



Rock varnish in New York: An accelerated snapshot of accretionary processes

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ABSTRACT

Samples of manganiferous rock varnish collected from fluvial, bedrock outcrop and Erie Barge Canal settings in New York state host a variety of diatom, fungal and bacterial microbial forms that are enhanced in manganese and iron. Use of a Dual-Beam Focused Ion Beam Scanning Electron Microscope to manipulate the varnish *in situ* reveals microbial forms that would not have otherwise been identified. The relative abundance of Mn–Fe-enriched biotic forms in New York samples is far greater than varnishes collected from warm deserts. Moisture availability has long been noted as a possible control on varnish growth rates, a hypothesis consistent with the greater abundance of Mn-enhancing bioforms. Sub-micron images of incipient varnish formation reveal that varnishing in New York probably starts with the mortality of microorganisms that enhanced Mn on bare mineral surfaces; microbial death results in the adsorption of the Mn-rich sheath onto the rock in the form of filamentous networks. Clay minerals are then cemented by remobilization of the Mn-rich material. Thus, the previously unanswered question of what comes first – clay mineral deposition or enhancement of Mn – can be answered in New York because of the faster rate of varnish growth. In contrast, very slow rates of varnishing seen in warm deserts, of microns per thousand years, make it less likely that collected samples will reveal varnish accretionary processes than samples collected from fast-accreting moist settings.

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1. Introduction

The scholarly study of manganese-rich rock coatings started with observations on rocks along the splash-zones of tropical rivers (von Humboldt, 1812; Darwin, 1897). The first monograph examining Mn-rich coatings focused on rocks along rivers in moisture-rich conditions (Lucas, 1905). Some of the first microscopic evidence of a biotic origin for Mn-rich coatings was found on stream-side rocks in a Queensland rainforest (Francis, 1921). A long tradition of basic and applied research on Mn-rich coatings in a wide variety of fluvial settings (Ball, 1903; Bhatt and Bhat, 1980; Blackwelder, 1948; Boussingault, 1882; Carpenter and Hayes, 1978; Carpenter and Hayes, 1980; Hem and Lind, 1994; Huelin et al., 2006; Hunt, 1954; Klute and Krasser, 1940; Potter, 1979; Robinson, 1981; Robinson, 1993; Tebo et al., 2005; Whalley et al., 1990; Zahn, 1929) contrasts with the common textbook and Internet perception that rock (or desert) varnish is a dryland phenomenon.

Black Mn-rich coatings have also been studied in non-arid settings other than stream sides, including: alpine (Dorn and Oberlander, 1982; Glazovskaya, 1968; Glazovskiy, 1985; Höllerman, 1963; Hooke et al., 1969; Hunt, 1954; Krinsley et al., 2009; Krumbein, 1969; Scheffer et al., 1963); Arctic (Büdel, 1960; Cailleaux, 1967; Rapp, 1960; Skarland

and Giddings, 1948; Washburn, 1969); Antarctic (Dorn et al., 1992; Glazovskaya, 1958; Glazovskaya, 1971); humid mid-latitude settings (Dorn and Meek, 1995; Douglas, 1987; Ha-mung, 1968; Krumbein, 1969; Tricart and Cailleaux, 1964); cold springs (Hunt, 1961; Hunt, 1972; Mustoe, 1981; Supplee et al., 1971); hot springs (Tazaki, 2000); fractures in regolith and bedrock in humid settings (Khak-mun, 1966; Kim et al., 2006; Weaver, 1978); as cutans in soils (Bolotina, 1976; Khak-mun, 1966; Huang et al., 2011); and caves (Moore, 1981; Northup et al., 2010; Peck, 1986; Rossi et al., 2010). The plethora of studies on Mn-rich coatings in non-arid settings led to the position advocating the term “rock varnish” in place of “desert varnish” (Krumbein and Jens, 1981; Dorn and Oberlander, 1982).

Despite two centuries of research on riverine and other non-arid rock varnishes, the last few decades have seen researchers focus on Mn-rich coatings in deserts (Boizumault et al., 2010; Christensen and Harrison, 1993; Flood et al., 2003; Garvie et al., 2008; Hodge et al., 2005; Kuhlman and McKay, 2007; Kuhlman et al., 2006a; Lee and Bland, 2003; Liu and Broecker, 2007; Liu and Broecker, 2008b; Nowinski et al., 2010; Patyk-Kara et al., 1997; Perry et al., 2006; Schelble et al., 2005; Wang et al., 2011; Zerboni, 2008; Zhang et al., 1990; Zhou et al., 2000). The reasons for the apparent recent bias toward desert settings are unclear; it could have to do with the sociology of science where researchers focus on a perceived funding source, for example NASA-supported research regarding Martian analogs (DiGregorio, 2002; DiGregorio, 2010; Marlow et al., 2011). A desert focus could

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also have to do with the greater biogeochemical stability of varnish in arid settings (Dorn, 1998; Dorn, 2007; Dorn, 2009). Alternatively, there is a point of view that the Mn-rich coating found in deserts is somehow distinct from similar coatings in non-arid settings (Blackwelder, 1948; Daveau, 1966; Loew, 1876; Peel, 1960; Lukashev, 1970; Moore and Elvidge, 1982; Perry et al., 2006).

Regardless of the rationale, the recent trend toward eschewing the study of varnish in non-arid settings may generate bias in theory development. Consider recent ground-breaking research on the microbial origin of varnish in caves and semi-arid environments (Northup et al., 2010; Rossi et al., 2010). While we consider cave-based and other mesic-setting research on microbial activity (Chafetz et al., 1998; Dorn, 1998; Dorn and Meek, 1995; Ha-mung, 1968; Krumbein, 1969; Mustoe, 1981) relevant to the issue of varnish formation in what are now deserts, this position is not shared universally.

Examination of varnish microlamination patterns in thousands of ultrathin cross-sections reveals rates of varnish formation in arid regions to be on the order of a just a few microns per millennia (Dorn, 1998; Liu and Broecker, 2000). Thus, an alternative view could be posed in the form of a question: how can the surfaces of rocks in hyperarid climates that varnish so slowly be considered similar to rocks that experience liquid water regularly and become coated within years to decades?

One potential answer rests in the thread of research finding that frequent moistening increases rates of varnish formation (Buchun et al., 1986; Capot-Rey, 1965; Dorn and Meek, 1995; Dorn and Oberlander, 1982; Goodwin, 1960; Hunt, 1954; Hunt and Mabey, 1966; Klute and Krasser, 1940). Using the Holocene calibration of varnish microlaminae (Liu and Broecker, 2007), a study of varnish on debris flows in Phoenix, Arizona revealed that varnish can form one to two orders of magnitude faster in particularly mesic microenvironments; these mesic settings, however, favor acid-producing lithobionts that typically out-complete and end up eroding most of the varnish (Dorn, 2010).

Fig. 1 explains this problem in a thought exercise of the continual interplay between varnish deposition, occupation of rock surfaces by organisms that erode or grow faster than varnish, and the role of rock hardness. In this conceptualization (Fig. 1), the ideal place to study accelerated varnish formation would be in a wet setting that does not foster the growth of epilithics that interfere with varnishing. Caves, alpine environments, and boulders in the splash zone of streams offer researchers the ability to study rapid varnishing while minimizing exposure to the erosive effects of faster-growing lithobiont competition. Thus, one answer to the question of relevance of mesic-based research to varnish formation in deserts climates is the ability to study rapid varnishing with lessened interference from varnish-destroying lithobionts.

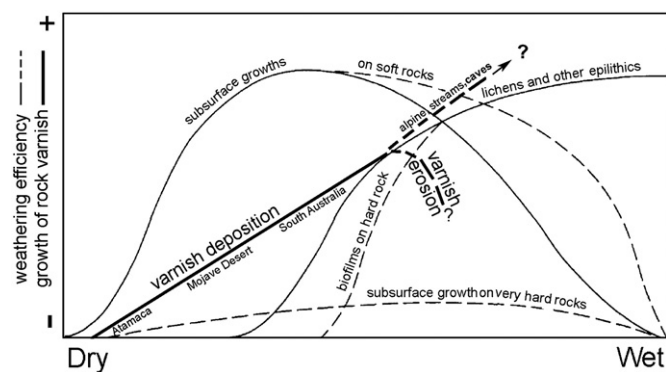


Fig. 1. Conceptual model, combining prior thoughts (Dorn and Oberlander, 1982; Viles, 1995), of how lithobionts and rock varnish interact together. The graph is a generalization of how effective moisture impacts the growth of rock varnish and the weathering efficiency of lithobionts. In the case of rock varnish, a second key factor other than moisture is competition from lithobionts. In the case of lithobionts, a second key factor is the hardness of the rock.

An even broader reason for continuing research on non-arid varnishes is that the study of Mn-rich rock coatings in a variety of climatic and environmental settings will promote the development of a more comprehensive theory of varnish formation. To that end, this paper returns to the tradition of studying varnishes in an area that few would associate with “desert varnish”, i.e. New York. Manganese-rich coatings on stream gravels are fairly common along streams in New York and elsewhere in northeastern North America (Carpenter et al., 1975; Huelin et al., 2006; Whitney, 1981). Our research hypothesis going into this investigation was that we would find substantial differences between New York and warm desert varnishes through the use of a new generation of scanning electron microscopes (SEM).

The study site section of this paper overviews the location and nature of sampling locales. In this initial investigation into New York varnishes, we did not employ a random or stratified random sampling technique. “Grab bag” samples were collected at places where dark Mn-rich rock coatings were visually obvious. The Methods section details the high-resolution electron microscope techniques used to examine New York samples. Results and discussion sections are combined in order to organize research findings into key themes and relate results to prior research.

2. Study sites

We collected samples from sites in New York that represent different environmental contexts. Settings include riverine settings where rock varnish forms in contact with flowing water, on rocks quarried a century ago for the Erie Barge Canal, on a glacial erratic, and subaerial varnishes that started inside opened bedrock fractures (Fig. 2). The riverine sites experience periodic high water inundation, but the other sites are in subaerial position. For the times of year when the surfaces are exposed only to the atmosphere, they are subject to precipitation in the range of 750 to 1500 mm that ranges between 3000 and 6000 mm of snowfall. Mean annual monthly temperatures range from -14°C in January to 26°C in July.

A site of interest is the Erie Canal, because it provides available chronological control in the region. Unweathered Silurian Keefer Formation sandstone of the Clinton Group was quarried a century before our sample collection (Fig. 3). Quarrying took place at a nearby stone quarry in Gasport between 1908 and 1917 (Jesse Bieber, Town of Royalton Historian, personal communication, 2011). The third version of the canal was completed in 1918, was approx. 3.5×36.5 m, and was engineered for powered boats instead of mule-drawn craft. Varnished clasts were collected from canal banks between Gasport and Middleport in a high enough position that was unlikely to have experienced splashing from barge movement.

A second sampling site is along NY route 458 in the Adirondack Northwest Lowlands, where joint faces of granitic gneiss appear to have been exposed during road construction (Fig. 2).

We also sampled two sites along the Raquette River, a perennial stream that initiates in the southern highlands of the Adirondack Mountains dominated by gneiss and flows into the lower drainage dominated by till, dolomite and sandstone. Our sampling sites on the Raquette are in the zone of transition from gneiss to glacial till. One environmental setting is a typical riverbank dominated by gneiss till boulders, and the second the environmental setting is more like a lake shoreline than a river bank (Fig. 2), also with gneissic till.

3. Methods

Randomly-selected rock fragments with rock coatings were taken from collected samples. All samples were analyzed using the latest electron microscope technology at the CAMCOR facility of the University of Oregon, including use of a Dual-Beam Focused Ion Beam (DB-FIB) Scanning Electron Microscope. The DB-FIB has a micromanipulator that digs into surfaces, and turns material over on the order of one



Fig. 2. Collection sites of rock varnishes in New York, where the left image provides an overview of the site and the right image presents a close-up of the sampling locale. Upper row: Erie Barge Canal region (N 43.18916 W 78.56873). Second row: Raquette River in a location of active turbulent flow (N 44.53372 W 74.92573). Third Row: Raquette River at Higley Flow State Park where the shoreline is almost lacustrine in terms of the low velocity (N 44.50434 W 74.92573). Fourth Row: New York route 458 between St. Regis Falls and Santa Clara (N 44.62762 W 74.42345), where joint faces appear to have been exposed by blasting during road construction.

micron to 30 μm wide. DB-FIB preparation of samples allows examination with scanning/transmission electron microscopy (STEM) and energy dispersive analysis of X-rays (EDS) — all while maintaining a vacuum. High resolution back-scattered electron microscopy was used on the surfaces of all samples, and in addition, one of the samples (Raquette River, quiet water site) was prepared by thinning it to approximately 100 nm with the focused ion beam portion of the DB-FIB instrument. We then used scanning transmission electron microscopy (STEM) to study the prepared cross-section at magnifications up to 500,000 times. The best spatial resolution obtained was about 1 nm. EDS elemental measurements were made on all

samples, using established geological standards, and results are normalized to 100%.

4. Results and discussion

Many papers published on varnish involve an unstated assumption that the few samples analyzed represent a general condition, allowing sweeping claims based on as few as three samples (Dorn and Krinsley, 2011; Garvie et al., 2008). A second issue with the vast majority of varnish studies derives from authors limiting themselves to familiar techniques — creating an often-unstated interpretive bias



Fig. 3. Historic photograph of boulders quarried in 1913 being placed along the Erie Canal, with a view of the boulders a century later. Rock varnish forms in the area experiencing periodic inundation and also in subaerial settings that do not experience splash. The sample analyzed here derived from a subaerial setting.

(Dorn and Krinsley, 2011). Here, we admit that the scope of this study is insufficient to claim that we analyzed anything but a small fraction of the different types of varnishes found in these sites and we limit ourselves here to a micron-scale perspective.

Since the goal of this paper rests in re-opening scholarly dialog on the relationship between Mn-rich coatings in humid settings and those varnishes found in warm arid settings, we combine results and discussion together in order to clarify intellectual threads. However, our findings apply only to a limited number of samples and offer a point of comparison for future research on riverine and other non-arid varnishes.

4.1. Layered texture of rock varnish

Not all manganese-rich rock coatings are considered rock varnish. True rock varnish is characterized by clay minerals that impose a layered structure to the varnish as seen in cross-sections at high magnification (Krinsley et al., 1995; Krinsley, 1998). Mn-rich coatings that lack clay minerals, and hence lack a layered cross-sectional texture, are heavy-metal skins (Dorn, 1998). The four samples analyzed here show the characteristic layering of rock varnish, illustrating that layering can appear differently from alternative sample preparation approaches (Fig. 4). Fig. 4A and C sections were turned over using the

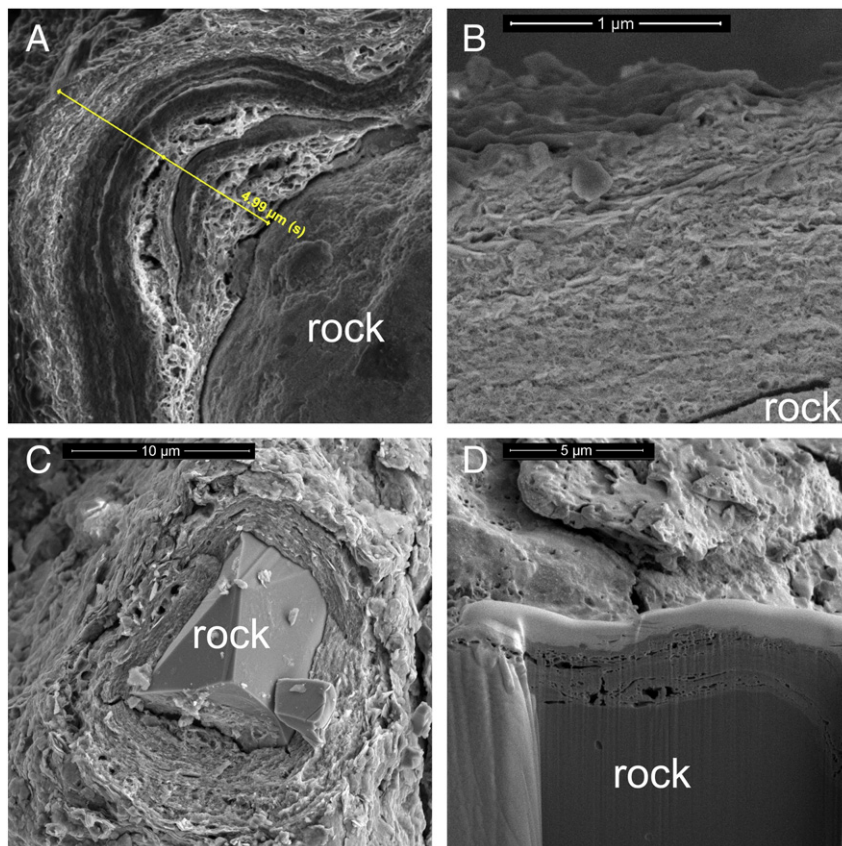


Fig. 4. Layered cross-sectional textures of rock varnishes collected from the Erie Barge Canal (A), New York Route 458 (B), active flow along the Raquette River (C), and low turbulence flow along the Raquette River (D). The layered nature of rock varnish is seen differently based on alternative sample preparation approaches. The micromanipulator was used to excavate portions of A and C, while B was simply an image of a physically broken surface. D is the result of DB-FIB use.

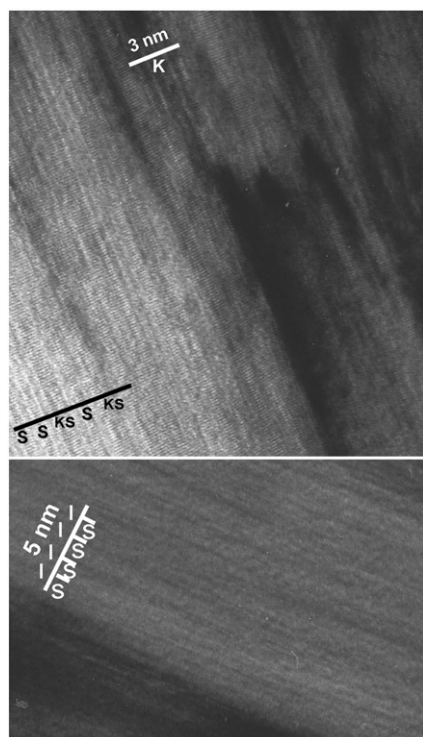


Fig. 5. Lattice fringe spacings in HRTEM images suggest the presence of a mixture of clays in the Erie Barge Canal varnish. The upper HRTEM indicates different interstratified kaolinite–smectites, where the individual kaolinite layers appear as ca. 0.7-nm-spaced fringes. The lower lattice fringe has spacings consistent with illite–smectite mixed-layer minerals.

micromanipulator, whereas Fig. 4B images a cross-section made by physical breakage of the sample prior to insertion into the microscope. The section displayed in Fig. 4D was made through the use of DB-FIB.

This layered texture is imposed by clay minerals and how they cement manganese to rock surfaces (Dorn, 2007; Krinsley, 1998; Krinsley et al., 1995; Potter and Rossman, 1977). High resolution transmission electron microscopy (HRTEM) reveals the presence of clay minerals similar to those found in other studies (Fig. 5). HRTEM imagery reveals lattice fringe spacings that are consistent with mixed-layer illite–smectite minerals as well as some kaolinite layers.

Table 1

EDS analyses of bioforms. Data are presented in weight percent, normalized to 100%, where elements below the limit of detection are indicated by no data. These analyses are based on mineral standards.

Element	Figure									
	Fig. 6A	Fig. 6B	Fig. 7	Fig. 8 Mn-rich	Fig. 8 Fe-rich	Fig. 9 smooth texture	Fig. 9 black arrow	Fig. 9 white arrow	Fig. 10A	Fig. 10B
C K				17.63	5.04	25.84				
Na K							0.12			
Mg K	0.81	0.36		0.14	1.84	0.17	1.99	1.74	0.50	0.80
Al K	0.85	2.19	0.21	0.39	2.70	0.11	2.61	3.36	2.23	4.45
Si K	6.59	37.62	0.69	0.37	9.85	0.34	12.92	16.32	2.28	6.56
P K	28.87	0.36		0.23		0.39			0.41	0.51
S K				0.28		0.37				
Cl K										
K K	1.93	1.15	0.18				0.19		0.43	0.99
Ca K	0.97	0.60	0.63	1.07	0.87	1.64	0.94	1.37	1.95	2.05
Ti K	0.25	0.16		0.19					0.58	0.41
Mn K	6.51	2.29	61.14	20.73	8.99		9.96	9.52	48.11	34.47
Fe K	7.31	6.61	7.45	2.23	30.69		38.53	32.36	16.53	19.14
Zn K			5.13	0.77					1.24	0.94
Ba L			1.89							
O	45.31	48.66	22.68	55.96	40.02	71.14	32.75	35.32	25.74	29.67

Physiochemical fixation of nanoscale oxides takes place through interaction with mixed-layered clays (Potter, 1979). Potter (1979: 174–175) explained the process:

“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...”

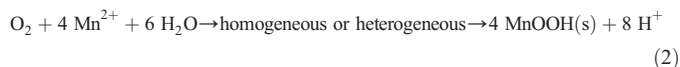
In the polygenetic model, rock varnish formation relies on ongoing nanoscale instability of manganese oxides that move from sources such as bacteria sheaths into clay minerals (Dorn, 1998; Dorn, 2007; Krinsley, 1998).

4.2. Mn-enhancement and *in situ* observations of microbial forms

Like varnishes found elsewhere, the New York samples are characterized by a great enhancement of manganese above levels found in the surrounding environment. The general Mn (II) oxidation reaction is:



for an oxidation state of (IV). In addition, heterogeneous oxidation can occur to accelerate the reaction rates where Mn (II) produces MnOOH (s), as follows:



The increasing surface area of MnOOH(s) increases heterogeneous reaction rates (Martin, 2005).

Mn must be transported to varnish surfaces in solution as Mn (II), and in natural waters Mn (II) oxidation requires pH values >8.5 to oxidize homogeneously without microbial assistance (Morgan and Stumm, 1965). Higher Eh values may also be important in the riverine settings studied here, since Mn (II) can oxidize at lower pH values with higher dissolved oxygen levels in the water. However, even given oxygen-rich waters, abiotic oxidation of Mn (II) has slow kinetics (Martin, 2005), thus requiring microbial mediation to produce the observed high concentrations of Mn oxides at pH values less than about 8.

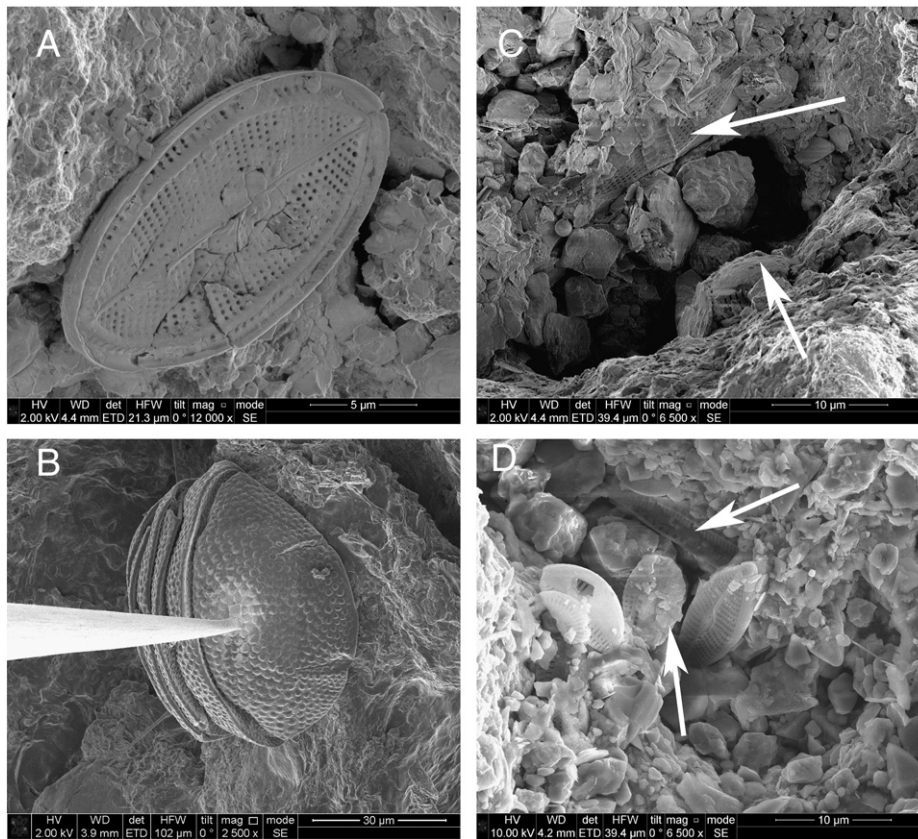


Fig. 6. Organisms enriched in manganese and iron are common on Raquette River and Erie Barge canal samples. Image A presents a diatom from Higley Flow State Park. The bioform's exterior in image B is enriched in Mn and Fe, sampled from a gneiss boulder along a fast-flowing section of the Raquette River; the bright filament extending from the left side is the Omniprobe pulling away a piece for *in situ* study. Diatomaceous forms break-apart and pieces are incorporated into varnishes (arrows) from the Raquette River (image C) and along the Erie Barge Canal (D).

Since general biogeochemical environment of the New York samples is not sufficient to abiotically oxidize and fix Mn or Fe (Krauskopf, 1957; Hem, 1964), the only other abiotic process known for Mn enhancement involves nanoscale hematite that can enhance Mn (II) oxidation greatly (Madden and Hochella, 2005). Unfortunately, the mineralogy of the iron in these varnishes is not known. However, if nanoscale hematite exists, it could possibly fix and enhance manganese. In contrast to the difficulty associated with explaining New York varnish formation through abiotic processes, we have found abundant and direct evidence for the role of microorganisms.

Varnish researchers have employed four general types of strategies to understand the role of organisms in the genesis of rock varnish:

- field observations (Laudermilk, 1931; White, 1924);
- culturing of organisms (Adams et al., 1992; Dorn and Oberlander, 1982; Eppard et al., 1996; Grote and Krumbein, 1992; Hungate et al., 1987; Krumbein, 1969; Northup et al., 2010; Palmer et al., 1985; Perry et al., 2004; Staley et al., 1991; Sterflinger et al., 1999; Taylor-George et al., 1983);

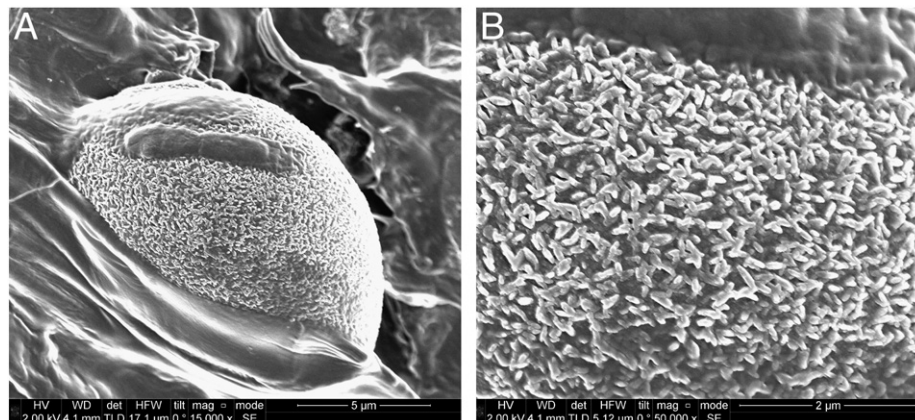


Fig. 7. On a gneissic boulder on the Raquette River, a fungal-sized form (left image) is encased in sub-micron particles (right image) that are composed of over 60% Mn. This ovoid form, in turn, is being coated by a film of carbon perhaps left by desiccating algae.

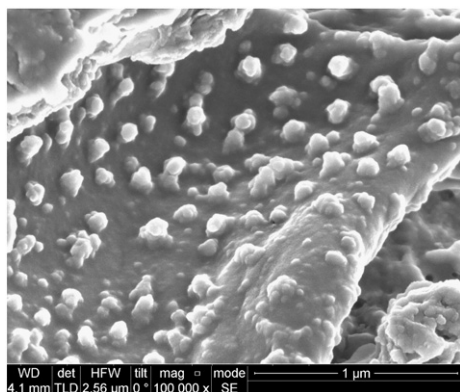


Fig. 8. Sub-micron spherical forms on the surface the NY Route 458 varnish are in size range of nanobacteria discussed in the literature (Chafetz et al., 1998; Folk, 1993). EDS analyses (Table 1) reveal that these forms can be Mn-rich or both Mn and Fe-rich; the smooth background is dominated by carbon.

- analysis of organics extracted from bulk samples (Benzerara et al., 2006; Eppard et al., 1996; Kuhlman et al., 2005; Kuhlman et al., 2006a; Kuhlman et al., 2006b; Northup et al., 2010; Perry et al., 2004; Spilde et al., 2005);
- and *in situ* observations.

In situ approaches can analyze the chemistry of microbial forms with EDS using secondary electron (Allen et al., 2004; Dorn, 2007; Dorn and Oberlander, 1982; Dorn et al., 1992; Flood et al., 2003; Northup et al., 2010; Wang et al., 2011), back-scattered electron (Dorn, 1998; Dorn and Meek, 1995; Krinsley et al., 2009), and transmission electron (Dorn, 1998; Krinsley, 1998; Perry and Kolb, 2003; Probst et al., 2001) microscopy.

Rather than undertake culturing or DNA analyses, we used the *in situ* strategy of making electron microscope observations and EDS analyses of forms that appear to be biotic. These forms include cocci or rod shapes of bacteria and fungal-sized filaments that are enriched in manganese, iron or both. Of course, the *in situ* approach to understand varnish genesis has an important limitation. Just because a form has the right size and shape to be bacteria, fungi, or other biotic-appearing forms does not prove that the forms are microorganisms or even Mn-encrusted sheaths of microorganisms. With this caveat,

this section presents STEM imagery and corresponding EDS analyses (Table 1) of New York varnish biotic forms.

Observed biological forms displaying Mn and Fe enhancement appear to be more common than warm desert varnishes discussed in the aforementioned references. Table 1 compiles EDS analyses associated with microbial forms seen in STEM imagery. For example, enhanced in Mn and Fe are associated with diatom and other organisms along a quiet-water stretch of the Raquette River (Fig. 6A, B). Spherical or ovoid forms displaying enrichments of Mn and Fe, in the size range of bacteria and fungi, are found colonizing surfaces of a boulder along the Raquette River (Fig. 7), along NY Route 458 (Figs. 8, 9), and along the Erie Barge Canal (Fig. 10),

4.3. Problem of microfossil preservation in varnish

In situ studies of Mn-enriched bacterial forms on warm desert surfaces reveal that bacteria are infrequently seen on varnish surfaces and even less commonly as fossils in cross-sections (Dorn, 1998; Dorn and Meek, 1995; Jones, 1991; Krinsley, 1998; Krinsley et al., 2009; Perry et al., 2004; Probst et al., 2002). This general paucity of Mn-rich bacterial-forms is consistent with rates of varnish formation on the order of microns per millennia in warm deserts (Dorn, 1998; Liu and Broecker, 2000) and with the polygenetic model of varnish formation (Krinsley, 1998; Dorn, 2007). Rarely found bacterial-encrusted Mn that undergoes a very slow diagenesis with relocation of Mn into clay minerals (Potter and Rossman, 1979) would generate these observed accretion rates (Dorn and Krinsley, 2011).

Still, it is possible that Mn-enriched bacterial forms have been missed in analyses of cross-sections, because the process of polishing varnish samples for cross-section and thin-section analysis might end up disturbing microbial fossils to the point where they might not be recognizable. To assess this hypothesis, we used the DB-FIB to disturb structures *in situ* in varnishes from NY Route 548 (Fig. 9) and the Erie Barge Canal (Fig. 10). DB-FIB digging into these samples did reveal bacterial-sized forms enhanced in Mn and Fe that were not noticeable prior to the disturbance. Thus, DB-FIB disturbance of varnish structures, in tandem with STEM/EDS offers a new way to search for microbial forms that are associated with Mn–Fe enrichment. By way of comparison, a DB-FIB study of warm arid varnish collected from Solitario Canyon in southern Nevada revealed almost no evidence of microbial forms.

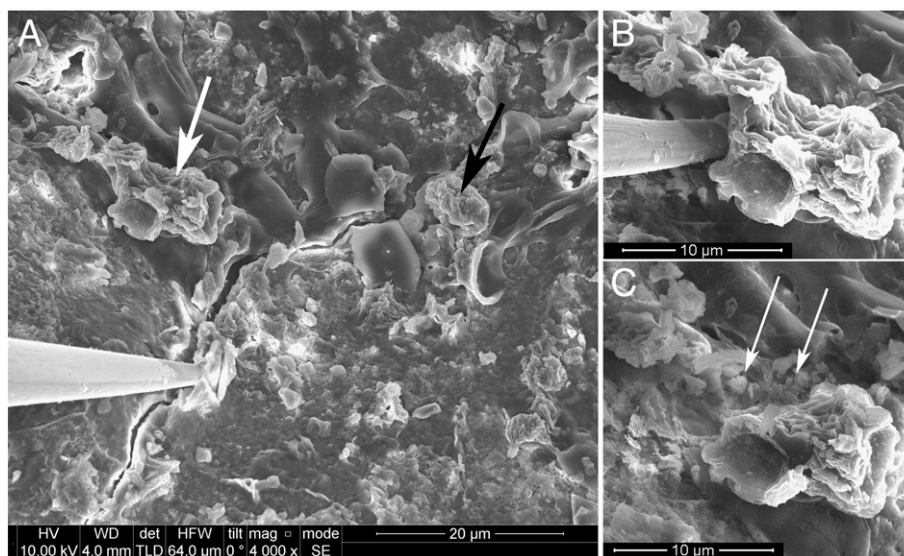


Fig. 9. Platelets that are adhering loosely to the surface of the NY Route 548 varnish are enriched in Mn (about 9% elemental), but much more so in Fe (~39% black arrow and ~32% white arrow in image A). The bright filament extending from the left side of image B is the Omniprobe used to break apart these platelets, exemplified by the white arrow. The close-up in image C suggests that bacterial-sized forms appear to be embedded in platelet structures.

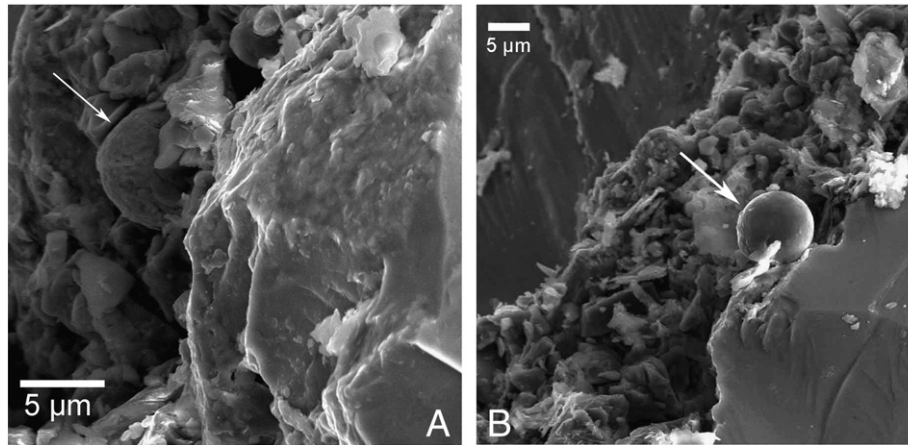


Fig. 10. Omniprobe disturbance of an Erie Barge Canal varnish exposed a number of microbial forms, such as the fungal-sized spherical shape in image A showing an abundance of over 48% Mn and the spherical shape in image B with over 34% Mn. The Omniprobe exposed a large fragment of detrital quartz (lower right in image B) mixed in with varnish fragments and possible microbial fossils.

Table 2
Examples of elemental variation exhibited in bulk chemical analyses of rock varnishes found in desert regions. Results are normalized to 100% with measurements by PIXE (Cahill, 1986), with 'na' indicating not available and a blank indicating below the limit of detection.

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

Table 3
EDS analyses of varnish spots without microbial forms where barium, zinc and rhenium are above the limit of detection. Data are presented in weight percent, normalized to 100%, where elements below the limit of detection are indicated by no data. These analyses are based on mineral standards.

Element	NY Route 548	NY Route 548	Raquette River	Erie Barge Canal	Erie Barge Canal
Na K					0.41
Mg K	1.94	1.88		0.87	
Al K	3.28	3.37		6.49	9.03
Si K	14.81	15.32	1.08	11.34	29.06
P K	0.53	0.49		0.79	
S K	0.34				
K K	0.31	0.36	0.29	2.41	9.43
Ca K	2.21	2.18	0.68	2.59	0.50
Ti K			1.10	0.85	
Mn K	9.23	9.04	59.24	30.91	4.83
Fe K	31.64	32.24	13.35	8.83	0.68
Zn K	0.60	0.63		0.50	
Ba L			0.89		0.93
Re M				0.30	
O	35.11	34.5	23.37	34.13	45.12
Totals	100.00	100.00		100.00	100.00

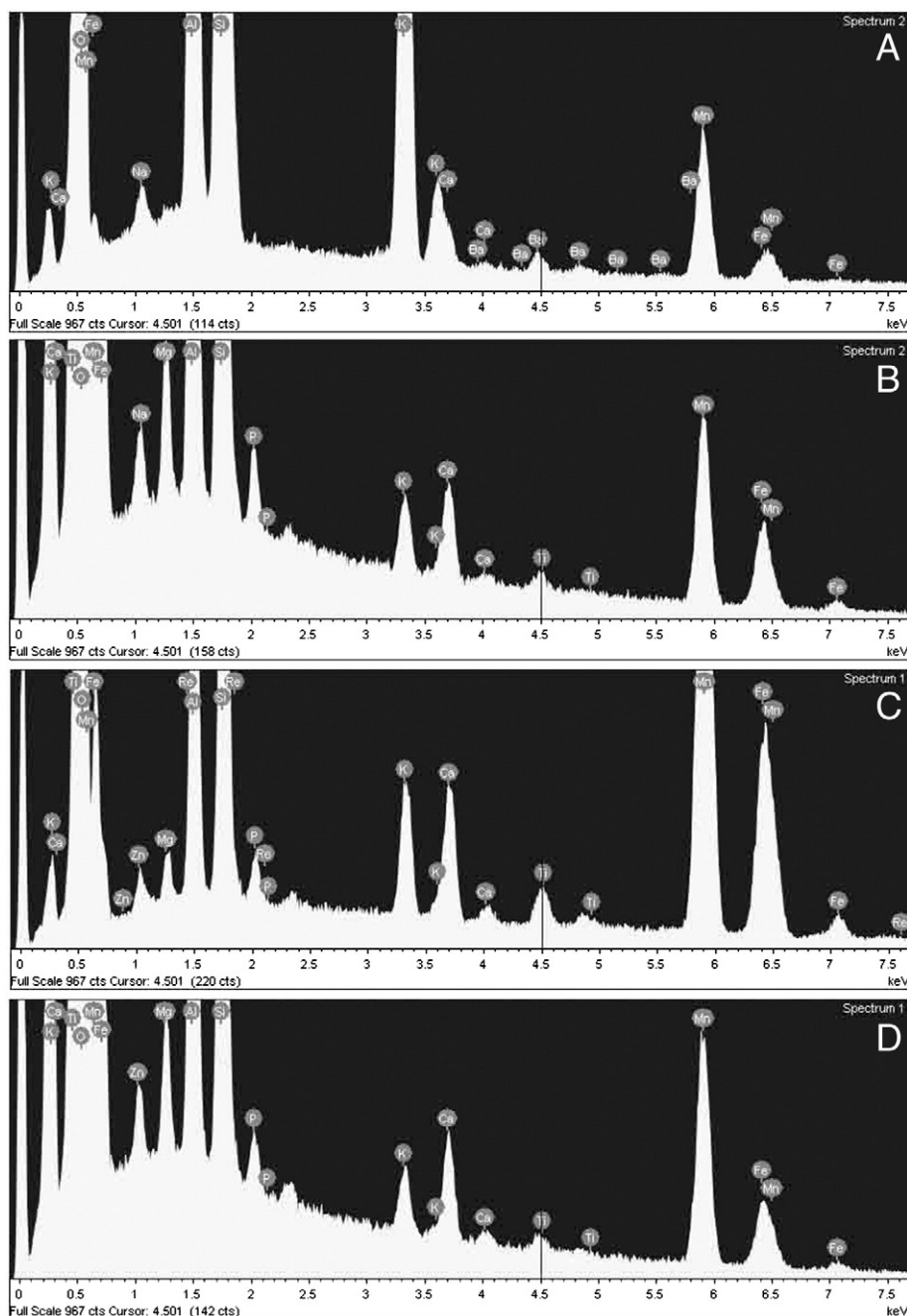


Fig. 11. Some of the Mn-rich Erie Barge Canal varnish analyses show enrichment of barium (A) along with Mn, but many do not (B–D).

4.4. Role of humid sites in understanding rates of varnish formation

The prior literature has established that varnishes in humid settings can form within decades to centuries (Buchan et al., 1986; Capot-Rey, 1965; Dorn and Meek, 1995; Dorn and Oberlander, 1982; Goodwin, 1960; Hunt, 1954; Hunt and Mabey, 1966; Klute and Krasser, 1940). This is the case for varnishes growing along the Erie Barge Canal (e.g. Fig. 4A). The sample analyzed here came from a site context that would not have been influenced by inundation. Rather, the setting is subaerial.

According to Jesse Bieber (personal communication, Town of Royalton Historian, 2011) a quarry near Gasport, Niagara County, provided the boulders that now line the Erie Barge Canal. This locality lies on the outcrop of the Clinton formation and was operated by the Wickwire Limestone Co. in 1913. These findings of subaerial varnish growth in a century are consistent with the prior literature that rapid varnish formation can occur in wet settings. Finding a much greater abundance of

Mn and Fe-enhanced bioforms in New York samples is consistent with a faster rate of varnishing. Thus, humid varnishes may offer a much greater potential to observe active varnish processes than varnishes collected from warm deserts.

4.5. Trace element enhancement: zinc, barium, and rhenium

Although zinc enhancement is well known in such settings as marine nodules (Wang and Müller, 2009), zinc is a trace or rare element in varnish collected from subaerial positions in warm deserts (Table 2). However, zinc has been noted more frequently in studies of Mn-rich coatings on river cobbles (Boonfueng et al., 2006; Huelin et al., 2006; Nowlan, 1976; Tani et al., 2003). Our EDS spot analyses associated with biotic forms (Table 1) and varnish surfaces without biotic forms (Table 3) are consistent with prior observations of both warm desert varnishes and Mn-rich coatings on river cobbles about zinc enhancement.

A misunderstanding has developed in the recent varnish literature regarding barium and whether or not it is a constant component of varnish that co-varies with manganese. Almost all recent papers reviewing rock varnish have referenced Mn–Ba connection presented by Tazhuo Liu and colleagues (Broecker and Liu, 2001; Liu and Broecker, 2000; Liu and Broecker, 2007; Liu and Broecker, 2008a; Liu and Broecker, 2008b). While Mn and Ba often display a spatial autocorrelation at the micron scale, this is not always the case. In other varnishes collected from arid regions, barium does not appear to be correlated with Mn (Dorn, 2007; Dorn et al., 1990; Krinsley et al., 1990).

Our analyses of New York varnishes (Tables 1, 3) reveal that Ba occurs along with Mn, but not always – consistent with patterns seen in varnishes collected from deserts. Fig. 11 exemplifies the micron-scale variability of different EDS spectra of varnishes collected from an Erie Barge Canal sample. The reasons for barium's bimodal behavior, in some cases greatly enriched and others not, have not yet been established. We suspect, however, the unstable nature of manganese oxides in varnish

(McKeown and Post, 2001) influences barium enrichment. Some manganese oxides such as romanechite do contain barium, while others such as birnessite do not.

An anomaly exists in the New York varnishes not reported elsewhere in the literature. Rhenium is a very rare element of substantive economic importance. We obtained one measurement (Table 3) where rhenium was enriched as high as 0.30% in elemental abundance. If future research replicates our finding of rhenium in humid-region settings, like that at the Erie Barge Canal, humid varnishes could be valuable economically.

4.6. Incipient accretionary processes

Prior studies examining incipient varnish accretion imaged with lower-resolution secondary electrons showed platelets of varnish accretion on mineral surfaces (Dorn and Oberlander, 1982) that were revealed to be mostly clays in HRTEM imagery (Krinsley et al., 1995). Here, we

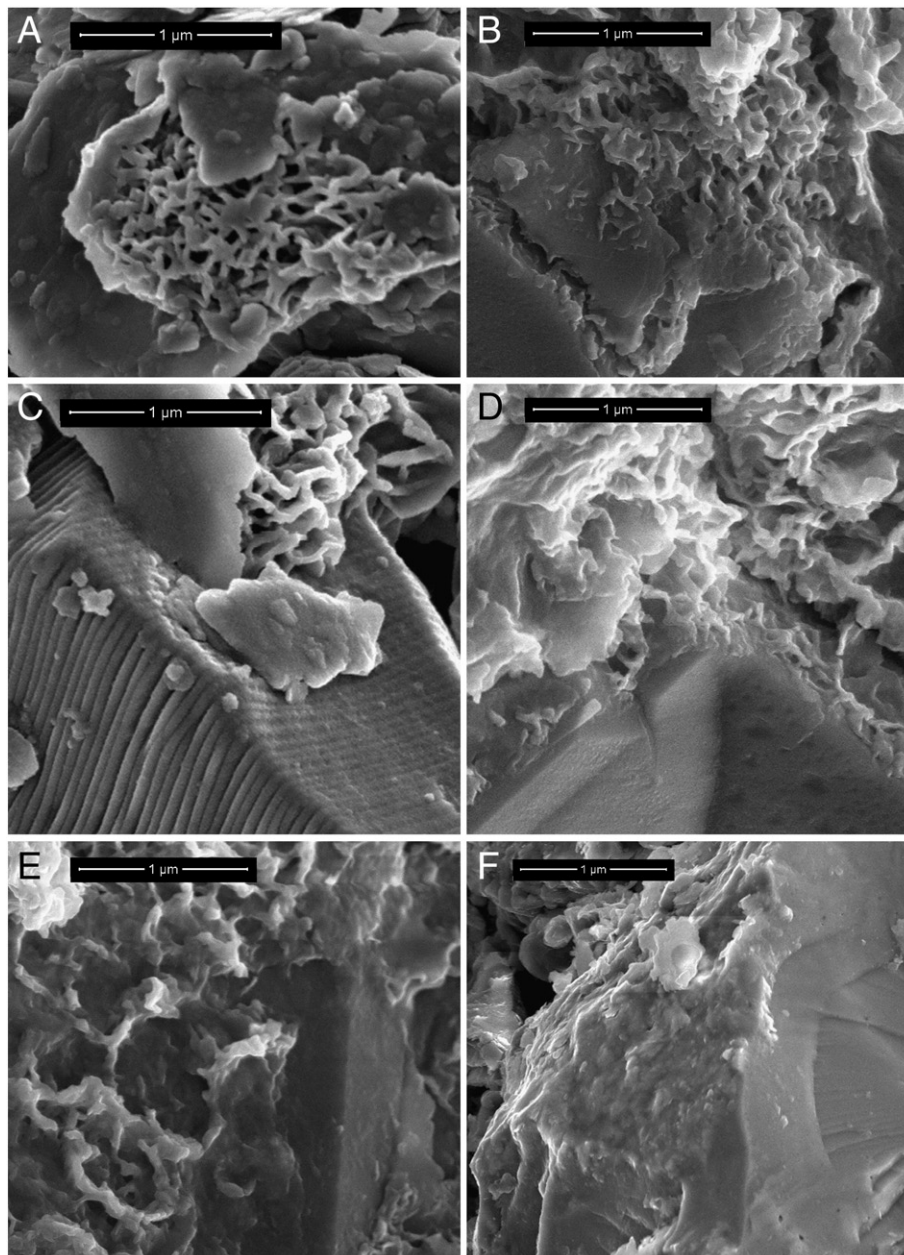


Fig. 12. Incipient varnish formation on minerals often takes the form of nanometer-scale filaments, displayed on Erie Barge Canal (A, B, D), Raquette River quiet water (E) and turbulent water (F), and New York route 458 (C) samples. The length of the scale bar is 1 μm in each image. The underlying minerals are quartz (A, B, E, F), biotite (C), and feldspar (D).

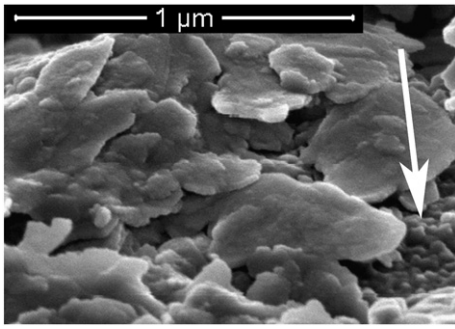


Fig. 13. Layered particles, with the texture of clay minerals, are accreting on top of Mn-rich material that has adsorbed to rock surfaces. The arrow points to Mn-rich hemispheres that are part of filamentous network adsorbed to the underlying rock.

used much higher resolution SEM to find that mineral surfaces are being initially colonized by networks of filaments (Fig. 12). The filaments, in turn, appear to be composed of spherical-shaped Mn-rich components. These filaments are too small to be microorganisms, since bacteria cell widths are typically a micron, and the filaments of EDS-determined Mn-rich material are tens of nanometers across.

It is possible that these Mn-rich filaments are produced by abiotic enhancement of Mn (II) by nanoscale hematite (Madden and Hochella, 2005). However, we favor the hypothesis that the filaments are the desiccated remains of microbial sheaths. The filamentous networks seen in Fig. 12 could have been the point of microbial adsorption on a mineral surface. Then, after the organisms died, the accumulated Mn would have remained in contact with the mineral surface. Varnish accretion would have then required clay minerals to then settle on these loci, and the Mn would have then cemented clay minerals to the mineral surface as seen in Fig. 13.

5. Conclusions

Varnish research in the last few decades has focused on manganese-rich coatings found in deserts, creating a possible bias in theory development. Thus, this research continues the tradition of varnish research in a wider variety of terrestrial weathering environments through the use of high resolution electron microscopy, with associated tools DB-FIB and EDS. Our research hypothesis going into this investigation was that we would find substantial differences between New York (humid) and warm desert varnishes.

There exist far more similarities between the observed humid and arid region varnishes than differences. New York varnishes display the same sub-micron cross-sectional texture of layering imposed by clay minerals, contain clay minerals as seen in HRTEM imagery, and host a variety of microbial forms that are enhanced in Mn in *in situ* EDS observations. There are dozens of elements enhanced in arid varnish over background values (Bard et al., 1978; Dorn et al., 1990; Lakin et al., 1963; Nowinski et al., 2010), including the zinc and barium observed here. However, rhenium enhancement has not been observed previously in arid varnishes.

Differences between humid and arid region varnishes include a much faster rate of formation in the wet settings of New York, the far superior preservation of microbial forms, and in finding diatoms enhancing Mn, in addition to bacteria and fungi.

However, the biggest difference is that Mn- and Fe-enhancing microbial forms are much more common in New York than samples collected from warm deserts — supporting a traditional hypothesis that moisture abundance is a key factor in accelerating rates of varnish formation. Humid varnishing appears to start with microorganisms enhancing Mn in an environment too acidic for physiochemical oxidation. Microbial mortality then results in Mn-rich sheath material adsorbing to mineral

surfaces, followed by the fixation of clay minerals by Mn that has remobilized at the nanometer scale. These observations are in accordance with observations on the importance of clay minerals in arid-region varnish formation (Dorn and Oberlander, 1982; Potter and Rossman, 1977) and with the polygenetic model of varnish formation minerals (Dorn, 2007; Dorn, 1998; Krinsley, 1998). However, more rapid varnishing and the superior preservation of microbial remains in the moist New York environment add a new piece to how varnishing initiates — starting with microorganisms enhancing manganese on bare mineral surfaces, followed by clay mineral adsorption.

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