Rock Varnish

Over thousands of years, a thin coating of clay, cemented to rocks by manganese and iron, records the history of landscape development and ancient cultures

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In July of 1799, Alexander von Humboldt, the German geographer, arrived in Cumaná in northeastern Venezuela. A hundred miles away, at the mouth of the Orinoco River, he found granite boulders that appeared "smooth, black, and as if coated with plumago." Indian legends explained that these rocks had been burnt by the hot tropical sun, and that they were dangerous to one's health. While investigating the origin of the rocks, von Humboldt and his crew scoffed at the local legends, but each night they retreated to white beaches, distant from the black boulders.

Von Humboldt’s boulders and similar rocks found elsewhere generated a scientific mystery that continued for nearly two centuries. Charles Darwin found dark coated rocks at Bahia in Brazil. Others found such coatings on rocks in the rain forest, underneath glaciers in the Alps, and even at the apex of the Pyramid of Cheops. Hypotheses about the origin of the black coating ranged from deposits left by ancient oceans to residues from decomposing organic matter, such as pollen. The most popular hypothesis attributed the coating to a process called sweating. According to the sweating hypothesis, water sweats out of the rocks under the hot sun, and precipitates are deposited as a black coating on the surface when the water evaporates. But was the sun hot enough to induce sweating of solutions from rocks in the rain forest or underneath glaciers?

The black coating has been known by various names, such as wustenlacken (desert varnish) and patina; only recently has the scientific community settled on a term that seems sufficiently broad and descriptive: rock varnish. Even while the origin of the rock varnish remained enigmatic, its physical and chemical structure came to be understood. Rock varnish consists of a thin layer, less than half a millimeter deep, on a rock’s surface. The coating is typically composed of about 60 percent clay minerals, 20 to 30 percent oxides of manganese and iron, and trace amounts of more than 30 minor compounds, such as copper and zinc oxides. It is the amount of manganese oxide that determines the color of the varnish. Often, the varnish concentrates manganese oxide to levels up to 100 times that found in surrounding rocks; such high concentrations of manganese oxide make the varnish black. Some varnish lacks manganese altogether and appears bright orange from the abundant iron oxides; this is particularly prevalent on the bottom of rocks and inside rock crevices. In other places, such as the hyperarid Peru Desert, the level of manganese oxide is intermediate, leaving the varnish a brownish orange.

The decisive clue to the mystery of rock varnish was a biological one. In 1981, T. M. Oberlander of the University of California at Berkeley and I suggested that bacteria concentrate manganese in rock varnish. We developed this hypothesis on strong circumstantial evidence. First, manganese-rich varnish often forms where water intermittently flows over rocks. The moisture provides a hospitable environment for microorganisms. Second, varnish develops well on porous surfaces that are easily flushed and, hence, are poor in nutrients. In such a harsh environment manganese-oxidizing mixotrophs (which derive some of their energy from inorganic manganese) are able to live; but fast-growing heterotrophic organisms (which rely entirely on organic nutrients) are unable to survive.

A third observation in support of the bacterial hypothesis is that dark varnish grows on rocks with a nearly neutral pH. Nonbiological mechanisms for oxidizing manganese operate only in an alkaline environment, where the pH exceeds 9. Thus, manganese-oxidizing bacteria are one plausible candidate. This line of argument is further supported by findings that varnish is orange when the local pH is too high to support manganese-oxidizing bacteria. Finally, there are many documented interactions between clay, the primary constituent of varnish, and bacteria. Clay particles are often adsorbed onto the surface of bacteria, and vice versa. Clay concentrates nutrients, a useful property in a nutrient-poor environment, and stimulates bacterial metabolism. And, a coating of clay can protect bacteria against desiccation and high temperatures. In combination, these factors supported the possibility that bacteria produce manganese-rich rock varnish.

With these ideas in mind, Oberlander and I examined rock varnish for the presence of bacteria. By searching through varnish with the aid of scanning electron microscopy, we found them—manganese-concentrating bacteria of the genus Metallogenium and other species. Fred Palmer and his colleagues
at the University of Washington found bacteria of the genus *Arthrobacter* in rock varnish. Next, we isolated living bacteria from natural rock varnish; when we grew these bacteria in laboratory cultures, they produced varnish that was morphologically similar to the natural product.

Given these discoveries, we formulated the following scenario. A wet period stimulates the proliferation of bacteria on rocks. The bacteria, then, secrete an enzyme that oxidizes manganese, forming a dark and immobile product. As dust blows across the rocks, the manganese oxide cements clay to the rock’s surface, producing varnish. The formation of the varnish begins in “nucleation centers,” or areas where bacteria are blooming, and spreads across the rock’s surface. Working in the coastal desert of Peru, Charlie Jones of the University of Oxford found that dew on rocks can release manganese that is then precipitated by bacteria. The local pH level affects the ratio of manganese to iron in the varnish. High alkalinity inhibits the manganese-concentrating bacteria, and so the manganese-to-iron ratio is low. The result is an orange varnish in which clay dust is rather poorly secured to the rock’s surface by iron oxides.

**Years beneath the Surface**

Even before the origin of rock varnish was fully understood, efforts were under way to turn the phenomenon into a tool, a useful indicator of something. In particular, rock varnish appeared to offer approaches to dating things because the varnish accumulates over time. Early attempts to date rock varnish concentrated on appearance because, with age, the varnish gets dark-
er and thicker and covers more of the rock. Kevin White of the University of Oxford is using satellite images to assess the visual changes in rock varnish over time.

Visual changes in rock varnish can provide relative ages between rocks, but the power of rock varnish as a dating tool would be enhanced if it alone could establish a specific age. In 1981, while working on the prehistoric shorelines of Pleistocene Lake Lahontan in Nevada, Oberlander and I sent samples of rock varnish to Tom Cahill of the University of California at Davis for analysis. The ratio of the cations potassium and calcium relative to titanium (that is, \((K + Ca)/Ti)\) in the varnish declines with time. We proposed that the major constituents of varnish—clays and oxides of manganese and iron—act as cation-exchange complexes, where potassium and calcium are replaced or depleted faster than titanium. This suggested that older varnish would have a lower cation ratio than newer varnish.

How much different would the ratios be? To obtain actual dates from measurements of the cation ratio, we would need to calibrate the measurements against those made by some other technique, such as radiocarbon dating, for a surface of the same age as the varnish. When carried across thousands of years, the cation ratio versus the radiocarbon date produce a dramatically linear relationship. This has been replicated at five different laboratories, including those of Carlos Pineda in South Africa and Yuming Zhang in China.

Recently, with my colleague David Krinsley at Arizona State University, I actually detected the removal of cations from rock varnish. We placed pieces of varnish in containers of deionized water for up to 100 days, and at various intervals tested the water for calcium and potassium. The abundance of both cations increased in the leaching water throughout the experiment, and their only potential source was the varnish. We also examined sections of the varnish after the leaching by means of electron microscopy and found two types of texture: layered and porous. We guessed that some constituent of the varnish had been removed from the porous areas and, therefore, measured the cation ratio. In all cases the porous areas of the varnish had a lower cation ratio than the layered areas. Thus through these experiments, one in the laboratory and the other carried out by nature, we essentially watched the cations being leached from the varnish over time.

The dominant technique for assigning dates to objects up to about 40,000 years old is the radiocarbon method, based on the decay of the radioactive carbon isotope \(^{14}C\). Of course this method can be employed only if an object contains carbon. Rock varnish does contain some carbon—it was first identified 60 years ago by J. D. Laudermilk of Pomona College—but the amounts are too small for the traditional method of analysis, which relies on direct detection of the radioactivity.
of $^{14}$C and requires gram quantities of material. In 1989, however, Tim Linck and his colleagues at the University of Arizona summarized a new revolution in radiocarbon dating, based on accelerator mass spectrometry. In this technique carbon atoms are ionized and accelerated to an energy of a few million electron-volts, then sorted according to mass in the magnetic field of a mass spectrometer. By counting atoms in this way, one can directly measure the ratio of $^{14}$C to the more abundant stable isotope $^{12}$C. The accelerator method allows precise analyses of radioactive carbon in samples weighing less than a milligram, like those found in rock varnish.

To apply radiocarbon dating to rock varnish, one must first isolate the organic materials that are the sources of carbon in the coating. At first, we did this by scraping the varnish to its lowest layer with a tungsten carbide needle and then chemically treating the scrapings to concentrate any organic material. About a year ago, however, I recognized that it is much easier to find the carbon-rich material through a microscopic examination, looking for organic mats and filaments that were buried by the varnish. These mats or filaments can be collected for radiocarbon dating.

Before leaving the subject of dating methodology, I should mention an inherent limitation of all techniques based on analysis of rock varnish. At best the rock varnish can provide a minimum age for an object. The rock’s surface must be exposed before the rock varnish can begin to form. So, if an ancient explorer’s arrowhead fell to the ground and bacteria immediately began producing varnish, analysis would reveal an age close to the time that the piece was produced or dropped. But the local environment determines when varnish begins to accumulate, and decades may pass before the process begins. Therefore, dating an object from rock varnish can never say more than, “It is at least this old.”

**Clues to Past Environments**

Beyond the passage of time, rock varnish records past environmental events—events from the so-called paleoenvironment. The local environment at the time the varnish is forming affects its composition. Therefore, sampling varnish on the tops of rocks, where they are exposed to airborne fallout, reveals fluctuations in the composition of the particles in the air. Only long-term variations in environment are readily observed because the varnish develops extremely slowly, at approximately two to five micrometers per thousand years in deserts.

Some environmental factors change the three-dimensional structure of the varnish. The rate of dust fallout, for example, affects the micromorphology of the varnish. When dust fallout is low, the varnish appears botryoidal, like a bunch of grapes. This structure develops because the low levels of dust cause the formation of varnish to concentrate at the nucleation centers, which later grow so large that they touch. If the dust fallout is high, however, the layers of varnish are lamellate, like a stack of papers. The high levels of dust cause clay deposition to overwhelm the botryoidal nucleation centers. In many cases, alternating layers of botryoidal and lamellate micromorphology appear in rock varnish, indicating paleoenvironmental variations in airborne dust. Orange varnish, however, is always lamellate because it lacks the manganese-oxidizing bacteria that create the nucleation centers.

Rock varnish also records blowing dust. In windy environments, dust

![Figure 4. Manganese and iron content of rock varnish was measured by energy-dispersive x-ray analysis, which reveals the presence of the metals and offers evidence of their biological origin. A measurement of the overall varnish (upper graph) reveals some manganese and iron, but analysis of varnish near a bacterial strand (lower graph) has much higher levels of the two metals.](image-url)
sweeps across rocks and, over centuries, sand the varnish from their surfaces and can whittle away at the rock as well, producing what is called eolian abrasion. Sometimes the abrasion fails to remove all of the varnish from a rock and, when the episode of erosion ends, new varnish begins to form on the exposed surface. The intersection of new and old varnish forms a discontinuity in the coating, much like a patched pothole on a highway. These distinctive features produce a record of the wind during the past.

Geochemical signals, including various pollutants, also accumulate in the rock varnish. In particular, heavy metals in the air, such as lead, become trapped by the oxides of manganese and iron in rock varnish. Consequently, monitoring the lead content in rock varnish may offer insight into relatively modern issues. Rocks adjacent to well-traveled roads, for example, often show variable concentrations of lead throughout their varnish. The very surface of the rock varnish can be 3 to 4 percent lead. But, just 20 micrometers below the surface of the varnish, the lead content drops below 0.1 percent. By better understanding the natural levels of lead throughout geological history, we might better understand the importance of modern increases.

A paleoenvironmental interpretation of varnish describes more than dangerous debris and dust. The varnish can even reconstruct an area’s past flora. This is possible because nearby plants shed micrometer-size airborne organic material that collects on rocks and becomes incorporated into the varnish. This organic material provides a rough environmental fingerprint of the local plants. Different types of plants capture different levels of stable carbon isotopes from atmospheric carbon dioxide. In general, two isotopes react in the same way in chemical reactions, but they may react at different rates. Therefore, a plant may incorporate one isotope more readily than another. This is called isotopic fractionation and is measured as a ratio, such as $^{13}$C/$^{12}$C, which is called the $\delta^{13}$C value.

Although measuring the $\delta^{13}$C value does not distinguish oaks from pines, the measurement can divide plants into two groups, based on their environmental requirements. One group, C$_3$ plants including wheat and beans, prospers in a humid environment. The other group is made up of C$_4$ plants such as corn and sugar cane and CAM
plants such as cacti. CAM plants use a special photosynthetic pathway called crassulacean acid metabolism. Through this pathway, CAM plants open the stomata on their leaves to capture carbon dioxide only during the coolness of the night. During the day, these plants close their stomata to conserve water. Both the C₄ and CAM plants thrive in arid habitats. Organic material from living C₄ plants has distinct δ¹³C values when compared to those found in C₄ and CAM plants.

In 1985, Michael DeNiro, now at the University of California at Santa Barbara, and I confirmed that δ¹³C values distinguish C₄ from C₃ and CAM plants. We conducted experiments on organic matter in modern rock varnish in western North America, Israel and the Sinai Peninsula. Here the δ¹³C values determine if C₄ or C₃ and CAM plants dominated an area during the formation of the rock varnish.

Still, some problems limit the potential of rock varnish as a tool for investigating the past. I have learned two hard lessons in trying to extract consistent and reproducible paleoenvironmental results from rock varnish. First, care must be taken to work with the right types of varnish. It is tempting to collect the best-looking varnish in the field; but often this varnish yields inconsistent data because it frequently originated in rock crevices or, as Deidre Dragovich of Sydney University has established, is heavily eroded by fungi or lichens. Only field experience and a careful evaluation of a cross section of the varnish can lead you to the right varnish, an evenly layered material. Second, fluctuations in any given cross section reflect only the environmental influences on that small area of rock surface. Profiles must be replicated from spot to spot on a rock, from rock to rock in an area and repeated from area to area in order to reconstruct a regional pattern of environmental change.

**Varnish in the Valley**

One intriguing environmental change for geomorphologists is the movement of sediment. Water, gravity and glaciers...
continually reshape the earth’s surface by moving sediment from one place to another. Alluvial fans—the conical deposits evident where a canyon emerges from a mountain range—provide a prime example of sedimentary deposits. These deposits develop from debris left by flowing water or sediment that tumbled down a hill under the force of gravity. Over thousands of years, the sediment amasses at the bottom of the canyon. The deposits settle into the shape of a fan, starting from the apex of a triangle called the fanhead to the broad base called the toes. The control of fan development over time remains largely a mystery because we lack knowledge of the dates and paleoenvironment of different deposits.

Southern Death Valley is a classic region for the study of alluvial fans in drylands. Alluvial fans emerge from the Panamint Mountains to the west and the Black Mountains to the east, leaving large deposits of sediment along the borders of the desert. These deposits offer a fantastic range of varnish development. So, I spent five years studying the varnish on rocks in alluvial fans around southern Death Valley.

The deposits in fans build up like the layers of a cake. Newer deposits sweep across older deposits. This creates a problem for assessing older deposits that have not only been covered but, perhaps, even eroded by newer flows. To limit this problem, I examined only the newest deposits, which are the best preserved and should possess keys to understanding the older deposits as well.

In Death Valley, I sampled varnish from the fanhead to the toes of the latest Pleistocene deposit and then dated the varnish with radiocarbon and cation-ratio techniques. Near the head I found varnish that was about 50,000 years old. Halfway down the fan the varnish was 30,000 years old. And at the bottom the varnish was about 14,000 years old. Then, a few points in between completed this essentially linear relationship between the age of the varnish and the height on the fan. Other workers had shown that deposits gradually shift down a fan, but no one had shown such continuous deposition along the fan over time. Nevertheless, deposition of sediment along a fan probably is episodic, but in a manner that escapes the resolution of my measurements.

If the deposition was continuous, what could have caused that? Roger Hooke of the University of Minnesota
suggested that tectonic uplift and tilting of the Panamint Range may have caused the gradual change. As the Range tipped more and more, alluvial deposits tumbled farther and farther down the fan, leaving the newest deposits closest to the bottom. If the uplift and tilting followed an essentially continuous course, so too would the relationship between the age of the varnish and its location on the fan.

Rock varnish on alluvial fans documents more than age alone. Moving from the fanhead to the toes of the latest Pleistocene deposit, δ13C values indicate a progressively more humid environment suitable to C3 plants. Moreover, this finding correlates well with the plant macrofossil record of the area. Work by Philip Wells and Deborah Woodcock of the University of Kansas showed that from 19,000 to 13,000 years ago a juniper woodland covered some slopes of the Panamint Range. Then, a climatic change produced the extremely arid environment now associated with Death Valley, and the junipers yielded to creosote bush.

This climatic change triggered the next alluvial deposit, the Holocene deposit. Here varnish at the fanhead indicates that this deposit began about 12,000 years ago. And δ13C values from the rock varnish on this younger fan unit indicate an arid climate and hot desert vegetation. The previously humid climate supported abundant vegetation on the slopes, which died when the desert heat arrived. The loss of vegetation probably enhanced erosion, which launched the new fan deposit. Such a scenario shows that dying plants, as well as moving mountains, affect the rate of sedimentation.

Lawrence Lustig of the U. S. Geological Survey presented a similar climatic interpretation. Twenty-five years ago, Lustig investigated the alluvial fans of Deep Springs Valley (northwest of Death Valley) without the aid of chronological or paleoclimatic data for insight or support. Based on the nature of the sediments, he concluded that extensive fan surfaces formed during a wetter period, followed by a wave of sediment deposition on the lower reaches of the fan at the onset of a drier period.

Raider of the Lost Rock
The moving earth moves more than sediment. It can also unearth archaeological objects, jostling them to the surface. In the past, any archaeological re-

Figure 11. Grooves in a boulder in the Mojave Desert were created by windblown sand, which scraped away layers of varnish and some of the underlying rock. When this eolian abrasion abated, the grooves were recoated with fresh deposits of rock varnish. Organic matter in the bottom of the grooves dates them at about 5,000 years old.

Figure 12. Discontinuities in layers of varnish are a result of intermittent eolian abrasion. Windblown sand often removes only portions of the varnish, leaving the once-continuous layer spotted with patches of bare rock. Once the windy conditions subside, a new layer of varnish begins forming and fills in the patches. After several thousand years and several episodes of windy weather, a cross section of the varnish resembles a bumpy road.
Figure 13. Satellite image of southern Death Valley in California shows numerous alluvial fans, whose history can be reconstructed in part from the rock varnish on their surfaces. From the west (left), dozens of alluvial deposits pour from the Panamint Mountains; from the east (right), smaller fans dot the border of the dried lake bed. On all of the fans, darker colors indicate older rock varnish. The photograph was made by the French SPOT satellite. It is a false-colored image, in which green vegetation, for example, appears bright red; but the muted tones of rocky landscapes appear similar to their natural colors.

mains found on the surface were a lost cause for dating procedures. Generally, the age of an artifact is determined by radiocarbon dating charcoal in the layer of soil in which the artifact is found. But remains found on the surface lack such chronological control and, therefore, are difficult to date. This problem arises with rock paintings (pictographs), rock engravings (petroglyphs) and stone alignments on the ground (geoglyphs). Recently, however, new techniques have allowed the dating of these surface features. An oxalate-rich skin that covers some rock art, and human blood extracted from pictographs, provide a source of carbon for radiocarbon dating methods. And now rock varnish can also date these objects.

Rock varnish is particularly well suited for dating archaeological material exposed in deserts. When people use rocks, fresh surfaces are exposed by etching boulders during the production of petroglyphs or to make stone tools. When etching or use of the artifact stops, rock varnish starts to grow again. Centuries later, the varnish can be dated. Perhaps even more importantly, a sample of rock varnish can be removed for analysis without destroying the underlying cultural resource.

Similar aspects of rock varnish apply equally well to the dating of geoglyphs. During the first millennium A.D., the people called the Nasca inhabited the desert coast of southern Peru. These people created complex geoglyphs with networks of geometric shapes and animal figures that are only recognizable from the air. Some archaeologists think the lines assisted in astronomical observations and that the animals were messages to gods in the sky. In any case, the Nazca geoglyphs were etched
into the desert pavement of Pampa San Jose by moving well-varnished cobbles to expose light-colored silt and the unvarnished cobbles below. Organic material accumulated on the newly exposed cobbles and was encapsulated by the growth of rock varnish. Persis Clarkson of Athabasca University and I dated the organic matter from several Nazca lines from about 190 B.C. to 660. These dates overlap those of the early Nasca culture.

Petroglyphs and surface artifacts often fail to provide sufficient organic material even for accelerator mass spectrometry. In such cases, cation-ratio dating may still be possible. Using this method, David Whitley of the University of North Dakota and I showed that petroglyph styles remained similar across thousands of years in the Coso Range and the Mojave Desert of eastern California. In addition, the cation-ratio technique dated petroglyphs in the arid zone of southern Australia at about 31,000 years old. Recently, Margaret Nobbs of Flinders University and I checked this date when we obtained organic material

Figure 15. The Nasca lines—a group of geometric shapes and animal figures in the desert of Pampa San Jose of southern Peru—vividly demonstrate the contrast between varnished and unvarnished rocks. The Nasca people created the figures by moving darkly varnished rocks to expose unvarnished rocks below. After the lines were created, varnish began forming on the exposed rocks, and the age of this varnish provides a minimum age of the lines. The varnish on the small bird has a radiocarbon date of about 1,500 years.
from the varnish of the Australian petroglyphs. Using accelerator radiocarbon dating, the Australian petroglyphs came in at about 36,000 years old. That makes this petroglyph the oldest known rock art in the world.

To further appraise the cation-ratio technique, my archaeological collaborators have completed a series of blind tests. Larry L. Loendorf of the University of North Dakota provided one of the most arduous tests of the accuracy of cation-ratio dating with archaeological material from the Pinon Canyon area of southeastern Colorado, which has hundreds of rock art sites. Independently, Loendorf radiocarbon dated material excavated near petroglyph panels, and I measured the cation ratio for the panels. In every case our results were consistent. At the Zookeeper site, for instance, I cation-ratio dated the main panel at between 900 and 1,000 years old. Loendorf, later, radiocarbon dated associated archaeological material and obtained a date of just over 1,000 years old.

Perhaps today even von Humboldt would sleep near a well-varnished rock, revering its retrospective rather than its repugnant power. Since his time, rock varnish has moved from a mysterious anomaly to a predictive tool. More than recalling the past, rock varnish can predict the future. It can identify stable landforms, which is increasingly useful to populations pushing onto alluvial fans that flank desert mountain ranges in such rapidly expanding metropolitan areas as Tucson and Phoenix. In such areas rock varnish can serve as a gauge of inactivity and, thereby, help people avoid building in areas of active flooding. Furthermore, rock varnish can indicate surface stability, a valuable factor in the search for stable sites for the disposal of nuclear and other toxic wastes. These features make rock varnish a useful tool for future development. Yet, this is just the beginning. The success of rock varnish as an indicator may predict similar futures for other rock coatings, such as calcium carbonate rinds, calcium oxalate skins, human-made pigments and silica glaze. Indeed, much of the beauty of rocks may be only skin deep.

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Bibliography


"Everywhere you look, there's the greenhouse effect. In here, we can't grow a damn thing."

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