Chadwick et al., 1994](#); [Quade et al., 1989](#); [Riebe et al., 2004](#)), including rock varnish ([Dorn, 1990](#)). For example, I have collected rock varnish every 200 m from below Sea Level in Death Valley, CA, to 3367 m at Telescope Peak, and the major difference at wetter/cooler altitudes is a reduction in the subaerial coverage of varnish due to more acid-producing lithobionts that dissolve subaerial varnish. I would challenge varnish researchers to carry out a similar collection of samples along a climatic transect before concluding that varnishes formed in hot deserts are somehow unique.

Despite abundant research on rock varnishes on subaerial surfaces in non-desert climates and research on varnish in subsurface positions analyzed in [Supplement File 1](#), a great many varnish studies show a systematic bias in sample collection avoiding non-desert locations. A mental framework focused on varnishes formed on subaerial surfaces in warm deserts may have led to: four of the eight hypotheses failing the test of explaining varnishes in different climates; five of the eight hypotheses failing the test of explaining varnishes formed in the subsurface; and seven of the eight failing to explain observed growth rates in non-desert settings.

Classification and the philosophy of science

Inevitably, failed hypothesis testing can lead to researchers reclassifying the subject of study into something that would not fail a test. Those studying the philosophy of science have long recognized that human “paradigms” drive the gathering and interpretation of data, and that even practicing hypothesis falsification can be delicately and sometimes unknowingly interwoven with the cultural background

of a scientist (Fuller, 2000; Kuhn, 1970; Popper, 1966, 1979).

Working in a discipline that mixes natural and social sciences, I am a physical geographer who accepts of importance of critical practice in natural science (Clifford, 2001; Demeritt, 1996; Rhoads, 1999; Rhoads and Thorn, 1996; Tadaki et al., 2015). I accept that all human-imposed classification of natural phenomena remains linked to the motives and beliefs of the scientist (Rhoads, 2010; Simpson, 2021). Thus, I acknowledge that the entire premise of this paper is founded on my inclusive view of rock varnish explained in the second part of this paper as a wide-ranging phenomenon found in almost all terrestrial weathering environments.

Analysis of proposed subclassification strategies. I proposed a four-tiered process-based classification of rock varnishes based on the principles of landscape geochemistry (Dorn, 1998: 223) that fell on unread eyes. Macholdt et al. (2017) proposed a second classification that subdivides rock varnish into five types. While welcoming a dialogue on how to subclassify varnish, I reject Macholdt et al.'s (2017) particular approach for the following reasons.

- (i) The techniques used by Macholdt et al. (2017) to subclassify varnish require state-of-the-art microscopy available to a few varnish scholars. A useful classification system requires the use of common scientific equipment.
- (ii) Subtypes II through V are based on samples from one or two study sites each, far too few to warrant a classification.
- (iii) Macholdt et al. (2017) did not analyze varnish along environmental transects. This traditional ecological approach used in other studies (Dorn, 1986, 1990) provides more than extremes.
- (iv) I have not found the same correlation between varnish type and climate as Macholdt et al. (2017). For example, their Type I occurs in Antarctica (Dorn et al., 1992), Greenland (Dorn and Jeong, 2018), Mediterranean climate of Southern California

(Dorn, 2019), and along the Orinoco River where von Humboldt initiated the scholarly study of rock varnish (Dorn et al., 2012b; Von Humboldt, 1812).

- (v) Macholdt et al. (2017) consider the Erie Canal location to be Type V, but Type I varnish also occurs this location (Krinley et al., 2012, 2017). Also, Macholdt et al. (2017) incorrectly consider Erie Canal equivalent to von Humboldt's original study area along the Orinoco River; they are not equivalent (Dorn et al., 2012b).
- (vi) I have observed the full range of Type I through Type V from different microenvironmental positions around a single rock outcrop.
- (vii) Macholdt et al. (2017) used rates of formation as a criterion, either Type I forming very slowly or Type V forming very fast. Supplemental File 1 and the fourth part of this paper presents data that rates of formation are not bimodal but much more nuanced.

Equifinality. After recognizing that their photo-catalysis hypothesis could not explain varnishes formed in wet (i.e., tree covered), low light, and subsurface locations, Xu et al. (2019: 68) proposed the notion that multiple "pathways" could produce rock varnishes found in different environmental settings.

Equifinality is the term for a final state reached from different initial conditions and in different ways that is traditionally applied to biological systems (Burton, 1939; Von Bertalanffy, 1950). At least three obstacles exist to applying equifinality as Xu et al. (2019) suggest.

First, equifinality carries with it a tremendous "baggage" of prior debate over its legitimacy. Simply examine the over 3000 citations of Von Bertalanffy (1950). As but one example in modern research, equifinality tends to reflect sloppy modeling (Marschmann et al., 2019; Tang and Zhuang, 2008).

Second, equifinality is being suggested by Xu et al. (2019) to address the problem of two failed hypothesis tests related to the location of varnish; it does not address the four other failed hypothesis tests of the photo-catalysis model.

Third, applying equifinality in varnish research poses a practical consequence of possibly rendering a varnish hypothesis invalid on Mars if varnish initiates in a subsurface position (Krinsley et al., 2009). Thus, an investigator with research interests regarding rock varnish on Mars would want to consider the implications of advocating equifinality.

The role of classification moving forward into the future. The classification approach I proposed a quarter century ago (Dorn, 1998) did not work, in that nobody used it. I do not think Macholdt et al.'s (2017) approach will work for the reasons explained above. The simplest solution at this point is to continue to use a broad view of rock varnish used by the vast majority of varnish researchers, as cited in the second part of this paper.

Conclusion

Many have used the word “mystery” to describe varnish formation (DiGregorio, 2010; Dorn, 1991; Fleisher et al., 1999; Kuhlman et al., 2006; Lingappa et al., 2021a; Perry and Sephton, 2008). As Forster et al. (2021: 22,685) noted, the “jury is still out on varnish genesis, which keeps inspiring researchers to apply cutting-edge techniques to solve this ‘old mystery’.”

There are a couple reasons why varnish formation is still considered mysterious by many. First and foremost, the traditional science tool of hypothesis testing has not been employed in rock varnish research. Without tests of proposed hypotheses, a mystery can remain a mystery. Thus, this paper presents nine independent tests of hypotheses proposed to explain the formation of rock varnish.

A second reason why varnish formation has been viewed as mysterious by many is not seeing the varnish-making processes, but only the result. Sometimes, the result consists of state-of-the-art magnificent electron microscope imagery. However, the only acceptable evidence of Mn-enhancement or Fe-enhancement involves “the gold standard” of seeing the process of making varnish in situ. Due to its slow rate of accretion, documenting in situ formation of rock varnish using electron microscopy can be a very time consuming

endeavor, sometimes taking weeks for just one desert site.

The purpose of this paper is not to strip away the mystery of varnishing, but to encourage the use of hypothesis testing. Basic characteristics of rock varnish documented by scholars over the past four decades led to the nine tests proposed here. These were then deployed to test eight hypotheses that researchers have advocated to explain rock varnish formation.

Seven of eight proposed hypotheses to explain varnish formation failed more than five of the tests, any one of which would falsify a hypothesis. Only one hypothesis “passed” all nine tests, the polygenetic model with budding bacteria as the active agent of Mn-Fe-enhancement. Chaddha et al. (2024) also advocate for the polygenetic model of varnish formation, as it combines both biotic and abiotic processes to explain varnish formation.

In the end, the most appealing aspect of the polygenetic model is that each step in varnish formation, both biotic and abiotic, has been seen “in the act” in situ in multiple environmental contexts. This brings to mind an appropriate popular phrase: “seeing is believing.”

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Supplemental Material

Supplemental material for this article is available online

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SUPPLEMENTAL FILE 1: Rock Varnish Revisited by Ronald Dorn

OVERVIEW OF THIS FILE:

The third section of the main paper presents nine key tests to adjudicate proposed hypotheses of rock varnish formation. This file starts with a duplication of section III in the main paper and then provides the background scholarship that supports the 9 tests.

III Key tests to adjudicate proposed hypotheses of rock varnish formation

A revisitation of the physical geography of rock varnish should ideally review advances in scholarship over 40 years. That is what this section accomplishes, but with a focused purpose of organizing this prior research into nine tests that must be met by researchers advocating a hypothesis that “solves the mystery” of rock varnish formation. These tests are formulated as questions. Does the proposed mechanism(s) explain:

- (i) the great enrichment in Mn compared with potential source materials?
- (ii) the substantial enrichment in Fe above potential source materials?
- (iii) the abundance of clay minerals?
- (iv) the nature of the contact between varnish and the underlying rock surface?
- (v) varnish occurrence on subaerial surfaces in all different climate regions?
- (vi) varnish occurrence in settings that have not been exposed to sunlight?
- (vii) the paucity of microfossils within varnish? [applies to biotic hypotheses only]
- (viii) ongoing diagenesis of varnish at the nanoscale?
- (ix) variable rates of accretion in various environmental settings?

What should be made clear, in this specific context of rock varnish research where hypothesis testing has not been a scholarly tradition, is that failing to pass a single test invalidates a hypothesis.

The rest of this section analyzes rock varnish scholarship that is the foundation of these tests. The rest of this section is the content of this **Supplemental File 1**. The level of detail explaining the background research leading to these tests is too extensive to include in the main paper.

3.1 Does the proposed mechanism(s) explain the great enrichment in manganese compared with potential source materials?

Early varnish scholarship established the great enrichment in Mn, compared to other potential source materials, no matter the climate or microenvironmental setting (Chaddha et al., 2023; Dietzel et al., 2008; Dorn and Oberlander, 1982; Dragovich, 1998; Engel and Sharp, 1958; Grote and Krumbein, 1992; Hooke et al., 1969; Jahn and Maneck, 1991; Krinsley, 1998; Linck, 1901; Lucas, 1905; Malherbe et al., 2015; Martínez-Pabello et al., 2021a; Merrill, 1898; Northup et al., 2010; Otter et al., 2020; Patyk-Kara et al., 1997; Potter and Rossman, 1979a; Sarmast et al., 2017; von Humboldt, 1812; Walther, 1912; Xu et al., 2019; Zahn, 1929; Zerboni, 2008).

Thus, any hypothesis proposed to form varnish must explain its enrichment in manganese.

3.2 Does the proposed mechanism(s) explain the enrichment in iron compared with potential source materials, albeit not as much as manganese?

Ongoing varnish research reveals that iron is enriched above other potential source materials such as dust or the surrounding soils, albeit not as much as manganese (Adams et al., 1992; Allen, 1978; Aulinas et al., 2015; Cremaschi, 1996; Dorn, 1990; Dorn and Dragovich, 1990; Dorn et al., 1992; Dragovich, 1988; Drake et al., 1993; Duerden et al., 1986; Edwards et al., 2004; Elvidge and Moore, 1980; Engel and Sharp, 1958; Forster et al., 2021; Garvie et al., 2008; Glazovskiy, 1985; Goosens et al., 2015; Harmon et al., 2021; Hooke et al., 1969; Jones, 1991; Liu and Broecker, 2007, 2013; Macholdt et al., 2015; Martínez-Pabello et al., 2021b; Moore and Elvidge, 1982; Potter and Rossman, 1979a; Rahim and Ismail, 2020; Ren et al., 2019; Sarmast et al., 2019; Xu et al., 2018; Zerboni, 2008).

As an example of the range of whole-varnish iron content, Dorn and Dragovich (1990) present FeO oxide weight percent for bulk varnish samples from Death Valley, CA (13.47%), Alibates National Monument, TX (8.90%), Negev Desert, Israel (14.17%), Khumbu in Nepal (9.24%), and the Atacama Desert in southern Peru (11.06%). Dorn et al. (1992) show FeO varies in Antarctic bulk varnish samples from 11% to 17%.

Just as important as bulk or whole-varnish abundance of iron, micron-scale electron microprobe transects show variability from varnishes from a mixture of 25 arid and humid global sites range from 7.51 ± 0.28 to $22.00 \pm 5.15\%$ (Dorn and Krinsley, 1991). Xu et al. (2019) show considerable micron-scale variability even at one study site location ranging from 7.00% to 15.33%. Nanoscale EDS elemental analyses show and even greater variability from less than 1 percent to almost 30% iron (Krinsley et al., 2017).

There exists a tendency for some varnish researchers to compare abundance in varnish with upper crustal abundance or even abundance in extraterrestrial meteors. Crustal abundance of iron varies depends on the reference. Older research puts crustal abundance at 5% (Fleischer, 1953). Of course, the relevance of crustal abundance is questionable, since the earth's upper crust has never been proposed as a source of rock varnish constituents.

Dust is thought to be a common source of varnish constituents on subaerial exposures in warm desert settings (Dorn, 1986; Dorn and Oberlander, 1982; Drake et al., 1993; Fleisher et al., 1999; Jones, 1991; Moore and Elvidge, 1982; Spilde et al., 2013; Thiagarajan and Lee, 2004). Xu et al. (2019), for example report pairs of bulk ICP-MS analyses reported as Fe₂O₃ of “varnish powders” (first value) and “soil dust” (second value) as 9.30-5.52%, 16.18-5.71%, 6.61-5.03%, 8.21-6.79%, and 9.62-5.20%. Goldschmidt et al. (2014) found a mixed signal of abundance, but they analyzed only 3 bulk varnish and 3 bulk dust samples in their comparison. Otter et al. (2020) report on iron relative abundance (compared to upper crust) of varnish and various soil size fractions less than and greater than 50 μm – generally finding more iron in varnish than dust, but with some exceptions.

The overall bulk concentration of iron in dust might not be as relevant as iron in the clay-sized fraction that is most easily incorporated into varnish. Bulk samples of dust or soil contain detrital Fe-rich minerals such as magnetite. Iron in the clay-sized fraction of Chinese desert dust ranges from 0.81% to 3.15% (Lu et al., 2017), while Canary Island dust from the Saharan Desert is on the order of 0.4% (Lázaro et al., 2008). Thus, the iron that is actually incorporated into varnish could be far more enriched than comparisons with dust or crustal abundance would suggest.

Of course, all of this focus on desert dust provides an inherent bias towards warm desert varnish formed in subaerial settings. For varnish varnishes formed in other environmental settings, whether they are subaerial humid or subsurface locations, little to no current insight exists to compare varnish iron abundance to various potential iron sources (precipitation, plant material, runoff, water permeating through soil or rock fractures).

In summary, any hypothesis proposed to explain varnish formation must be able to explain iron enrichment at the nanoscale, micron scale and bulk varnish scale.

3.3 Does the proposed mechanism explain the abundance of clay minerals?

Potter and Rossman used samples from a wide range of environmental settings (Potter, 1979; Potter and Rossman, 1977, 1979b) to establish clay minerals as the dominant component of varnish, comprising more than half of varnish and sometimes as high as 70%. The dominance of clay minerals is a characteristic that has been confirmed using different techniques and in a variety of different climates and microenvironmental settings

(Chaddha et al., 2021; Chaddha et al., 2022; Diaz et al., 2002; Dietzel et al., 2008; Dorn and Krinsley, 2019; Dorn et al., 2012c; Dorn and Oberlander, 1982; Drake et al., 1993; Duerden et al., 1986; Fang et al., 2023; Haberland, 1975; Israel et al., 1997; Johnson et al., 2002; Krinsley, 1998; Krinsley et al., 2012; Krinsley et al., 1995; Liu and Broecker, 2007; Martínez-Pabello et al., 2022; Probst et al., 2002; Sarmast et al., 2017; Spilde et al., 2007).

Put another way, Mn-Fe skins are a type of rock coating that does not include clay minerals (Dorn, 1998, 2022). Whatever process forms varnish must explain the great abundance of clays in rock varnish.

3.4 Does the proposed mechanism explain the nature of the contact between varnish and the underlying rock surface?

The nature of the varnish/rock contact or boundary depends on whether rock type, mineralogy, and especially the existence and nature of the weathering rinds (Gordon and Dorn, 2005; Oguchi, 2013) on which varnish can accrete. Light and secondary electron imagery in the 1970s and 1980s showed dramatic contrasts of fresh minerals and varnish textures (Allen, 1978; Dorn and Oberlander, 1982; Perry and Adams, 1978; Potter and Rossman, 1977; Soleilhavoup, 1986). Back-scattered electron (BSE) imagery revealed presence of the same dramatic contact where underlying minerals were relatively undecayed (Dorn and Krinsley, 1991; Dorn et al., 2012c; Dorn et al., 1992; Krinsley and Dorn, 1991; Raymond et al., 1991). The same held true for high resolution transmission electron microscope (HRTEM) imagery (Krinsley, 1998; Krinsley et al., 1995; Sharps et al., 2020). Studies of trace elements accumulating in varnish also indicate the source of varnish is not from the underlying rock, but an external source (Fleisher et al., 1999; Hodge et al., 2005; Moore et al., 2001). Thus, the primary observation in scholarship since the 1970s is that varnish does not derive its constituents from the underlying rock.

This is not to say that there is always a clean contact. The varnish-rock boundary can appear chaotic at the nanoscale (Forster et al., 2021). This is where varnish either formed on partially decayed rock material (Dorn et al., 2013b; Krinsley et al., 1990; Krinsley et al., 2009; Nobbs and Dorn, 1993; Sharps et al., 2020) or where the underlying rock underwent decay after varnishing started (Dorn et al., 2013a; Dorn and Krinsley, 2019; Dorn et al., 2017; Nobbs and

Dorn, 1993; Whitley et al., 1999). A chaotic contact can also occur where post-depositional modification of varnish has resulted in Mn and Fe migrating down into the weathering rind of the host rock, producing a case hardening effect (Dorn, 2022; Dorn et al., 2017).

3.5 Does the proposed mechanism explain varnish occurrence on subaerial surfaces in different climate regions?

Rock varnish is found in a host of different environmental settings on exposed subaerial surfaces other than hot and warm deserts. Examples include:

- Mediterranean climates (Dorn, 2019; Dorn and Meek, 1995);
- paraglacial conditions such as those found in high Arctic (Dorn and Jeong, 2018; Jahn and Maneck, 1991; Washburn, 1969);
- humid temperate climates (Krinsley et al., 2017);
- tropical humid climates such as Cambodia (Municchia et al., 2016) and Malaysia (Rahim and Ismail, 2020);
- temperate subalpine settings such as Yosemite Valley (Larson and Dorn, 2012);
- in the splash zone of tropical rivers like the Nile (Lucas, 1905) and Orinoco (Dorn et al., 2012c; von Humboldt, 1812), as well as temperate rivers (Dorn, 2005);
- the high alpine (Glazovskaya, 1968) including where changing geomorphology can change water flow (Chaddha et al., 2023);
- continental semiarid settings like southern Idaho (Merrell and Dorn, 2009) and Argentina (Baied and Somonte, 2013; Somonte and Baied, 2013);
- high altitude arid Tibet (Krinsley et al., 2009; Wang et al., 2023; Wang et al., 2011), arid Ladakh, India (Chaddha et al., 2023) and the arid high altitude of Mauna Kea (Dorn et al., 1991);
- Antarctica (Dorn et al., 1992);
- semiarid tropical settings like Lake Turkana basin in East Africa (Liu et al., 2021) and Kaho'olawe Island, Hawaii (Stasack, 2006); and
- from multiple sampling sites along environmental gradients from humid to arid in altitude transects of western USA mountain ranges (Dorn, 1986, 1990).

Thus, any hypothesis proposed to form varnish must explain varnishes formation in a wide range of subaerial environments.

3.6 Does the proposed mechanism explain varnish occurrence in settings that have not been exposed to sunlight?

Varnish with the same characteristics and variety as those found in classic subaerial settings in warm deserts occur in locations that do not experience sunlight (Anderson and Sollid, 1971; Bolotina, 1976; Dorn and Jeong, 2018; Douglas, 1987; Elshabrawy and Ali, 2021; Eren et al., 2014; Goosens et al., 2015; Ha-mung, 1968; Huang et al., 2011; Hunt, 1972; Khak-mun, 1966; Krinsley et al., 2012; Li et al., 2017; Lozano and Rossi, 2012; Moore, 1981; Northrup et al., 2003; Potter, 1979; Spilde et al., 2005; Spilde et al., 2002; Villa et al., 1995; Weaver, 1978; Whalley et al., 1990).

Thus, any hypothesis proposed to form varnish must explain its occurrence without insolation.

3.7 Does the proposed mechanism explain the paucity of microfossils within varnish?

High resolution imaging of nanoscale structures found in warm desert varnishes, that accrete at rates on the order of microns per millennia, consistently reveal a paucity of intact microbial fossils (Dorn, 1998; Forster et al., 2021; Krinsley, 1998; Krinsley et al., 2013; Krinsley et al., 1995; Macholdt et al., 2017; Macholdt et al., 2015). These nanoscale observations are consistent with lower resolution back-scattered and secondary electron microscope imagery, also showing the paucity of microfossils (Dorn and Krinsley, 1991; Dorn et al., 2013b; Krinsley et al., 2012; Raymond et al., 1989).

Certainly some rock varnishes collected from non-desert locations can display an abundance of microfossils (Dorn and Meek, 1995; Krinsley et al., 2017). Also, some have found abundant cyanobacterial structures in warm desert varnishes (Krumbein, 1969; Lingappa et al., 2021). While the paucity of microfossils is a test that is not relevant to abiotic hypotheses, all hypotheses proposing that varnish forms via biotic processes must explain the paucity of those microfossils in older varnish (lower layers in varnish cross-sections).

3.8 Does the proposed mechanism explain ongoing diagenesis of varnish at the nanoscale?

The processes of varnish accretion on rock surfaces operate in tandem with diagenesis of varnish at micron and nanometer scales. Water flowing through varnish leads to leaching of Mn, Fe, Ca, K and other cations (Dorn and Krinsley, 1991; Krinsley et al., 1990), that then precipitates in opened fractures (Krinsley et al., 1990). Some of the leached materials infuse into weathering-rind in the underlying rock can lead to case hardening (Dorn et al., 2012a; Dorn et al., 2017). Micron-scale diagenesis often confounds microlamination dating, because the microlamination patterns disappear in response to remobilization of varnish constituents (Dorn, 2009, 2023; Dorn and Krinsley, 2011; Liu and Dorn, 1996; Moore et al., 2012). Micron-scale diagenesis results from changes in the varnish environment, such as colonization of acid-producing microcolonial fungi, lichen or environmental changes that result in more water flow or acidification of water sources (Dorn, 1998, 2019).

The above summary of micron-scale varnish diagenesis was presented first in order to clarify that the issue of diagenesis pertaining to varnish formation is not at the micron scale – where mobility occurs after varnish accretion. Rather, different processes of diagenesis occur at the nanoscale that must articulate to whatever process generates varnish.

Fragments of nanoscale Mn-Fe-rich granules release smaller fragments into adjacent clay minerals (Dorn, 1998, 2007; Krinsley, 1998). At the nanoscale, irregular layers of Mn-Fe-cemented clays rest next to regularly spaced lattice fringes with spacing that is consistent with illite, smectite, chlorite, and interstratified clay-textural interstratification (Krinsley, 1998).

Potter (1979: 174-175) argued for this step without the benefit of supporting HRTEM imagery:

"Deposition of the manganese and iron oxides within the clay matrix might then cement the clay layer...the hexagonal arrangement of the oxygens in either the tetrahedral or octahedral layers of the clay minerals could form a suitable template for crystallization of the layered structures of birnessite. The average 0-0 distance of the tetrahedral layer is 3.00 Å in illite-montmorillonite mixed-layered clays, which differs only 3.4 percent from the 2.90 Å distance of the hexagonally closed-packed oxygens in birnessite..." (Potter, 1979)

These nanoscale transformations continue, as interlayer cation exchange with slight changes in chemistry shifts manganese mineralogy between todorokite or birnessite-like phases at the

nanoscale (McKeown and Post, 2001). Förster et al. (2021) use ptychography on a nanoscale laminations of rock varnish from Death Valley to map clusters of Mn(II), Mn(IV), and mixed valence that interfinger with one another; this mixing of Mn-clusters with different valences is fully consistent with ongoing nanoscale diagenesis (Dorn and Krinsley, 2011; Garvie et al., 2008).

Another component of ongoing nanoscale diagenesis involves the enhancement of trace elements in rock varnish (Bard, 1979; Engel and Sharp, 1958; Fleisher et al., 1999; Hodge et al., 2005; Lakin et al., 1963; Otter et al., 2020; Sims et al., 2022; Thiagarajan and Lee, 2004; Wayne et al., 2006; Xu et al., 2019). This includes lead that is due to 20th century air pollution in the varnish surface-most layers of incipient varnish (Dorn, 1998) – in a finding replicated many times (Dorn et al., 2012b; Hoar et al., 2011; Nowinski et al., 2010; Spilde et al., 2007; Wayne et al., 2004).

This pattern of element enrichment, including rare earth elements, is considered by several to mean that aqueous processes must be involved (Fleisher et al., 1999; Otter et al., 2020; Thiagarajan and Lee, 2004; Xu et al., 2019). However, these scholars are constrained by a mental picture of a rock surface sitting in a dusty desert exposed to minimal precipitation. Certainly, nothing in scholarship would preclude an important role for aqueous deposition in non-desert and subsurface locations, but these geographic settings have not been part of scholarship on this topic.

Thus, any hypothesis proposed to form varnish must explain how the proposed formative process(es) articulates to diagenetic processes that occur as a part of varnish formation.

3.9 Does the proposed mechanism explain variable rates of accretion in various desert and non-desert settings?

Determining rate of varnish formation requires independent age control when varnish started to form, and also evidence that varnishing did not experience interruptions or erosional episodes such as from aeolian abrasion (Dorn, 1986) or periodic dissolution (Krinsley et al., 1990). This was accomplished when Dorn (1998) published rates of formation varnish in warm deserts to be a few microns per millennia, a finding confirmed later (Liu and Broecker, 2000) using independent age controls for the onset of varnishing and finding a range of ~1-40 $\mu\text{m}/\text{millennia}$. The condition of establishing no interruption to varnish formation is usually met through analysis of varnish microlaminations (Dorn, 2014; Liu and Broecker, 2008a, b, 2013). Unfortunately, no data exists for rates of varnish accretion in non-subaerial settings.

Comparatively little data exists for rates of formation in humid settings. Available data indicate that accretion rates can be as fast as 422 $\mu\text{m}/\text{millennia}$ (Dorn and Meek, 1995; Krinsley et al., 2017; Spilde et al., 2013).

Similarly, little data exists for varnish accretion rates in semi-arid settings. Bishop Creek glacial moraines of the eastern Sierra Nevada, California, have independent age control from ^{36}Cl surface exposure ages (Phillips et al., 2009) and ^{14}C ages on the aeolian biome (Dorn, 1996). Rock varnish formed on the same morainal boulders sampled for ^{36}Cl in a semi-arid climate that allows growth of *Pinus ponderosa* in ecoregion dominated by sagebrush. Rates of this varnish formation range in this semiarid setting from 10 to 65 $\mu\text{m}/\text{ka}$.

Even less insight exists for varnishes formed in mesic (wetter) microenvironments in a warm desert, such as on the shaded north-sides of boulders. In such a setting, radiocarbon ages for wood crushed by rock falls in the Sonoran Desert (Dorn, 2014) yield rates of varnish

formation on those rock falls during the Holocene of 12, 16, 24-36, and 50 microns per millennia.

Any universally applicable process of varnish formation must be able to explain very slow rates of varnish in warm deserts, very fast rates of formation in much wetter locations, as well as intermediate rates of formation in mesic microsites in deserts and semi-arid settings. Put another way, whatever makes varnish must have a rate-limiting step in warm deserts, as well as the capacity to accelerate varnish formation as moisture abundance increases.

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SUPPLEMENTAL FILE 2: Rock Varnish Revisited by Ronald Dorn

OVERVIEW OF THIS FILE:

The fifth section of the main paper presents a summary of tests of hypotheses proposed and discussed in scholarship over the last 40 years to explain how rock varnish forms. The detailed testing is too long for inclusion in the main paper. Thus, the purpose of this supplemental file is to present details on the hypothesis testing.

In review, the nine tests based on varnish scholarship presented in Supplemental File 1 are presented here in the form of nine questions. Does the proposed hypothesis explain:

- (i) the great enrichment in Mn compared with potential source materials?
- (ii) the substantial enrichment in Fe above potential source materials?
- (iii) the abundance of clay minerals?
- (iv) the nature of the contact between varnish and the underlying rock surface?
- (v) varnish occurrence on subaerial surfaces in all different climate regions?
- (vi) varnish occurrence in settings that have not been exposed to sunlight?
- (vii) the paucity of microfossils within varnish? [applies to biotic hypotheses only]
- (viii) ongoing diagenesis of varnish at the nanoscale?
- (ix) variable rates of accretion in various environmental settings?

Failing to pass one test invalidates the hypothesis.

This file starts with a duplication of section V in the main paper and then goes into detail on nine tests of seven hypotheses proposed to explain varnish formation.

Introduction to Supplemental file 2:

Varnish scholars have advocated a wide variety of hypotheses to explain how rock varnish forms. This section presents a summary analysis of hypotheses proposed or discussed over the past four decades to the falsification tests explained in section III and detailed in **Supplemental File 1**. A full analysis of each alternative hypothesis is the length of a separate paper and presented here in **Supplemental File 2**.

This section, thus, is just a synopsis of **Supplemental File 2**, starting with a brief summary of each hypothesis. The remainder of this supplemental file then explains which (if any) of these hypotheses pass a test, which hypotheses are in the realm of speculation with little or no support, and hypotheses that clearly fail particular tests.

These are the various hypotheses that have been proposed and discussed over the last four decades in varnish scholarship.

Microbial Community: An extensive microbial community exists on and within rock varnish, with inference that microbial processes play a role in varnish formation.

Culturing Mn-Fe organisms: A variety of Mn-Fe-concentrating microorganisms have been cultured from rock varnish.

Silica binding hypothesis: slow dissolution of silica and its subsequent gelling, condensation, and induration, provides a likely mechanism for the formation of desert varnish and silica glazes (Perry et al., 2006).

From the rock: A role for the underlying rock as a source of varnish ingredients continues in more modern scholarship (Lebedeva et al., 2019; Municchia et al., 2016; Raymond et al., 1988; Soleilhavoup, 1986; Thiagarajan and Lee, 2004).

Photo-oxidation of manganese: certain minerals in varnish such as birnessite and hematite promote Mn(II) oxidation in 1-5 μ m “tunnels” in existing varnish (Xu et al., 2019).

Cyanobacteria. Cyanobacteria growing on sunlit rocks sequester manganese in their cells. (Lingappa et al., 2021b).

Fluctuations in acidity: This abiotic process was proposed 65 years ago (Engel and Sharp, 1958) and starts with a shift to slightly acidic conditions that leaches Mn from its source material, followed by oxidation to Mn(IV) that then fixes Mn in varnish after water evaporation or an increase in pH (Goldsmith et al., 2014; Otter et al., 2020; Thiagarajan and Lee, 2004).

None of the hypotheses presented above and explained in detail below in this **Supplemental File 2** passed all nine tests. The microbial community hypothesis did not pass any of the nine tests. Culturing Mn-Fe organisms passed the greatest number of tests, 4 of 9. Full details are provided in **Supplemental File 2. Table 1** summarizes the results of this hypothesis testing.

Table 1. Summary of falsification testing results for the various hypotheses analyzed in this section. “No” indicates that currently available evidence on a test falsifies the hypothesis. Yes indicates currently available evidence on the test is consistent with the hypothesis. U (for uncertain) is that currently available evidence provides uncertain support in that test of the hypothesis.

Tested Hypothesis	Mn-rich	Fe-rich	Clay abundance	Rock contact	Different climates	No light	Few microfossils	Nanoscale diagenesis	Variable rates
Microbial biome	No	No	No	U	No	No	U	No	No
Cultured Mn oxidizers	Yes	Yes	No	No	Yes	Yes	No	No	No
Silica binding	No	No	No	Yes	No	No	U	No	No
Underlying rock	No	No	No	No	Yes	Yes	No	No	No
Photocatalysis	Yes	No	No	Yes	No	No	Yes	No	No
Cyanobacteria	Yes	No	No	U	U	No	No	No	No
Abiotic acidity fluctuations	U	No	U	U	No	No	Yes	No	No

The remainder of this supplemental file details the testing of these alternative explanations for varnish formation.

Hypothesis: An extensive microbial community exists on and within rock varnish, with inference that microbial processes play a role in varnish formation

A wide variety of different microorganisms grow on, or in rock varnish (Allen et al., 2004; Brewer and Fierer, 2018; Esposito et al., 2015; Esposito et al., 2019; Flood et al., 2003; Gleeson et al., 2018; Hirsch et al., 1995; Krumbein, 1969; Kuhlman et al., 2005; Kuhlman et al.,

2006a; Kuhlman et al., 2006b; Kutovaya et al., 2015; Lang-Yona et al., 2018; Lingappa et al., 2021a; Martínez-Pabello et al., 2021a; Nir et al., 2019; Northup et al., 2010; Palmer et al., 1985; Parchert et al., 2012; Paulino-Lima et al., 2016; Perry et al., 2004a; Perry et al., 2002; Perry et al., 2004b; Perry and Kolb, 2003; Powers et al., 2018; Ren et al., 2019; Schelble et al., 2005; Sterflinger et al., 1999; Sun et al., 2020; Taylor-George et al., 1983; Warsheid, 1990; Zhang et al., 2012).

There is a long tradition in varnish research of inferring that just the presence of organisms and organic material on or in varnish might indicate a role in varnish formation, but not explaining the process that connects this spatial autocorrelation to varnish formation. For example, a century ago, field observations noted that pollen and other organics deposit on varnish, and this material sometimes contains abundant manganese, but with no clear way to get the Mn into the varnish (White, 1924). Lichens grow on varnish-covered rocks leading to a suggested origin (Laudermilk, 1931); in reality lichen-generated acids dissolve varnish (Dragovich, 1987) and other rock surfaces (Fabero-Longo et al., 2011).

An example of this tradition of spatial autocorrelation that keeps emerging in the varnish literature started with research noting “black globular units” growing on varnish (Borns et al., 1980), later classified as microcolonial fungi (Staley et al., 1983). No purpose would be served in citing over a dozen papers in the last two decades making a suggested connection between microcolonial fungi and varnish formation, but without any evidence and failing to cite prior scholarship that these organisms do not enhance Mn or Fe (Dragovich, 1993). In contrast, these fungi destroy varnish; the acids they secrete erode pits into varnish (Krinsley et al., 1990; Oberlander, 1982).

Lang-Yona et al. (2018, p. 269) used metagenomic shotgun sequencing to identify an extensive varnish microbial community, but lacked evidence for “direct enzymatic involvement in varnish formation”; still, they suggest that “an indirect influence of the detected microorganisms could not be excluded.” Esposito et al. (2019, p. 7) also used shotgun metagenomics to note the absence of a manganese-oxidizing enzyme, but also speculate that “Fe and Mn accretion could be biological catalyzed by distinct microbial communities”. Thus, while the growing genetic literature on varnish microbial communities cannot pass a test of Mn-enrichment, many papers still speculate that there could be some unclear role for all of these organisms.

The microbial community hypothesis also fails tests to explain Fe enrichment, the abundance of clays, the presence of varnish in different climates and in settings lacking exposure to light, and the role of nanoscale diagenesis. Although some discussion over microbial fossils exists (Flood et al., 2003; Probst et al., 2001; Stein and Neilson, 1999), one of the biggest obstacles to the general involvement of the greater varnish microbial community rests in the extremely slow rate of varnish formation in the desert locations where most of the analyzed sample were collected. If this extensive microbial community is involved, some unknown process(es) would have to explain slow growth deserts and faster growth in wetter locations. In summary, a microbial community explanation is falsified by seven tests.

Hypothesis: A variety of Mn-Fe-concentrating microorganisms have been cultured from rock varnish

Culturing Mn-oxidizing organisms from on (or within) rock varnish reveals a number of microorganisms capable of concentrating Mn (Bolotina, 1976; Dorn and Oberlander, 1981; Glazovskaya, 1958; Glazovski, 1985; Grote and Krumbein, 1993; Hungate et al., 1987; Jones,

1991; Khak-mun, 1968; Krumbein, 1969, 1971; Krumbein and Jens, 1981; Mustoe, 1981; Northup et al., 2010; Palmer et al., 1985; Perfil'ev et al., 1965; Perry et al., 2004a; Staley et al., 1991; Zhang et al., 2012). A number of studies also indicate that Fe is also concentrated by microorganisms cultured from varnish and other coatings (Adams et al., 1992; Aguirre-Ramírez et al., 2022; Alnaimat et al., 2017; Marnocha and Dixon, 2013, 2014; Sterflinger et al., 1999).

This research certainly “passes” the first two tests of both Mn and Fe enhancement. These papers also answer affirmative the question of occurrence on subaerial surfaces in different climates (Glazovskaya, 1958; Glazovskiy, 1985; Mustoe, 1981) and also occurrence in settings not expose to sunlight (Khak-mun, 1968; Perfil'ev et al., 1965).

Certainly, there is nothing to preclude a role for other types of microorganisms concentrating Mn-Fe. In other words, the sorts of processes and forms presented in section 4 might also occur or microbes other than budding bacteria. The “problem” is that I have encountered only a few contexts where cocci- and rod-shaped bacterial encrustations of Mn-Fe oxides occur on the varnish surface or as partially preserved fragments in cross-sections. Nor have I encountered more than a few fungi or Cyanobacteria with casts of Mn-Fe. As infrequently as I observe budding bacterial Mn-Fe sheaths, I encounter other microbial Mn-Fe sheaths two orders of magnitude less frequently.

Existing research on culturing microbes able to oxidize and enhance Mn-Fe, but the role of these microbes is currently falsified by five of the tests because scholars do not present information pertaining to the following tests: explaining the abundance of clay mineral in varnish; explaining the nature of the varnish-rock contact; explaining the paucity of microfossils within varnish; explaining ongoing nanoscale diagenesis; or explaining variable rates of varnish accretion.

Hypothesis: Silica binding hypothesis

In the paper “baking black opal in the desert sun” Perry et al. (2006, p. 539) write: “[i]t is proposed here that the slow dissolution of silica (as hypothesized earlier; (Perry and Kolb, 2003)) from both anhydrous and hydrous minerals, and its subsequent gelling, condensation, and induration, provides a likely mechanism for the formation of desert varnish and silica glazes.” Even though the researchers documented that they studied Mn-rich varnishes in energy dispersive spectrometry (EDS) spectra (Perry et al., 2006), the hypothesis does not discuss how their proposed mechanism explains Mn-enrichment. Furthermore, no aspect of the proposed process explains Fe-enrichment in varnish. Thus, this hypothesis is falsified by the first two tests.

The third test links the proposed process of varnish formation to the dominance of clay minerals. The silica binding model depends on the interpretation that clay minerals are not a dominant part of rock varnish (Perry et al., 2006) — an interpretation that is contradicted by prior scholarship (Potter, 1979; Potter and Rossman, 1977, 1979b) establishing clay minerals as the dominant component (Chaddha et al., 2021; Chaddha et al., 2022; Diaz et al., 2002; Dietzel et al., 2008; Dorn and Krinsley, 2019; Dorn et al., 2012; Dorn and Oberlander, 1982; Drake et al., 1993; Duerden et al., 1986; Fang et al., 2023; Haberland, 1975; Israel et al., 1997; Johnson et al., 2002; Krinsley, 1998; Krinsley et al., 2012; Krinsley et al., 1995; Liu and Broecker, 2007; Martínez-Pabello et al., 2022; Probst et al., 2002; Sarmast et al., 2017; Spilde et al., 2007). Thus, the third test falsifies the silica-binding hypothesis.

The romantic article title ‘baking black opal in the desert sun’ (Perry et al., 2006) emphasizes the importance of the hot desert environment. Nothing in the proposed process (Perry and Kolb, 2003; Perry et al., 2006) relates to varnishes in geographic settings other than

hot deserts, providing another test that falsifies the silica-binding hypothesis.

Similarly, nothing in the proposed process explains the presence of rock varnish in a great many different subsurface settings (see section 3.6) that are not exposed to light or to the requisite baking in the heat, providing another test falsifying the hypothesis.

The silica-binding hypothesis involves ongoing diagenesis where water movement remobilizes silica, the key component of varnish in this hypothesis (Perry et al., 2006). Also, in this hypothesis, silica glaze and rock varnish are essentially a similar type of rock coating. However, nanoscale studies of the texture of silica glaze (Dorn et al., 2013a; Langworthy et al., 2010) reveal it to be stunningly different from rock varnish (Dorn et al., 2013b; Krinsley et al., 2013; Krinsley et al., 1995) that involve very different nanoscale diagenesis processes detailed in section 3.8. The silica-binding hypothesis is falsified by the nanoscale diagenesis test.

The hypothesis that silica binding forms rock varnish, focusing on hot desert surfaces, means that the processes proposed of silica dissolution, gelling, condensing and hardening would require that there be a severe rate-limiting step to explain very slow rates of varnish accretion of microns/millennia in hot deserts (Dorn, 1998; Liu and Broecker, 2000). However, studies of silica glaze on surfaces of known age (e.g., lava flows located in the hot, dry desert settings in Hawai'i) indicate it can form within decades (Curtiss et al., 1985; Dorn et al., 2013a; Gordon and Dorn, 2005), providing a seventh test that falsifies the silica-binding hypothesis.

Hypothesis: The underlying rock plays an important role in varnish formation

A persistent explanation for varnish formation focuses on the idea that the underlying rock somehow supplies the raw ingredients to make rock varnish. Almost all of the proponents for rock as the source of at least some varnish constituents published prior to the original rock varnish paper that reviewed problems with this hypothesis (Dorn and Oberlander, 1982).

A role for the underlying rock as a source of varnish ingredients, however, still continues in more modern scholarship (Lebedeva et al., 2019; Municchia et al., 2016; Raymond et al., 1988; Soleilhavoup, 1986; Thiagarajan and Lee, 2004). These papers present no empirical data that supports a role for the underlying rock. Geochemical modeling (Thiagarajan and Lee, 2004), finding some Mn-Fe rich rock material (Municchia et al., 2016) and speculating based on light and SEM microscope observations (Soleilhavoup, 1986) (Raymond et al., 1988) provide no clear process(es) by which rock varnish results from underlying rock constituents. The most specific process, albeit unsupported by data, comes from Lebedeva et al. (2019) who proposed that heavy brief summer precipitation events reduce Mn and Fe from the rock, leading to migration to the surface. Then, Ba and Mn re-oxidize with Fe and titanium as co-precipitates. The next effect is precipitation of rock varnish on the surface of rocks in desert pavements. None of these papers address the arguments made in the origin rock varnish paper (Dorn and Oberlander, 1982) or scholarship reviewed in section 3.4.

In the end, these speculative papers on a role for the underlying rock only present evidence that meets two of the falsification tests: presence in different climate regions; and occurrence on surfaces not exposed to sunlight. The other seven tests falsify the continuing notion that the underlying rock somehow plays a role in varnish formation

Hypothesis: Photo-oxidation of manganese

Studying five varnishes on the surface of desert pavement clasts in the Gobi Desert, Xu et al. (2019) found that certain minerals in varnish such as birnessite and hematite promote Mn(II)

oxidation in 1-5 μm “tunnels” in existing varnish. This, of course, produces a “chicken vs. egg” problem: if existing varnish is required to oxidize Mn, how does that first existing varnish form?

Xu et al. (2019) also report that metal oxide-mediated photocatalysis produces the typical slow growth of varnish found in warm deserts (Xu et al., 2019). Xu et al. (2019) carried out laboratory experiments of their proposed photo-oxidative hypothesis using purchased standard minerals rather than those extracted from varnish, to demonstrate faster Mn(II) oxidation than a homogenous solution under controlled conditions. Like most other hypotheses, the photo-oxidative model focuses on only the first test of explaining Mn-enrichment.

Xu et al. (2019) present bulk ICP-MS data and also microprobe data, demonstrating similar Fe enrichment found in other rock varnishes. Their data includes comparisons between bulk varnish and bulk soil dust, indicating Fe enhancement in varnish compare to dust as a potential source material. However, nothing in the proposed photo-oxidative hypothesis relates to explaining Fe enrichment, resulting in a failed test given available evidence.

A second failed test involves not explaining the abundance of clays in varnish. In fact, Xu et al. (2019 p. 55) assert that the light-responsive semiconducting minerals (birnessite, hematite, goethite, rutile, anatase) are “the major components of rock varnish”. This assertion is not consistent with their microprobe data showing fairly typical oxide weight percentages for clay-bearing Si-Al-Mg. This assertion is also not consistent with their ICP-MS bulk analyses showing the clay-bearing Si-Al-Mg percentages of 60-80%.

Xu et al. (2019, p. 68) recognized that their proposed formation mechanism does not explain varnishes in the subsurface, in low-light settings like Antarctica, or in humid regions with abundant tree cover. Thus, Xu et al. (2019) acknowledge their hypothesis does not meet the tests of varnishes formed in different climates and in settings with no light.

Xu et al. (2019) did not address explaining the nature of the contact between varnish and the underlying rock. This is not a trivial issue with this hypothesis, because the photo-oxidative model requires pre-existing “tunnels” of varnish on the order of a few microns in diameter. Thus, how does rock varnish start to form on a bare-rock surface without these pre-existing varnish tunnels? Given the lack of attention to how the model starts up, this test also currently falsifies the hypothesis.

Another failed test that rejects the hypothesis involves not linking photocatalysis as a process to nanoscale diagenesis as a key aspect of varnish formation. Xu et al. (2019) do not address how the oxidized Mn becomes incorporated into varnish via nanoscale ongoing diagenesis. Put more simply, the photo-oxidative hypothesis generates Mn(IV), but does not explain how it inserts into the structure of varnish.

Hypothesis: Cyanobacteria

Studying seven subaerial varnish samples from arid and semiarid locales in the southwestern USA, Lingappa et al (2021a p. 6) proposed the following hypothesis:

“Cyanobacteria grow on sunlit rock surfaces with intermittent access to water, sequestering high concentrations of manganese in their cells and exploiting the unique redox chemistry of manganese complexes as a catalytic antioxidant system that enables their survival in such a harsh environment. When they die, the residue from their biomass provides an enriched manganese source that is ultimately oxidized to form the oxide mineral cements that comprise varnish. Since varnish forms over timescales of millennia, a well-developed varnish sample represents the time integrated manganese accumulation of many, many generations of cells, which are sparsely distributed at any given time.”

Lines 275-276 in the Lingappa et al. (2021b) supplementary file continues: “The Cyanobacteria provide an additional mechanism for Mn oxidation that has not previously been discussed in the context of varnish” (Lingappa et al., 2021b). Cyanobacteria (formerly called blue-green algae), however, have been one of several proposed agents of varnish formation for the last half-century (Krumbein, 1969; Krumbein and Jens, 1981; Scheffer et al., 1963).

Lingappa et al.’s (2021a) Cyanobacteria hypothesis fails to meet the test of explaining substantial enrichment of Fe in varnish. Their paper notes that Fe is an important component of varnish, but they do not explain how Cyanobacteria generates iron’s enhancement.

Lingappa et al.’s (2021a) Cyanobacteria hypothesis fails to meet the test of explaining the abundance of clay minerals in varnish. Simply indicating that Cyanobacteria residue ultimately cements varnish is speculation, without any evidence to indicate how cellular residue interacts with clays to produce rock varnish.

Lingappa et al.’s (2021a) Cyanobacteria hypothesis does operate in semiarid climates. Prior Cyanobacteria research indicates activity in wetter climatic regions as well (Krumbein, 1969; Krumbein and Jens, 1981; Scheffer et al., 1963). However, no prior scholarship addresses the role of Cyanobacteria in colder settings like Antarctica and Greenland. Thus, “U” for uncertain would be an appropriate result for the test of non-desert subaerial settings.

Lingappa et al.’s (2021a)’s Cyanobacteria hypothesis starts with the observation that they grow on “sunlit rocks”. Thus, this hypothesis fails the test of explaining rock varnishes in subsurface positions such as on the sides of rock fractures (Dorn and Oberlander, 1982; Douglas, 1987; Eren et al., 2014; Hunt, 1972; Weaver, 1978), under glaciers (Surdam et al., 1989; Whalley et al., 1990), on the walls of subterranean pukios (Clarkson and Dorn, 1991), on ancient Egyptian walls (Elshabrawy and Ali, 2021), on rock surfaces in soils (Bolotina, 1976; Hamung, 1968; Huang et al., 2011; Khak-mun, 1966; Li et al., 2017; Xu et al., 2018), and in caves (Boston et al., 2008; Northrup et al., 2003).

Similarly, explaining why few microfossils occur within the internal structure of rock varnish would be a failed test. Lingappa et al. (2021a) assert that the Cyanobacteria would breakdown into residue. However, no evidence or even speculation connects the hypothesis to the lack of microfossils, especially where Cyanobacteria appear to be so abundant.

Lingappa et al.’s (2021a) did not address how Cyanobacteria’s role links to ongoing nanoscale diagenesis process that produce rock varnish. Simply asserting that residue somehow interacts with the rest of varnish constituent to cement the coating is speculative. Without evidence, this would be considered a failed test.

Hypothesis: Fluctuations in acidity generate rock varnish abiotically

A persistent geochemical explanation for varnish formation has focused on the tremendous enhancement of Mn compared to all potential source constituents, without the need for any biological processes (Engel and Sharp, 1958; Hooke et al., 1969; Linck, 1901; Moore and Elvidge, 1982; Smith and Whalley, 1988; Whalley, 1983). This abiotic process starts with a shift to slightly acidic conditions that leaches Mn from its source material, followed by oxidation to Mn(IV) that then fixes Mn in varnish after water evaporation or an increase in pH.

After a hiatus of a few decades, geochemists working on rock varnish have refocused on this acidity fluctuation hypothesis, but with some refinements based on observations made in warm deserts in this dusty setting (Goldsmith et al., 2014; Otter et al., 2020; Thiagarajan and Lee, 2004). For example, one refinement involves the idea of acidification of surface water via

uptake of atmospheric carbon dioxide, that can then leach a host of metals from the desert dust, with subsequent moisture evaporation leading to deflation of the leached dust (Otter et al., 2020).

The aforementioned scholarship offers a theoretical explanation for the strong Mn enrichment in rock varnish. However, the basic hypothesis has been “hanging around” for over a half century without any empirical evidence that this process actually operates on or in rock varnish. The following seven reasons indicate why fluctuations in acidity remains a speculative idea:

(i) No proponents of acidity fluctuations have shown *in situ* evidence of the proposed process operating. In contrast, research into the budding bacteria-polygenetic hypothesis focused much effort on whether or not budding bacteria can be “caught in the act of Mn enhancement”. Proponents of acidity fluctuations often present extensive electron microscopy of varnish cross-sections; but this research simply studies varnishing that took place thousands of years ago. It's the equivalent of trying to find a murder weapon in a bank vault instead of dredging the lake where the accused murderer was seen. Certainly, studying the surface of rock varnishes in warm deserts for a “smoking gun” would be time consuming. That nobody has tried to find clear *in situ* evidence of the proposed process in 65 years (Engel and Sharp, 1958) is the first reason why acidity fluctuations remain only speculation.

(ii) Where are the actual field measurements of the biogeochemical conditions that the acidity fluctuation hypothesis requires? Do pH/Eh shifts in these field data match model requirements? Are such measurements made at one point in time, or over a week or longer to monitor frequently and nature of the changes? Are such measurements made at multiple sites in different environmental conditions, and in what season? The lack of key field data on geochemical conditions is the second reason why acidity fluctuations remain a speculative notion.

(iii) Proponents of acidity fluctuation research simply cite experimental data for laboratory studies on abiotic oxidation rates of Mn that have nothing to do with varnish materials (Goldsmith et al., 2004: 103). Only a series unstated assumptions infer that these laboratory studies reflect the realities of the varnish environment. Why not conduct oxidation rate studies using real materials collected from field settings?

(iv) Organic acids certainly exist on rock varnish surfaces, even in hot warm deserts, as evidenced by organic remains (Nagy et al., 1991). Consider that microcolonial fungi are common on hot desert surfaces (Staley et al., 1982) and that varnish hosts a microbial biome (Esposito et al., 2019; Kuhlman et al., 2006a). Yet, no proponents of acidity fluctuations evaluated potential confounding factors associated with the presence of organic acids.

(v) Recent research reveals that rock varnish has extreme hydrophobic properties (Chaddha et al., 2023). There are theoretical effects of hydrophobicity on the proposed acidification hypothesis that need to be simulated in the lab, and perhaps data gathered in the field.

(vi) Proponents of other hypotheses have attempted to simulate the formation of varnish in a laboratory setting (Dorn and Oberlander, 1982; Krumbein and Jens, 1981; Xu et al., 2018). The only experimental support for a purely geochemical process of Mn-enrichment come from laboratory and field experiments to cover graffiti with “artificial desert varnish” (Elvidge and Moore, 1980) by spraying an alkaline agent on rock surfaces, followed by a solution of divalent Fe and manganese. This experiment was never intended to simulate real-world varnish, only come up with a solution to landscape scars and graffiti in deserts. The lack of an attempt at

simulating artificial varnish growth via acidity fluctuations in 65 years reflects the speculative nature of the hypothesis.

(vii) My strong preference would have been for advocates of abiotic Mn-enhancement via acidification to carry out a field or lab experiment to assess whether or not acidity fluctuations can actually enhance Mn using real varnish samples. Since this experiment has not yet been conducted by proponents, and since I live in the dusty, hot Sonoran Desert, I felt compelled to see if simulating the proposed processes showed any evidence of Mn-enhancement in a field-based experiment.

Step 1: I started the experiment by collecting winter precipitation with a pH of 6.3 from South Mountains. This is a region with abundant desert dust fallout, and I focused the experiment on stable well-varnished gneiss boulders more than 1.5 m in diameter (Dorn, 2016).

Step 2: I pounded the boulders with a rock hammer to the point where fractures would form on the margins of 3-5 mm diameter depressions with abundant dust and well varnished pockets. The idea was to be able to place the acidic precipitation droplets in these depressions, have the water not penetrate down the fractures, but be able to wiggle samples out with a tweezer after the precipitation dried. There were plenty of boulders, and ten such depressions were located on 10 separate boulders.

Step 3. With a pipette, the tiniest of droplets were placed gently and bit-by-bit filled up the tiny depressions. This took place on a cloudy winter day with an air temperature of 10 °C. It took about 10 minutes to fill up a depression, and it took between 40 and 90 minutes for the water to fully evaporate.

Step 4. The samples were gently wiggled out via tweezers as slivers of rock and varnish less than a centimeter long in the maximum dimension.

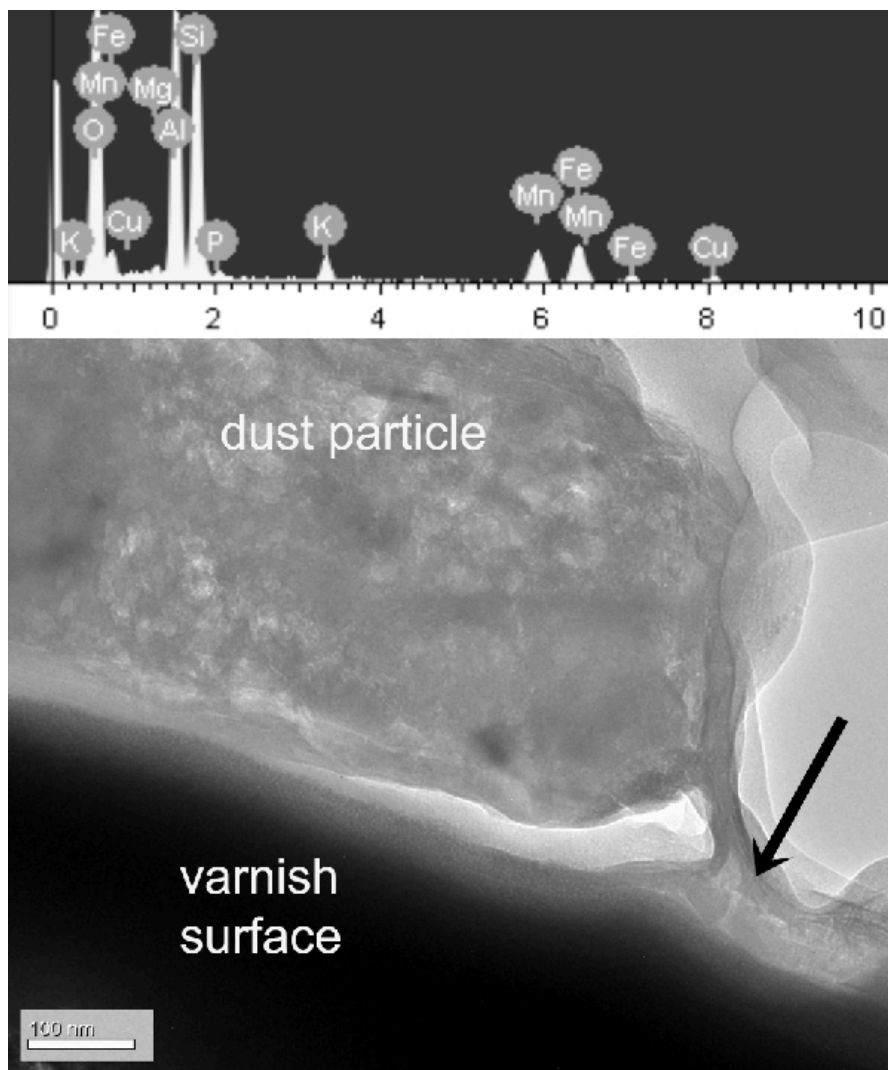
Step 5. Samples were subject to STEM microscopy with EDS. The idea was to examine the nanoscale interface between dust and pre-existing varnish for any evidence of chemical release of Mn from the dust grain into the varnish.

None of the 10 samples showed any evidence of Mn release or reprecipitation via the process of abiotic shifts in acidity. One of the 10 samples showed the possibility of iron release from a dust particle being adsorbed onto a rock varnish surface.

One of the 10 samples showed evidence of the development of budding bacteria. **Figure S1** shows a HRTEM image of a dust particle that landed on a varnish surface. A hyphae-form appears to be attaching itself to this particle, and also enhancing both Mn and Fe. Some smaller budding hyphae can have diameters of 100 to 200 nm when they are alive thus, the hyphae form in **Figure S1** must have experienced severe desiccation, in the field and in sample preparation. EDS analyses of the budding hyphae shows both Mn and Fe enhancement, and the adsorbed dust particle did not. The source of the Mn and Fe enhanced by the budding bacteria could have been the acidic wetting.

Figure S1 (Figure in Supplemental File):

Although there was no evidence that abiotic fluctuations in pH could enhance Mn in a field experiment conducted in the Sonoran Desert, there was one sample that showed growth of budding bacteria (arrow), as evidenced by this image of a desiccated budding hyphae that shows both Mn and Fe enrichment in the EDS obtained at the arrow. The hyphae appears to be adsorbed to a dust particle.



In summary, the first test of the acidity fluctuation hypothesis is whether it explains Mn-enhancement in varnish. The answer is “uncertain”. Theoretically, over sixty years of scholarship continues to speculate that small shifts in acidity could potentially enhance Mn in varnish. However, the complete lack of field-based empirical support for this mechanism leads to the conclusion that hypothesis is still speculative. Without clear *in situ* evidence of the release of Mn from dust and subsequent reprecipitation in varnish, without experimental support showing such a process in the laboratory, relying on Mn-oxidation laboratory experiments unrelated to varnishing conditions, and failing to consider a number of confounding factors like organic acids leaves the test findings as “U” for uncertain. Simply repeating a reasonable process again and again begins to fall on deaf ears when there’s a complete lack of empirical evidence that the process occurs at the surface of rock varnish.

The second test is whether the acidity fluctuation hypothesis explains the substantial enrichment of Fe at bulk, micron, and nanoscales? The answer is a clear no. Nothing in the acidity fluctuation hypothesis can explain how Fe is enhanced, especially not observed abundances of Fe explained in section 2.2.

The third test is whether the proposed hypothesis explains the dominance of clay minerals as the major component of rock varnish. Since hypothesis proponents focus almost

exclusively on warm and dusty desert surfaces, the assertion is that some of the dust that releases Mn is clay-rich and is incorporated into varnish (Goldsmith et al., 2014; Otter et al., 2020; Smith and Whalley, 1988). Thiagarajan and Lee (2004) present a variety of theoretical interactions of aeolian clay-rich fallout and possible varnish processes. However, theoretical interactions and a spatial autocorrelation with dust fails to offer a real-world explanation of how slight acidity fluctuations might result in clays comprising over half and sometimes up to 70% of rock varnish (section 2.3). Thus, the test result is best summarized as U or uncertain.

The fourth test is whether acidity fluctuations explain the nature of the varnish/rock contact. Certainly, recent proponents of abiotic acidification argued for an external origin of varnish constituents (Goldsmith et al., 2014; Otter et al., 2020). However, abiotic acidification proponents still argue that this process could be consistent with an internal origin for varnish constituents (Engel and Sharp, 1958; Smith and Whalley, 1988; Thiagarajan and Lee, 2004; Whalley, 1983). Given the internal ambiguity of hypothesis proponents, the test result would best be “U” for uncertain.

Fifth, the abiotic acidification hypothesis will not work on subaerial surfaces in the many humid regions, or in the many subaerial rock surfaces in all regions that experience geochemical conditions too acidic to oxidize Mn(II) (Dorn, 1990). Thus, rock varnish formation outside of warm and dust desert surfaces fails this test.

Otter et al. (2020) did note that the conditions that occur on warm desert surfaces exposed to abundant dust fallout differed substantially at one particular study site. Thus, they proposed similar, albeit slightly different processes of abiotic leaching, to explain greater Mn abundance and probable faster rate of accretion at a single quartz-rich study site. Whether the ideas of Otter et al. (2020) could be applied to any other semi-arid locations, or to wetter humid locations, was not addressed.

The fundamental problem with the acidification hypothesis for non-deserts is that it relies on an abiotic process of oxidizing Mn in settings that receive an abundance of naturally acidic precipitation, without any alkaline dust. These wetter subaerial settings also have the challenge of epilithic organisms that secrete acids like fungi (Fabero-Longo et al., 2011; Gadd, 2007, 2017), lichens (Aghamiri and Schwartzman, 2002; Armstrong and Bradwell, 2010), and other epilithic organisms (Viles, 2011, 2013).

Sixth, as proposed by its proponents, the abiotic acidification hypothesis works only on subaerial rock surfaces. The extensive scholarship on rock varnish cited in section 3.6 of this paper includes rocks found in soils, subterranean Egyptian tombs, subterranean prehistoric canals, fractures in bedrock of different types and other subsurface settings. Nothing in scholarship explains how slight acidity fluctuations might explain varnishes in subsurface settings.

Since this is an abiotic hypothesis, the seventh test related to the paucity of microfossil is not relevant.

The eighth test deals with what happens after Mn-Fe enrichment occurs when ongoing diagenesis occur at the nanoscale. Certainly, nothing in the abiotic acidification literature focuses on what happens after enhancement (Goldsmith et al., 2014; Otter et al., 2020; Thiagarajan and Lee, 2004). While slight acidity fluctuations would not preclude post-enrichment diagenesis processes reviewed in section 3.8, this test cannot be “assumed away”. Given the lack of focus on details of what happens after the proposed process operates, the best result at this time is “no” or does not explain ongoing nanoscale diagenesis.

The ninth test is whether the proposed hypothesis explains variable rates of varnish accretion in different environmental settings. Goldsmith et al. (2014) and Otter et al. (2020) make theoretical arguments why the proposed process of varnish leached from dust could explain varnish rates of accretion on the scale of microns per millennia in warm deserts (Dorn, 1998; Liu and Broecker, 2000). Otter et al. (2020) proposed that a variation on this model for a South African semi-arid study site could explain a faster rate of growth at that location. However, how this model could explain faster rates of varnish growth in various humid locations (Dorn and Meek, 1995; Krinsley et al., 2017; Spilde et al., 2013) remains unaddressed. At the present time, thus, the abiotic acidification hypothesis cannot explain observed variability in rock growth rates.

Summary of Supplemental file 2:

Rock varnish consists of over half clay minerals, about a third Mn and Fe oxides, as well as minor and trace elements that deposits as a paper-thin accretion on an underlying rock. This definition has been adopted widely:

(Andreae et al., 2023; Aulinas et al., 2015; Chaddha et al., 2021; Chaddha et al., 2022; Dietzel et al., 2004; Dorn and Oberlander, 1982; Dragovich, 1988a; Drake et al., 1993; Elshabrawy and Ali, 2021; Esposito et al., 2019; Forster et al., 2021; Glazovskiy, 1985; Harrington, 1987; Hodge et al., 2005; Hungate et al., 1987; Jahn and Maneck, 1991; Jones, 1991; Krinsley, 1998; Krinsley et al., 2013; Krumbein and Jens, 1981; Kuhlman and Abrecht, 2008; Kuhlman et al., 2006a; Lingappa et al., 2021a; Liu et al., 2021; Martínez-Pabello et al., 2021a; Martínez-Pabello et al., 2021b; McKeown and Post, 2001; Nagy et al., 1991; Northup et al., 2010; Otter et al., 2020; Pineda et al., 1988; Reneau et al., 1992; Spilde et al., 2007; Spilde et al., 2013; Wang et al., 2011; Wayne et al., 2004; Whalley et al., 1990; Xu et al., 2019; Zerboni et al., 2022; Zhang et al., 2012; Zhou et al., 2000).

Overwhelming scholarship indicates that Fe-enhancement is one of the defining characteristics of rock varnish:

(Adams et al., 1992; Allen, 1978; Aulinas et al., 2015; Cremaschi, 1996; Dorn, 1990; Dorn and Dragovich, 1990; Dorn et al., 1992; Dragovich, 1988b; Drake et al., 1993; Duerden et al., 1986; Edwards et al., 2004; Elvidge and Moore, 1980; Engel and Sharp, 1958; Forster et al., 2021; Garvie et al., 2008; Glazovskiy, 1985; Goosens et al., 2015; Harmon et al., 2021; Hooke et al., 1969; Jones, 1991; Liu and Broecker, 2007, 2013; Macholdt et al., 2015; Martínez-Pabello et al., 2021b; Moore and Elvidge, 1982; Potter and Rossman, 1979a; Rahim and Ismail, 2020; Ren et al., 2019; Sarmast et al., 2019; Xu et al., 2018; Zerboni, 2008).

Furthermore, scholarship in rock varnish reveals that the dominance of clay minerals is a characteristic that has been confirmed using different techniques and in a variety of different climates and microenvironmental settings

(Chaddha et al., 2021; Chaddha et al., 2022; Diaz et al., 2002; Dietzel et al., 2008; Dorn and Krinsley, 2019; Dorn et al., 2012; Dorn and Oberlander, 1982; Drake et al., 1993; Duerden et al., 1986; Fang et al., 2023; Haberland, 1975; Israel et al., 1997; Johnson et al., 2002; Krinsley, 1998; Krinsley et al., 2012; Krinsley et al., 1995; Liu and Broecker, 2007; Martínez-Pabello et al., 2022; Probst et al., 2002; Sarmast et al., 2017; Spilde et al., 2007).

Put another way, Mn-Fe skins are a type of rock coating that does not include clay minerals and is not considered to be rock varnish (Dorn, 1998, 2022).

What is particularly perplexing is that only one of the proposed hypotheses analyzed in this Supplemental File 2 dealt with major components of rock varnish other than Mn. Only one hypothesis dealt with Fe-enhancement: culturing organisms that enhanced Fe. None of the proposed hypotheses analyzed in this Supplemental File 2 linked specific varnish-forming processes to the dominance of clay minerals. In the end, all of the proposed hypotheses analyzed in this supplemental file failed five or more tests.

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