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ARTICLES

Revisiting Alexander von Humboldt's Initiation of Rock Coating Research

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ABSTRACT

Secondary, backscattered, high-resolution transmission, and energy-dispersive spectroscopy tools of electron microscopy reexamined Alexander von Humboldt's field site of "brownish black crust[s]" covering rocks along cataracts of the Orinoco River. Modern tools confirm eighteenth-century analysis that the basic composition includes an abundance of manganese, iron, and carbon. Additional major constituents include clay minerals, calcium, and sometimes barium and cobalt. Backscattered and secondary electron imaging confirms the 2-century-old hypothesis of an accretionary nature of the Orinoco coating. The remarkable Orinoco sheen is produced by a smooth lamellate micro-morphology and high concentrations of manganese—the same conditions required to produce lustrous varnishes formed in warm deserts. Although von Humboldt deduced, and we agree, that coating constituents must derive from the Orinoco, electron microscope observations of Mn-enriched diatom fragments, Mn-enriched cocci-bacterial forms, and microstromatolitic textures suggests a role for microorganisms in the 60- to 70-times enhancement of Mn over Fe in these varnishes. With the retrospect of 2 centuries of scholarship, Alexander von Humboldt rightfully deserves to be considered the father of rock coating research.

Online enhancement: appendix.

Introduction

Two hundred years have passed since Alexander von Humboldt's *Personal Narrative of Travels to the Equinoctial Regions of America During the Years 1799–1804* was first published. Volume 2 initiated the scholarly study of rock coatings with observations of "brownish black crust[s]" along the cataracts of the Orinoco between the missions of Carichana and Santa Barbara. Von Humboldt and Aimé Bonpland explored several research topics, on pages 242–246 of the second volume of an English translation (von Humboldt 1812), which are quoted below and are still discussed in today's scholarship.

Thickness. An important issue to von Humboldt was the apparent uniform thickness: "The black crust is 0.3 of a line in thickness." Before the metric system, the French *toise* (~1949 mm) was subdivided into 6 Paris feet, each of which contained 12

pouces, again divided into 12 *lignes*. Since each *ligne* is ~2.25 mm, 0.3 *ligne* would be about two-thirds of a millimeter.

Composition. Working with two chemists, Berzelius and del Rio, and referring to research on dark rock coatings elsewhere in the world, von Humboldt indicated that the Orinoco "rock encrustations" are composed of oxides of manganese and iron, and also carbon.

Luster. Alexander von Humboldt indicated the coating was particularly remarkable because of its "lustre," although no cause was suggested for the notable sheen.

Underlying rock as a potential source for the coating. Von Humboldt noted "brownish black crust" rests on minerals "without any trace of decomposition." He referred to other research that

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the underlying quartz and feldspar contains “five or six thousandths of oxide of iron and of manganese,” but mica and hornblende contain more manganese—“fifteen or twenty parts in a hundred.” He reasoned, “How is it to be conceived that these oxides are spread so uniformly over the whole surface of the stony masses, and are not more abundant round a crystal of mica or hornblende than on the feldspar and milky quartz?” Thus, von Humboldt was the first to propose that rock coatings can be externally applied as accretions.

Depositional processes. Alexander von Humboldt wrote,

In reflecting upon the lustre and equal thickness of the crusts, we are rather inclined to think that this matter is deposited by the Orinoco. Adopting this hypothesis, it may be asked whether the river holds the oxides suspended like sand and other earthy substances, or whether they are found in a state of chemical solution. The first supposition is less admissible, on account of the homogeneity of the crusts, which contain neither grains of sand, nor spangles of mica, mixed with the oxides. We must then recur to the idea of a chemical solution; and this idea is no way at variance with the phenomena daily observable in our laboratories.

Alexander von Humboldt went on to ask, “Is this phenomenon independent of the nature of the rocks?” and answers with the conclusion that external “cementation seems to explain why the crusts augment so little in thickness.”

Following von Humboldt’s pioneering observations on the nature of rock coatings, Charles Darwin found and briefly discussed “rich brown”-coated rocks at Bahia, Brazil, that were composed of primarily iron (Darwin 1897, p. 22). The first monograph examining Mn-rich coatings followed a century after von Humboldt and focused on rocks along tropical rivers in moisture-rich conditions (Lucas 1905).

For many years much rock coating research followed von Humboldt and focused on stream-side settings. Some of the first microscopic evidence of a biotic origin for Mn-rich coatings was discovered in association with algae on stream-side rocks in a Queensland rainforest (Francis 1921). Since von Humboldt’s observations, many others contributed basic and applied research on Mn-rich coatings in fluvial settings (Boussingault 1882; Ball 1903; Zahn 1929; Klute and Krasser 1940; Blackwelder 1948; Hunt 1954; Carpenter and Hayes 1978, 1980; Potter 1979; Bhatt and Bhat 1980; Robinson 1981, 1993; Whalley et al. 1990; Hem and Lind 1994; Tebo et al. 2005; Huelin et al. 2006).

Beyond investigations of riverine accretions, and commensurate with other fields of science, there has been an expansion of research in the last 2 centuries with the identification of 14 broad categories of rock coatings including carbonate skins, case hardening agents, dust films, heavy metal skins, iron films, lithobiontic coatings, nitrate crusts, oxalate crusts, phosphate skins, pigments, rock varnish, salt crust, silica glaze, and sulfate crust (Dorn 1998). The study of rock coatings now encompasses a diverse set of disciplines including air pollution (Potgieter-Vermaak et al. 2004), archaeology (Whitley 2008), astronomy (Krinsley et al. 2009), biology (Kuhlman et al. 2006), geography (Perel’man 1966), geochemistry (Robinson 1993), geomorphology (Fairbridge 1968), geology (Longwell et al. 1950), history (Dorn et al. 2012), paleoclimatology (Liu et al. 2000; Dietzel et al. 2008), seismology (Stirling et al. 2010), stone conservation (Price 1996), soils (Ha-mung 1968), and other fields.

Despite the intellectual expansion of research initiated by Alexander von Humboldt, we are unaware of any attempts to reexamine the Orinoco “brownish black crust.” Thus, after 2 centuries of scholarship, we return to the site where the scholarly study of rock coatings initiated. We use modern analytical equipment of scanning/transmission electron microscopy, backscattered electron microscopy (BSE), high-resolution transmission electron microscopy (HRTEM), and energy-dispersive spectroscopy analysis of x-rays (EDS) to revisit the fundamental research issues first identified by von Humboldt.

The organization of this article derives from von Humboldt’s original research questions relating to coating thickness, coating composition, luster, whether coatings derive from the underlying rock or external sources, and processes responsible for coating deposition. In each section, we present new evidence on the Orinoco coating and analyze this new evidence with the aid of 2 centuries of scholarship on von Humboldt’s original questions.

Thickness

Common Orinoco coating thicknesses that we observed rest at ~30–40 μm (fig. 1), or less than <10% of von Humboldt’s original estimate of 0.3 *lignes*. The thinnest coating we observed is <100 nm (fig. 2). This sort of variability is typical for rock varnish (Dorn 1998) and for manganese-rich coatings on river cobbles (Carpenter and Hayes 1978, 1980). Rock varnish and heavy metal skins of the thicknesses suggested by von Humboldt, >670 μm , do exist, but they are rare (Dorn 1998). A reasonable

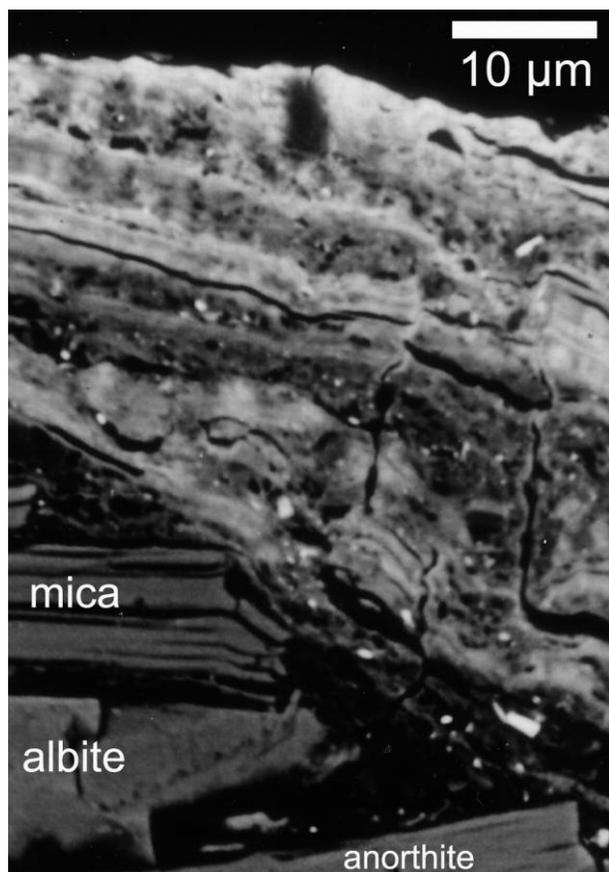


Figure 1. Rock varnish accreting on top of minerals that are undergoing chemical dissolution, imaged with back-scattered electrons. Note how the varnish appears to be collapsing into void space generated by the loss of mica (muscovite) and albite. Mineral compositions were inferred through energy-dispersive spectroscopy.

supposition is that von Humboldt did not have the instrumentation able to measure coating thickness accurately.

Alexander von Humboldt's focus on the apparent uniform thickness of the coating was used, in part, to support his hypothesis of external accretion. Specifically, no clear difference in thickness was found in association with mica and hornblende—minerals thought to contain more manganese (von Humboldt 1812). A BSE micrograph image of varnish formed on top of mica (fig. 1) and albite minerals supports von Humboldt's original conclusion, even if his observations were limited by instrumentation. There is no textural evidence that the chemical weathering of minerals in the underlying rock is supplying the raw ingredients for the Orinoco coating. Instead, it appears as though the coating originally formed on top of less weathered minerals. Then, after the accretion process started, min-

eral decay continued to the point where voids have been created and the varnish appears to be collapsing into these voids.

Thickness is still a relevant issue in the contemporary literature on rock varnish. Rates of varnish accretion in desert regions in dry microenvironments are on the order of microns per millennia (Liu and Broecker 2000), although faster growth rates occur in wetter microenvironments (Dorn and Meek 1995; Dorn et al. 2012). Because the rate of growth of varnish is heavily dependent on micro-environmental setting, it is not possible to use thickness or thickness-dependent measurements like bulk concentrations of manganese or general appearance (McFadden et al. 1989; Lytle et al. 2002) to obtain a reliable age estimate (Dorn 2007).

Composition: Is It Rock Varnish or a Heavy Metal Skin?

The early nineteenth-century chemical analyses of von Humboldt's Orinoco coating, being composed of manganese, iron, and carbon, appears to be correct. Table A1, available online or from the *Journal of Geology* office, presents proton-induced x-ray emission (PIXE; Cahill et al. 1984) analyses of bulk samples of rock varnish scraped from von Humboldt's Orinoco coating, along with varnishes collected from different desert locations for comparison. In this bulk analysis of ~20 mg of scraped coating material, manganese and iron comprise about half of the Orinoco varnish; carbon is not measured by PIXE. Elements connected with clay minerals (Al, Si, Mg) make up ~30% of the Orinoco coating.

Tremendous chemical variability exists in rock varnish at the scale of microns (Dorn and Krinsley 1991; Liu and Broecker 2008; Nowinski et al. 2010; Wang et al. 2011). This is true for the Orinoco coating, as well. Table A2, available online, presents EDS analyses obtained within a few microns of one another. While points 1, 5, and 6 seem similar to the bulk PIXE analysis in table A1 with respect of Mn and Fe abundance, concentrations of Si and Al are lower. Cobalt—not measured by PIXE—is an important element in the Orinoco varnish, likely connected to scavenging by Mn hydroxides (Jenne 1968).

Like rock varnishes formed in deserts, barium is sometimes correlated with manganese (Dorn et al. 1990; Liu 2003). This can be seen in the bulk PIXE analysis (table A1); in points 1, 5, and 6 in table A2, available online); and EDS spectra (fig. 3). In other varnishes, barium does not appear to be correlated with Mn (Dorn et al. 1990; Krinsley et al. 1990;

Dorn 2007). This can be seen in points 2, 3, and 4 where barium is below the limit of detection, despite abundant manganese. The reasons for barium's bimodal behavior has not been established, but it could have to do with the unstable nature of manganese oxides in varnish (McKeown and Post 2001).

Von Humboldt also specifically noted carbon as an abundant constituent. Carbon is only a minor to trace element within varnishes found in warm deserts (Dorn and DeNiro 1985). While PIXE did not measure carbon, EDS analyses did detect carbon in an abundance of over 10% by weight in the spots that lacked barium (table A2)—confirming the presence of carbon within Orinoco coatings and also distinguishing this tropical coating from varnishes found in drylands.

An important issue related to varnish composition concerns the presence of clay minerals. Manganese and iron-rich rock coatings that do not contain clay minerals are not considered rock varnish (Dorn 1998); instead, they are heavy metal skins. The processes that cement rock varnish (or desert varnish) relies on the presence of clay minerals.

Physical, biological and physiochemical barriers are all needed to form true rock varnish (fig. 4). First, physical barriers trap raw constituents on rock surfaces; these barriers can include physical forces that hold particles together (Jordan 1954; Bishop et al. 2002; Ganor et al. 2009). Then, bacteria concentrate manganese and iron (Dorn and Oberlander 1981; Hungate et al. 1987; Dorn 2007; Northup et al. 2010; Wang et al. 2011). Some of the bacterial sheaths are fossilized (Dorn and Meek 1995; Dorn 1998; Krinsley 1998), and fossil casts dissolve slowly. Decay of Mn-Fe casts remobilize fragments at the nanometer scale (Dorn and Meek 1995; Dorn 1998; Krinsley 1998). Physiochemical fixation of nanoscale oxides takes place through interaction with mixed-layered clays (Potter 1979). HRTEM imagery (e.g., fig. 4) shows Mn and Fe inserted into mixed-layered clays. Potter (1979, pp. 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 this polygenetic model, rock (or desert) varnish formation is the result of a sequence of barriers to transport and ongoing nanometer-scale instability (Dorn 1998; Krinsley 1998).

In the case of the Orinoco sample, collected from the splash zone of the river, the bulk PIXE analysis indicates that clays (Al, Si, Mg) could comprise up to 30% of the composition of the rock coatings—even if EDS analyses indicate that some portions of the varnish lack Al and Si in abundance. Distinguishing whether or not von Humboldt's coating is true varnish requires HRTEM analyses. Clay minerals impose a layered structure to the varnish (Krinsley et al. 1995; Krinsley 1998; Dorn 2007), and this nanoscale layering does occur in the Orinoco coating (fig. 5). Heavy metal skins, in contrast, do not display this type of nanometer-scale layering (Dorn 1998). Thus, von Humboldt's Orinoco coating does appear to be rock varnish and not a heavy metal skin.

Luster of the Varnish

The cause of the luster or sheen of the Orinoco coating, as well as many other dark manganese-rich coatings is one of the most misunderstood aspects of rock varnish. Many have thought sheen to be caused by dust polishing (Hunt 1954; Goudie and Wilkinson 1977), sand blasting (Blake 1905; Begole 1973), the presence of goethite (Kelly 1956), or metabolic products of cyanobacteria (Scheffer et al. 1963). None of these hypotheses are correct. Varnishes shine when surfaces have a smooth lamellate micromorphology (Krumbein 1969) combined with a surface rich in manganese (Dorn and Oberlander 1982).

Rock varnishes have two general types of textures, a smooth lamellate surface and a tendency to nucleate at discrete locations followed by growth into a botryoidal texture (Dorn 1986). The Orinoco varnish displays both of these textures (fig. 6). Much of the surface is quite smooth (fig. 6A) and rich in manganese (tables A1, A2). These portions of the surface are responsible for von Humboldt's observation of "lustre."

In addition, pockets of microbotryoidal texture also exist (fig. 6B). Typical botryoids in varnish on the order of 10 or so microns in diameter, but some have been noted at $<5 \mu\text{m}$ (Dorn 1986). These microbotryoidal textures contain nucleation clusters that have the size and form of bacteria cocci, which

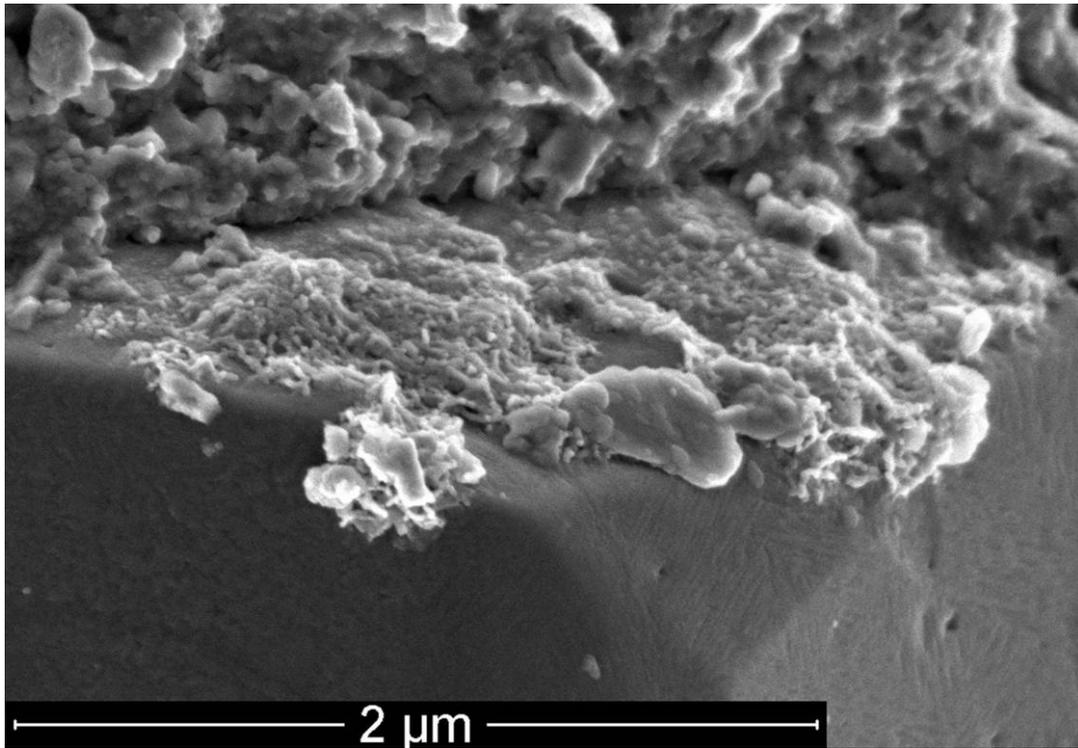


Figure 2. Secondary electron image of varnish formed on quartz, where the thinnest coating appears to be incipient deposits <100 nm thick.

grow together into larger botryoidal forms with diameters of $\sim 5 \mu\text{m}$. Some hand samples of the Orinoco varnish do not display a strong luster, and these contain more areas botryoidal textures.

An Accretion or Derived from Weathering of the Underlying Rock?

The debate over whether rock varnish forms by

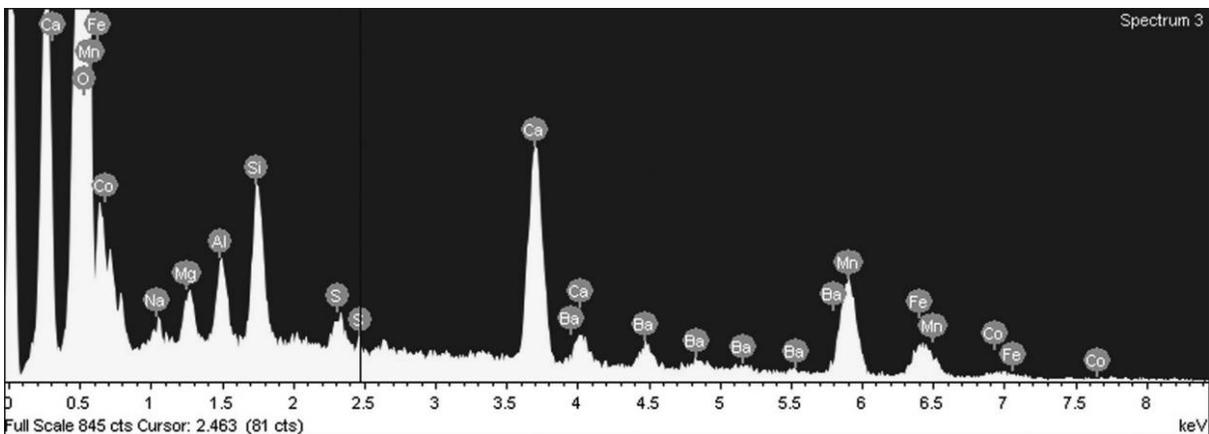
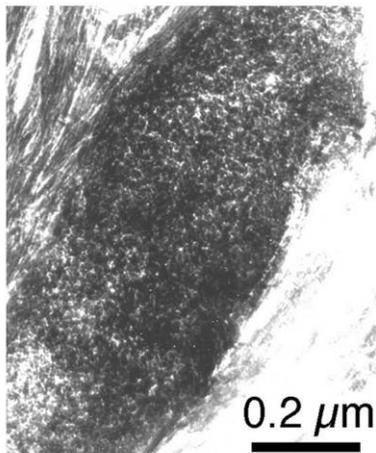
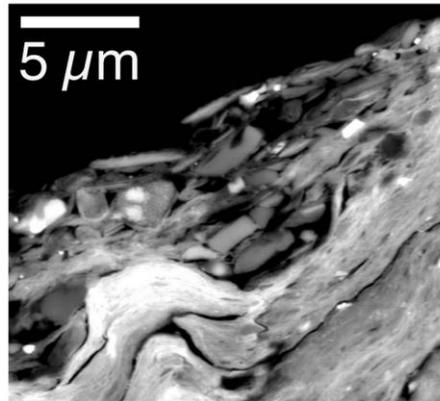
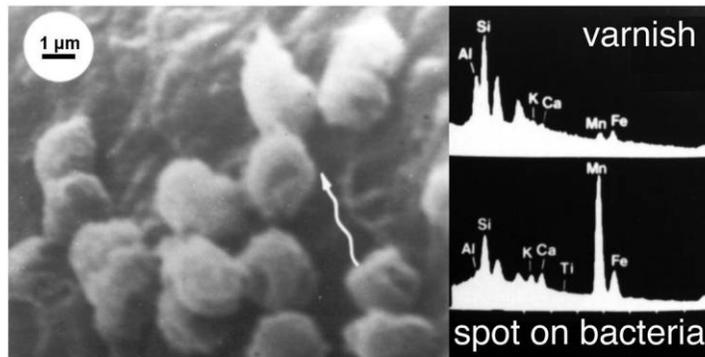


Figure 3. Energy-dispersive spectroscopy spectra of point 6 in table A2, available online or from the *Journal of Geology* office. Note the presence of Ba.

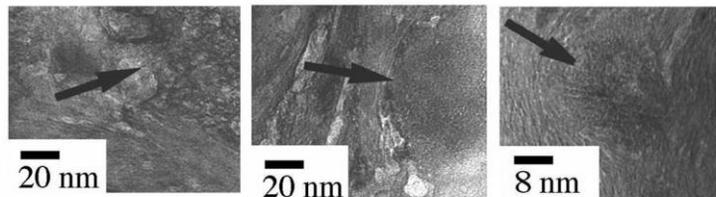
Physical Barrier: van der Waals force promotes dust accumulation, providing raw ingredients of clays



Biological Barrier: Mn and Fe fixation in bacteria sheaths

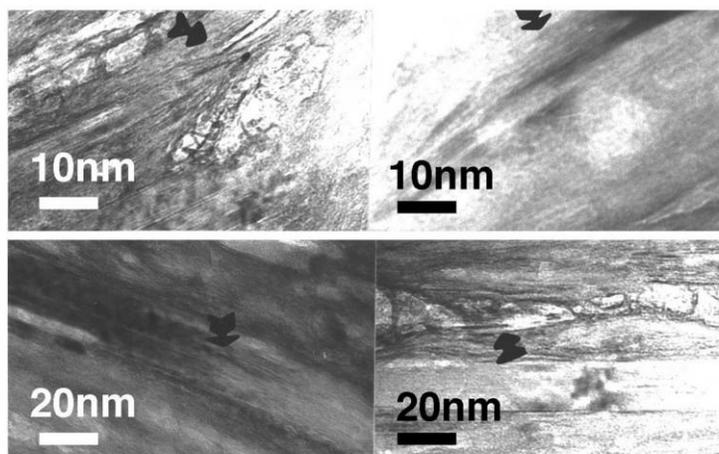


Dissolution from cell wall (granular fragments)



&

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



weathering of the underlying minerals or as an accretion started with von Humboldt, who favored an external origin. In contrast, most observers in the nineteenth and twentieth centuries favored the notion that varnish constituents derived from the underlying rock (Walther 1891; Linck 1900; Hume 1925; Longwell et al. 1950; Glennie 1970; Goudie and Wilkinson 1977; Shlemon 1978; Besler 1979).

The debate was resolved efficiently through electron microscopy. Studies of the interface between varnish and the underlying rock all reveal extremely clear contacts indicative of accretion (Potter and Rossman 1977; Dorn and Oberlander 1982), even at the nanometer scale (Krinsley et al. 1995; Dorn 1998, 2009). In addition, vivid microsedimentary structures (Perry and Adams 1978) also demonstrated the accretionary nature of varnishing. Imagery of the coating-rock contact of von Humboldt's Orinoco varnish tells the same story (figs. 1, 2, 7). In every image acquired for this study, there exists a very clear contact between the overlying varnish and the underlying rock, all indicating that varnish is an externally applied accretion. The only evidence for the role of weathering is that mineral decay in the underlying rock can collapse the rock varnish into voids created by mineral dissolution (fig. 1). Thus, von Humboldt's original hypothesis of an external accretion is accurate, for the varnish field as a whole and for the Orinoco site.

Depositional Processes

Alexander von Humboldt reasoned that Orinoco coatings are chemically precipitated out of the waters of the Orinoco. Although the chemistry of the Orinoco varies tremendously from location to location and seasonally, the average pH of the river at 6.77 in one study (Lewis and Saunders 1989) and 5.76 in another (Mora et al. 2009) is not sufficient to abiotically oxidize and fix Mn or Fe (Krauskopf 1957; Hem 1964). In natural waters, Mn (II) oxidation requires pH values >8.5 to oxidize homogeneously without microbial assistance (Morgan and Stumm 1965).

In addition, the ratio of Mn to Fe in Orinoco is approximately 1 : 38 in suspended sediments

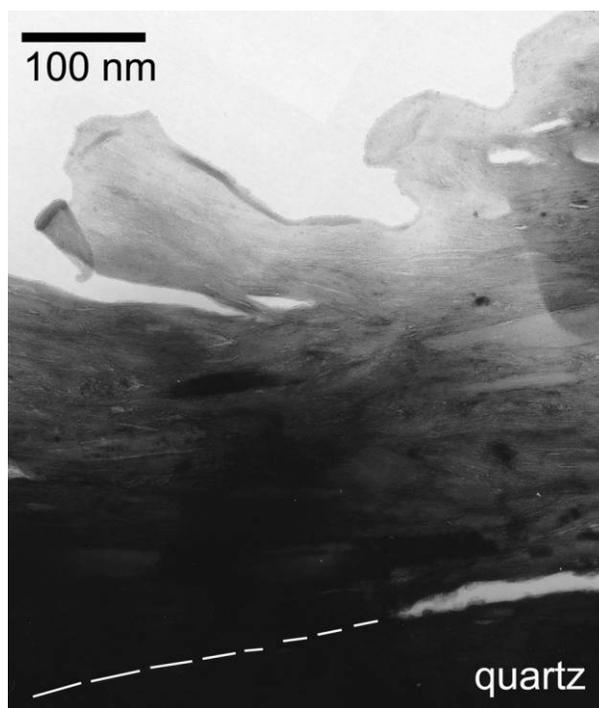


Figure 5. High-resolution transmission electron microscopy image of the Orinoco coating on quartz. Thick areas, such as the quartz, are not electron beam transparent. In the brighter regions, the typical layered texture of clay-hosting varnish (Krinsley et al. 1995) dominates the texture.

(Lewis and Saunders 1989) and 1 : 33 dissolved in water (Mora et al. 2009). Since the Mn to Fe ratio in the bulk analysis of the Orinoco coating is about 2 : 1 (tables A1, A2), whatever processes fix manganese and iron also need to enhance Mn 60–70 times over iron. The first step in enhancement must be to immobilize the manganese through oxidation, preferentially over iron.

Since the Orinoco's pH is insufficient for physiochemical oxidation by normal redox processes, the only other abiotic process known for Mn enhancement involves nanoscale hematite. Nanoscale hematite can enhance Mn (II) oxidation greatly (Madden and Hochella 2005). Unfortunately, the mineralogy of the iron in the Orinoco

Figure 4. Rock varnish formation requires that clay minerals be present, along with a sequence of barriers to the transport of varnish constituents. First, the raw ingredients must be transported to the rock surface and must be physically constrained. In the case of typical rock varnish formed on subaerial surfaces in deserts, this occurs by van der Waals force promoting the adhesion of dust. However, in the case of the Orinoco varnish, it might be the physical action of splashing water transporting clays in the suspended load to rock surfaces. Then, manganese must be concentrated by a biological or a physical-chemical process. After the concentrated manganese is remobilized over a scale of nanometers, it is fixed into mixed-layered illite-montmorillonite clay minerals.

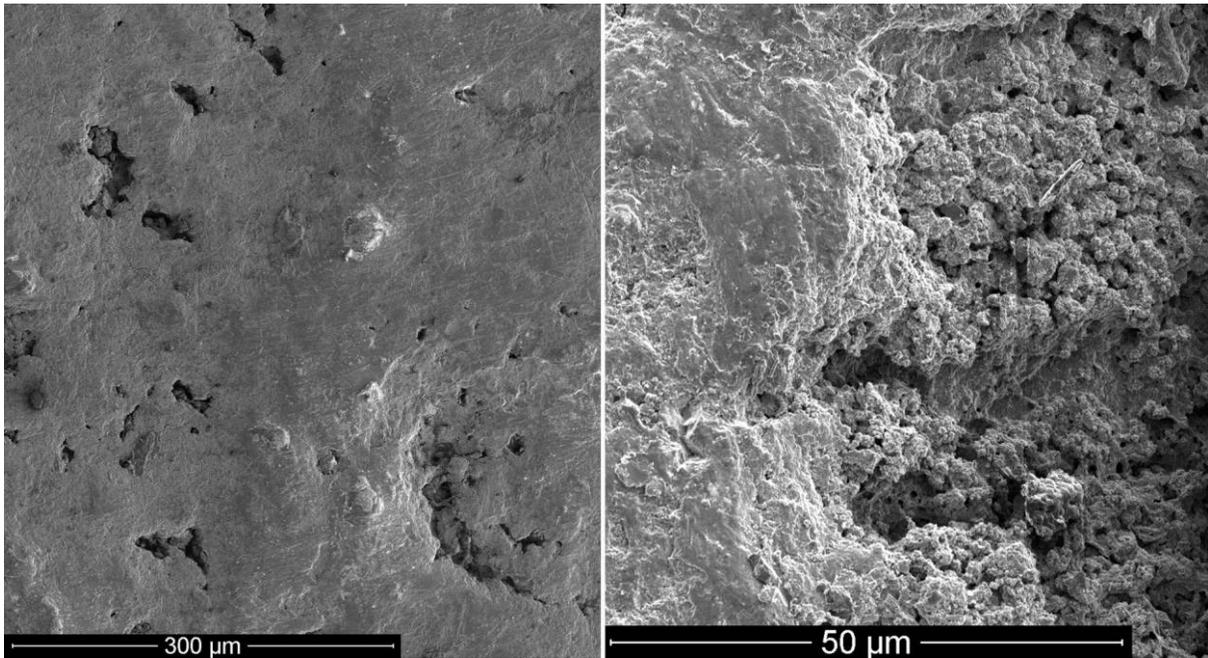


Figure 6. Micromorphology textures observed through secondary electrons reveal the presence of lamellate (*left*) and a mixture of lamellate and botryoidal forms (*right*) in the Orinoco varnish.

varnish is not known. However, if nanoscale hematite exists, it could play a role in Mn fixation and enhancement.

One speculative possibility is that nanoscale precipitates seen in figure 8 of Mn and Fe could possibly be related to hematite-fostered oxidation. Spherical and filamentous precipitates are tens of nanometers in scale, and they are far too small to

be biotic forms; these could be abiotically generated Mn precipitation. However, the framework structures and hemispherical forms in figure 8 could also be the remains of decayed bacteria; for example, EDS analyses reveal that the network of filaments (fig. 8A) are Mn rich and could be the remains of a bacterial sheath.

Another aspect of Mn enhancement could be the

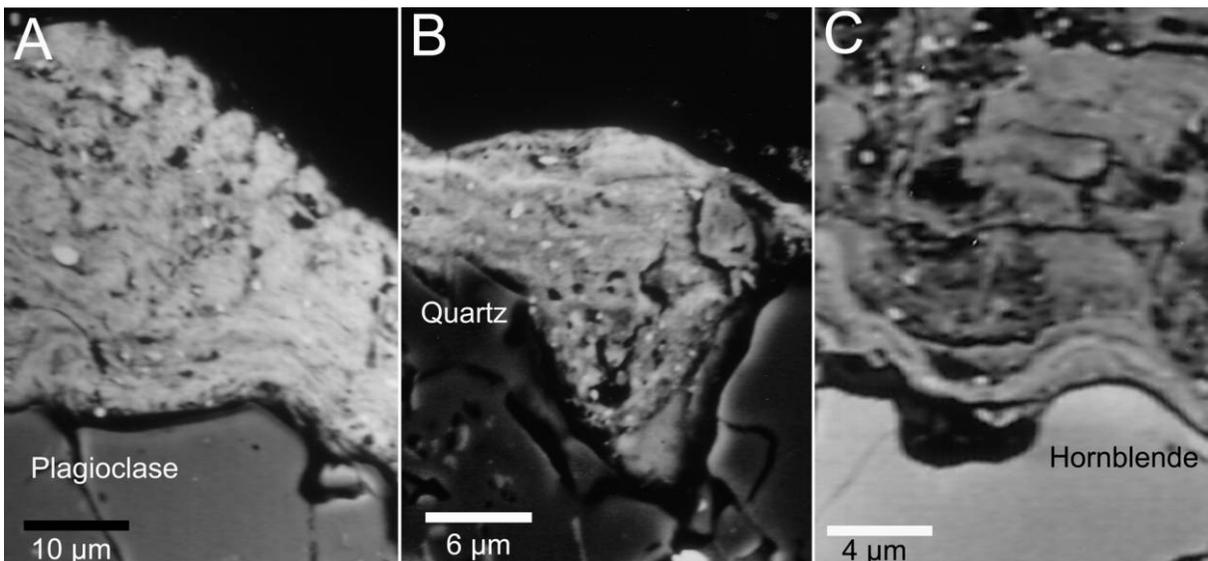


Figure 7. BSE images of Orinoco varnish formed on plagioclase, quartz, and hornblende minerals.

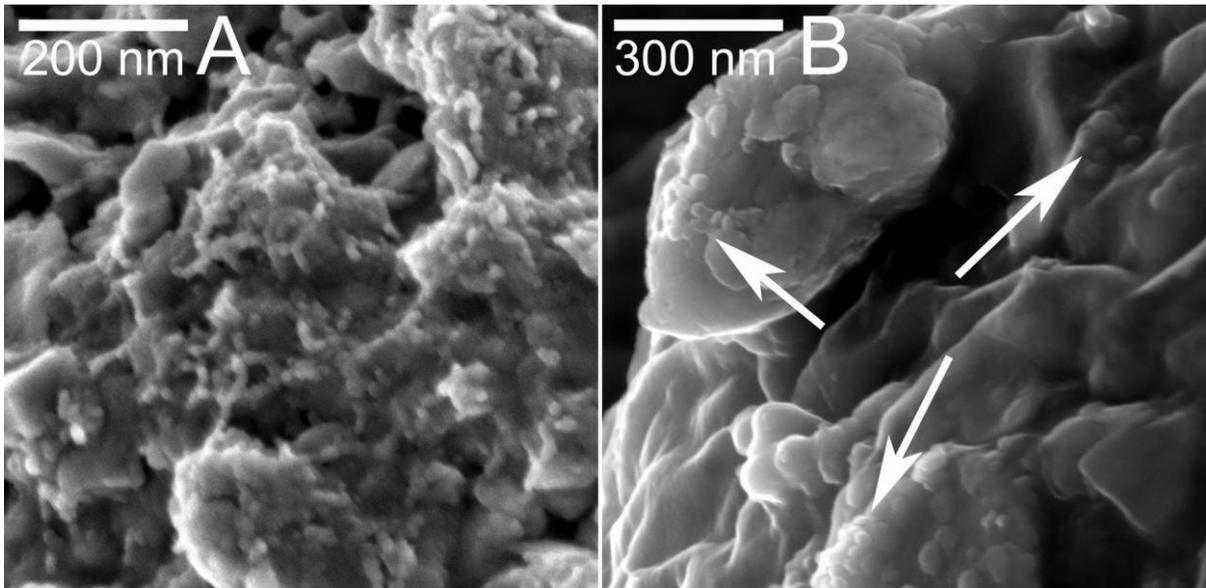


Figure 8. Secondary electron images of nanoscale forms of Mn-Fe precipitates that occur on Orinoco varnish. Some are hemispherical in shape (arrows in *B*), while others are networks of filaments (*A*). These forms are too small to be bacteria, but they could be the remains of a bacterial sheath.

splash zone location of the Orinoco varnish. Since rock coatings are most common in the high-water splash zone of tropical rivers (von Humboldt 1812; Boussingault 1882; Lucas 1905; Francis 1921), recent research has found that manganese and iron concentrations are highest during the high-water stage in the Orinoco (Mora et al. 2009), because dissolved Mn concentrations are pH dependent

(Mora et al. 2010). Lower pH values during high water increase the solubility of Mn. Thus, some Mn enhancement could be from this abiotic seasonal process. Still, even if Mn concentrations are a bit higher, a mechanism to immobilize and also enhance Mn is required—either nanoscale hematite or biotically.

In contrast to the uncertainty of abiotic fixation

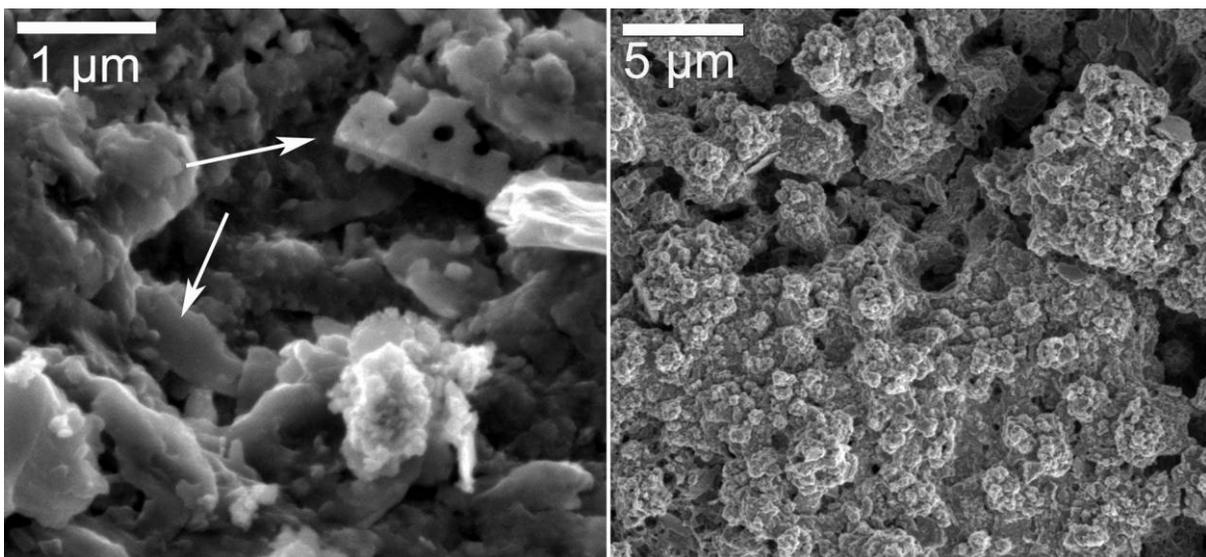


Figure 9. Secondary electrons image diatom fragments (*left*) and cocci bacterial forms (*right*) could both be responsible for Mn enhancement.

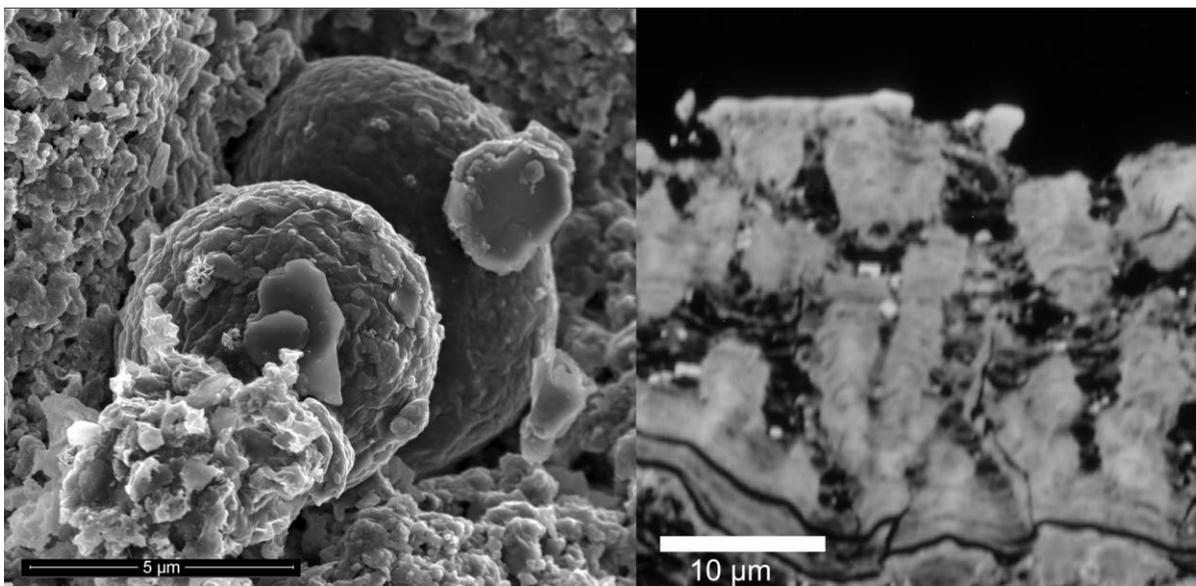


Figure 10. Secondary electrons image botryoidal varnish structures (*left*) and backscattered electron imaging in cross sections of these forms reveal a stromatolitic appearance (*right*).

of Mn in the Orinoco splash zone environment, microbial oxidation of Mn (II) to Mn (IV) is quite rapid at Orinoco pH values (Tebo et al. 1997; 2004). Environmental and laboratory studies suggest that the microbial oxidation of Mn (II) results in the formation of Mn (IV) without lower Mn (III) valences (Tebo and He 1998; Tebo et al. 2004). Both gram-positive and gram-negative bacteria form a diverse phylogenetic group of sheathed and appendaged bacteria capable of oxidizing Mn (Perfil'ev et al. 1965; Khak-mun 1966; Dorn and Oberlander 1981, 1982; Hungate et al. 1987; Ivanova et al. 2010; Northup et al. 2010).

While we have not conducted any culturing studies on Orinoco samples, we note three types of evidence suggesting that microbial processes could be important. First, we have observed fragments of diatoms incorporated into the Orinoco coating (fig. 9), noting that algae are implicated in the formation of tropical riverine varnish (Francis 1921). Second, we have observed an abundance of cocci-sized bacterial forms where EDS measurements (e.g., point 3 in table A2) indicate that they are enriched in Mn and Fe (fig. 9). We also note that the abundance of Mn can vary tremendously from cocci form to cocci form over a distance of nanometers and microns.

A third piece of evidence suggesting the importance of microbial processes is the presence of stromatolite forms. Botryoidal forms in the size range of 5 μm have a stromatolitic appearance when viewed in cross section (fig. 10). Although stro-

matolitic forms can form by purely abiotic processes (McLoughlin et al. 2008), these forms are often suggestive of a biotic role in depositional processes (Klappa 1979; Urzì et al. 1992; Arp et al. 1999).

We do not have any definitive explanations for the depositional processes responsible for the Orinoco coatings. There are morphological suggestions that a nanoscale abiotic process could exist, and there are textural and biotic form indicating that microbial processes could be important. The exact processes of Mn and Fe enhancement in von Humboldt's Orinoco coatings remain to be elucidated in future studies.

Conclusion

Two centuries have passed since publication of *Personal Narrative of Travels to the Equinoctial Regions of America During the Years 1799–1804* initiated formal scientific scholarship into rock coatings, as well as many other fields of science. Alexander von Humboldt and Aimé Bonpland discussed five topics on pages 242–246 of the second volume of an English translation (von Humboldt 1812): coating thickness, coating composition, luster, whether coatings derive from the underlying rock or external sources, and processes responsible for coating deposition.

Based on an analysis of the scholarly literature (Lucas 1905; Dorn and Oberlander 1982; Dorn

1998, 2009), we estimate researchers exploring various aspects of rock coatings have visited and analyzed samples from several thousand field sites in the last 200 yr. However, we cannot find one study that has revisited or reanalyzed von Humboldt's "brownish black crust[s]". Thus, this article returns to the Orinoco cataracts and presents a new analysis of von Humboldt's crust and his ideas.

Alexander von Humboldt's basic hypothesis, that manganese-, iron-, and carbon-containing rock coatings are formed by accretionary processes and not by weathering of the underlying rock, remains valid under the lens of modern electron microscopy. Bulk PIXE analyses and point-specific EDS analyses confirm wet chemical analyses conducted in the eighteenth century, that showed manganese, iron, and carbon are major constituents. HRTEM images reveal that clays produce a nanometer-scale texture of layering seen in rock varnishes formed in warm deserts. Backscattered and secondary electrons imaging the varnish-rock contact reveal the external nature of the accretion.

Although von Humboldt thought that chemical precipitation from water is the likely process of formation, this notion is not compatible with modern understanding that the acidity of the Orinoco cannot immobilize manganese through abiotic oxidation of Mn (II) to Mn (IV). Alexander von Humboldt's attributing the Orinoco water as the source of the coating is still reasonable, since the concentrated Mn would have to derive from suspended sediment or dissolved Mn. However, imaging with secondary and backscattered electrons does not re-

veal definitive evidence of how Mn has been enhanced 60–70 times over Mn concentrations in Orinoco water and suspended sediment. There are, however, electron microscope observations that biotic processes may be involved, including Mn enhancement associated with cocci bacterial forms, Mn-enriched diatom fragments, and the presence of microstromatolitic textures.

Two aspects of the coating particularly impressed von Humboldt: its apparent uniform thickness <1 mm and its sheen. Although the coating thickness is not uniform, varying from nanometers to up to 50 μm , apparent uniformity likely reflects limitations of eighteenth-century instrumentation. The remarkable Orinoco sheen derives from two features, a very smooth lamellate micromorphology and high concentrations of manganese—the same features needed to produce a lustrous appearance of rock varnishes formed in warm deserts.

Alexander von Humboldt truly deserves credit for initiating the study of rock varnish, specifically, and rock coatings in general. After 2 centuries of scholarship, his writings are a reminder of the timelessness of careful field-based observations.

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