4.5 Rock Coatings

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Glossary

Carbonate skin Coating composed primarily of carbonate, usually $CaCO_3$, but sometimes $MgCO_3$.

Case hardening Addition of cementing agent to rock matrix material; the agent may be manganese, sulfate, carbonate, silica, iron, oxalate, organisms, or anthropogenic.

Dust film Light powder of clay- and silt-sized particles attached to rough surfaces and in rock fractures.

Heavy metal skins Coatings of iron, manganese, copper, zinc, nickel, mercury, lead, and other heavy metals on rocks in natural and human-altered settings.

Iron film Coating composed primarily of iron oxides or oxyhydroxides.

Lithobiontic coatings Organisms forming rock coatings, for example, lichens, moss, fungi, cyanobacteria, and algae.

Nitrate crust Potassium and calcium nitrate coatings on rocks, commonly in caves and rock shelters in limestone areas.

Oxalate crust Mostly calcium oxalate and silica with variable concentrations of magnesium, aluminum, potassium, phosphorus, sulfur, barium, and manganese. Commonly found forming near or with lichens.

Phosphate skin Various phosphate minerals (e.g., iron phosphates or apatite) sometimes mixed with clays and sometimes manganese.

Pigment Human-manufactured material placed on rock surfaces by people.

Rock varnish Clay minerals, Mn and Fe oxides, and minor and trace elements; color ranges from orange to black in color produced by variable concentrations of different manganese and iron oxides.

Salt crust Chloride precipitates formed on rock surfaces.

Silica glaze Coating that is generally clear white to orange shiny luster, but can be darker in appearance, composed primarily of amorphous silica and aluminum, but commonly with iron.

Sulfate crust Sulfates (e.g., barite and gypsum) on rocks; not gypsum crusts that are sedimentary deposits.

Abstract

Fourteen different types of coatings cover rock surfaces in every terrestrial weathering environment, altering the appearance of the underlying landform. Some accretions interdigitate, whereas others blend together, creating a great number of variations. Rock coatings are important in geomorphology because coatings: alter weathering rates; play a role in case-hardening surfaces; offer clues to understanding environmental change; and can provide chronometric insight into the exposure of the underlying rock surface. Following a landscape geochemistry paradigm, five general hierarchies of control explain the occurrence of different types of rock coatings: first order – geomorphic processes control the stability of bedrock surfaces on which coatings form; second order – coatings originating in rock fissures occur on subaerial surfaces when erosion of the overlying rock occurs; third order – the habitability of surfaces for fast-growing lithobionts such as lichens determines whether slowly accreting coatings occur; fourth order – the raw ingredients must have a transport pathway to the rock surface, and of course, they must be present; fifth order – physical, geochemical, or biological barriers to transport then result in the accretion of the coating.

4.5.1   Introduction to Rock Coatings

Bare rock surfaces rarely display a lithology's true appearance, where rhyolite appears pink, gneiss displays dark and light banding or basalt is black. As surfaces accrete rock coatings (Table 1), appearances can change dramatically. Consider three examples. The sandstone of Petra, Jordan, is generally darkened by case hardening caused by the accumulation of iron and manganese in the upper millimeter of sandstone (upper row in Figure 1). The light-colored granodiorite at Stone Mountain, Georgia, is streaked by several different types of rock coatings, including calcium oxalate (middle row in Figure 1). Black basalt lava flows on the rainshadow side of Hualalai and Mauna Loa volcanoes, Hawaii, are gradually lightened in color as silica glaze accretes on lava flow surfaces (lower row in Figure 1). The geomorphic reality is that coated surfaces are far more common than uncoated rocks. Because these accretions influence the weathering of the underlying rock, a full understanding of the terrestrial weathering environment must consider rock coatings.

This chapter organizes rock coatings through a paradigm of landscape geochemistry, as developed by Soviet geography (Polynov, 1937; Perel'man, 1961, 1966; Glazovskaya, 1968, 1973) with some adoption outside of Russia (Fortescue, 1980). This theoretical framework provides a way by which rock coatings can be interpreted in terms of element abundance, element migration, geochemical flows, geochemical gradients, and geochemical barriers with the classification, interpretation, and spatial laws pertaining to geochemical landscapes. At its simplest, a landscape geochemical approach interprets the occurrence of rock coatings as being caused by physical, chemical, or biological barriers to the transport of elements. This chapter interprets rock coatings from the perspective of five different landscape geochemistry hierarchies of controls on rock-coating formation.

4.5.2   Interpreting Rock Coatings through a Landscape Geochemistry Approach

What influences the formation of a rock coating? Phrased more empirically, what processes generate silica glaze on one surface, case hardening on another, and oxalate crusts on a third – as exemplified by the three different types of rock coatings seen in Figure 1. The answer characteristically ends up being an encyclopedic approach of analyzing unique site-specific factors. In the case of case-hardened rock at Petra (upper row in Figure 1), rock varnish once formed on a sandstone surface. Manganese and iron were leached out of the varnish and reprecipitated inside the pore spaces of the sandstone. Granular disintegration of the sandstone surface eroded much of the varnish, but case hardening by heavy metals including manganese stabilized the outer millimeter. Another coating is the oxalate crust on Stone Mountain, Georgia (middle row in Figure 1); this oxalate, composed primarily of hydrated calcium oxalate ($CaC_2O_4 \cdot H_2O$), accreted about a meter downslope from a patch of lichens. Overland flow carried oxalate from the lichens, and evaporation assisted in the accretion of

Table 1   Major types of rock coatings

| Coating	Description	Related terms
Carbonate skin	Composed primarily of carbonate, usually $CaCO_3$, but sometimes $MgCO_3$	Calcrete, travertine
Case hardening	Addition of cementing agent to rock matrix material; the agent may be manganese, sulfate, carbonate, silica, iron, oxalate, organisms, or anthropogenic.	Sometimes called a particular type of rock coating
Dust film	Light powder of clay- and silt-sized particles attached to rough surfaces and in rock fractures.	Clay skins, clay films, soiling
Heavy metal skins	Coatings of iron, manganese, copper, zinc, nickel, mercury, lead and other heavy metals on rocks in natural and human-altered settings.	Also described by chemical composition
Iron film	Composed primarily of iron oxides or oxyhydroxides.	Ferric oxide, iron staining
Lithobiontic coatings	Organisms forming rock coatings, for example, lichens, moss, fungi, cyanobacteria, algae.	Organic mat, biofilms, biotic crust
Nitrate crust	Potassium and calcium nitrate coatings on rocks, often in caves and rock shelters in limestone areas.	Saltpeter, niter, icing
Oxalate crust	Mostly calcium oxalate and silica with variable concentrations of magnesium, aluminum, potassium, phosphorus, sulfur, barium, and manganese. Often found forming near or with lichens.	Oxalate patina, lichen-produced crusts, patina, scialbatura
Phosphate skin	Various phosphate minerals (e.g., iron phosphates or apatite) sometimes mixed with clays and sometimes manganese.	Organophosphate film, epilithic biofilm
Pigment	Human-manufactured material placed on rock surfaces by people.	Pictograph, paint, graffiti
Rock varnish	Clay minerals, Mn and Fe oxides, and minor and trace elements; color ranges from orange to black in color produced by variable concentrations of different manganese and iron oxides.	Desert varnish, patina, Wüstenlack
Salt crust	Chloride precipitates formed on rock surfaces.	Halite crust, efflorescence
Silica glaze	Usually clear white to orange shiny luster, but can be darker in appearance, composed primarily of amorphous silica and aluminum, but often with iron.	Desert glaze, turtle-skin patina, siliceous crusts, silica–alumina coating, silica skins
Sulfate crust	Sulfates (e.g., barite, gypsum) on rocks, not gypsum crusts that are sedimentary deposits.	Sulfate skin
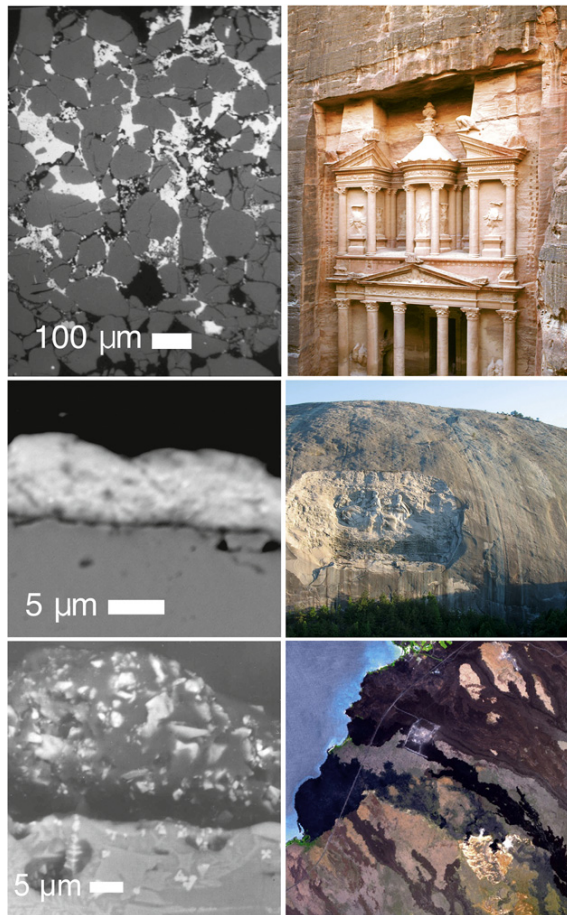
Figure 1   Rock coatings alter the appearance of bare-rock landforms. The left column is the rock coating as seen through back-scattered electron (BSE) microscopy. The right column illustrates how thin rock coatings alter the visual appearance of rock. Top row: case hardening by heavy metals seen through darkens the appearance of a pink sandstone at Petra, Jordan. Middle row: calcium oxalate on quartz illustrates how even thin coatings create dark streaks on granodiorite at Stone Mountain, Georgia, USA. Bottom row: silica glaze lightens the appearance of basalt flows as seen in an ASTER image of the rainshadow of Hualalai Volcano, Hawaii, courtesy of NASA (NASA, 2010), where even the 1859 Mauna Loa lava flow has a thin silica glaze coating.

the oxalate crust. Silica glaze that has formed on the 1859 Mauna Loa lava flow (lower row in Figure 1) likely started with soluble Al–Si complexes $[Al(OSi(OH)^3)^{2+}]$ that are ubiquitous on silicate mineral surfaces. Gentle wetting from dew or even water vapor is enough to mobilize these Al–Si complexes. There is a transition between complete and partial wetting; this transition rests at about 20–70 nm. When this transition is crossed, the metastable wetting film on the silica surface is then ruptured and silica precipitates.

Taken separately, each site-specific study represents an empirical exemplar of inductive science. Such cases dominate the rock-coating literature, but do not contribute to the development of any broader theory explaining the geography of rock coatings – or why different types of rock coatings form in

specific places. Because the science of weathering in geomorphology is a search for broader explanatory patterns, case studies do not typically advance the development of any general theory that explains rock coatings.

The field of landscape geochemistry (Polynov, 1937; Perel'man, 1961, 1966; Glazovskaya, 1968, 1973) offers one systematic way of analyzing the geography rock coatings, working toward a model that can predict what types of rock coatings would develop in different locations. Using this spatial approach to understanding biogeochemistry, Dorn (1998) proposed five general hierarchies of controls on the development of rock coatings. No alternative theoretical approach has yet been posited, although a dialog on development of theory on rock coatings would be a welcome development.

A hierarchical approach necessarily orders the way of analyzing rock coatings. For example, first and foremost, bare rock faces must exist – exposed by geomorphic processes such as landsliding or glaciation. It is an obvious statement that without the exposure of bare rocks, we would not see subaerial exposures of rock coatings. As exposures of bare rock are most common in deserts and alpine settings, rock coatings are more commonly seen in these environments.

Second-order controls are exhibited where erosion exposes rock surfaces that already had rock coatings that formed in the subsurface. The subaerial exposure of coatings that formed in rock fractures is a second-order control, because a great many now-exposed coatings originated at depth.

Third-order controls come into play when fast-growing lithobionts colonize rock faces, and lichens, fungi, and algae effectively outcompete slower-growing inorganic rock coatings. Lithobionts are a third-order control, because they can dramatically alter the biogeochemistry of rock surfaces. This chemical change can often dissolve inorganic coatings or can prevent them from accreting.

Fourth and fifth orders become relevant only if bare rock faces occur (first order), if rock coatings are not exposed by an erosional event (second order), and if fast-growing lithobionts do not grow over the rock face (third order). All three of these conditions must be for the development of many of the subaerial rock coatings listed in Table 1. For example, the silica glaze on Stone Mountain (Figure 1) could accrete, because a bare rock surface was not already coated by lithobionts or an accretion formed originally in the subsurface.

The fourth and fifth orders of control focus on element abundance, element migration, geochemical flows, geochemical gradients, and geochemical barriers associated with different types of inorganic rock coatings. The fourth order focuses on the issue of whether or not the elemental ingredients of a rock coating are present and have a transport pathway to a site; for example, the iron and manganese present in rock varnish at Petra was mobilized down into sandstone pores (upper row in Figure 1). However, just because the elements of rock coatings occur and are transported to a site does not mean that these elements will accrete.

The fifth order of control involves barriers to transport that fix the coating's constituents. The transport barrier might be physical, such as electrostatic or physical forces that hold dust particles together (Jordan, 1954; Bishop et al., 2002; Ganor et al., 2009). Another barrier could be geochemical, such as a change in pH/Eh oxidizing and fixing (NIAIST, 2005) iron in films. Still
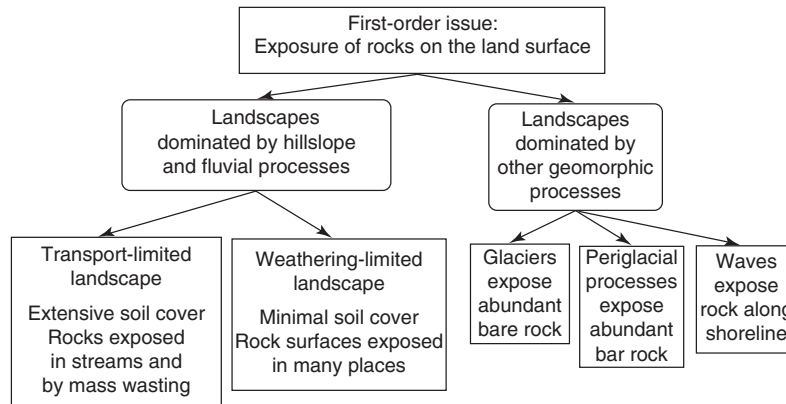
First-order issue:
Exposure of rocks on the land surface

Landscapes dominated by hillslope and fluvial processes

Landscapes dominated by other geomorphic processes

Transport-limited landscape

Extensive soil cover
Rocks exposed in streams and by mass wasting

Weathering-limited landscape

Minimal soil cover
Rock surfaces exposed in many places

Glaciers expose abundant bare rock

Periglacial processes expose abundant bar rock

Waves expose rock along shoreline

Figure 2 Subaerial rock coatings can only occur where bare rock faces have been exposed by geomorphic processes.

another barrier could be biological, exemplified by bacteria oxidizing manganese in rock varnish (Northup et al., 2010). Barriers to transport resulting in rock coatings generally require combinations of biological, chemical, and physical processes.

4.5.2.1   First-Order Control: Geomorphic Stability

The first-order control on whether rock coatings occur is whether bare rock surfaces exist. Rock control is an important concept in geomorphology (Suzuki, 2002), and it is especially critical for rock coatings. After all, a cover of soil, vegetation, or regolith means that rock coatings have no subaerial exposure. Glaciers, waves, landslides, and overland flow in weathering-limited landscapes all exemplify geomorphic processes that expose rocks to the atmosphere – the primary precondition for the occurrence of subaerial rock coatings.

Thus, the first order of control rests with geomorphic processes that generate bare rock surfaces for subaerial rock coatings (**Figure 2**). A wide variety of geomorphic processes expose bedrock surfaces (Ehlen and Wohl, 2002). Mass wasting, glacial, periglacial, volcanic, faulting, flooding, and coastal processes can all bring rocks into the subaerial environment. Bare exposures are most common in arid regions, because deserts are weathering-limited landscapes (Gilbert, 1877).

4.5.2.2   Second-Order Control: Subaerial Exposure of Subsurface Coatings

Rock coatings do develop in the subsurface and are exposed at the surface by erosion of the overlying soil or rock material. For example, iron films develop on clasts in the B-horizon of soils (Haberland, 1975; Hayden, 1976) and are then exposed at the surface through soil erosion (Hunt and Wu, 2004). Manganiferous rock varnish forms in mountain soils (Ha-mung, 1968). Weathered rock fractures are lined with Mn–Fe coatings (Weaver, 1978; Kim et al., 2006), dendrites or branching structures (Xu et al., 2010), and silica glazes (Milnes et al., 1991; Frazier and Graham, 2000). Clay-coated surfaces can be a common component of fractured bedrock (Frazier and Graham, 2000) and weathered minerals in general (Meunier et al., 2007). Fissures in less-weathered bedrock host iron films, rock varnish, laminar calcrete, silica glaze, and
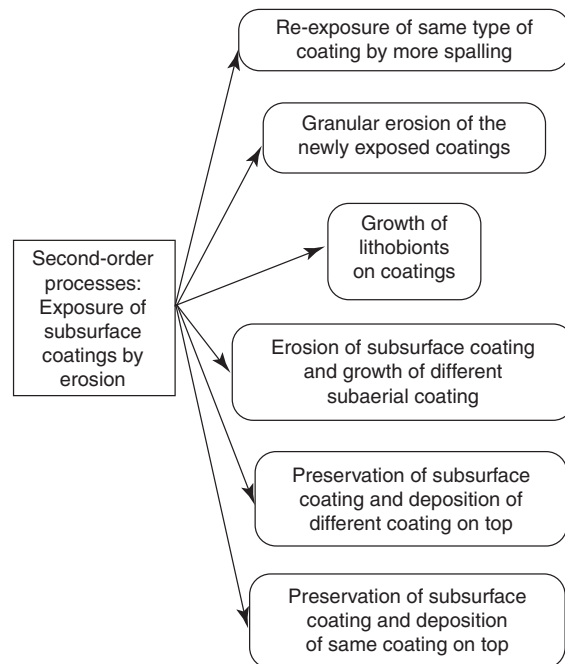
Second-order processes: Exposure of subsurface coatings by erosion

Re-exposure of same type of coating by more spalling

Granular erosion of the newly exposed coatings

Growth of lithobionts on coatings

Erosion of subsurface coating and growth of different subaerial coating

Preservation of subsurface coating and deposition of different coating on top

Preservation of subsurface coating and deposition of same coating on top

Figure 3 Possible pathways of subsurface-formed coatings upon exposure in the subaerial environment. Further erosion may lead to exposure of other subsurface rock coatings. The joint face might erode by millimeter-scale flaking, removing the surficial coating. Lichens and other lithobionts might form on top of inorganic rock coatings, potentially leading to dissolution from the secretion of organic acids. A former subsurface coating might be dissolved by carbonic acid in rainwater, freeing up the surface for the growth of a subaerial coating more in equilibrium with the surficial environment. A new rock coating might form or, in some cases, the same rock coating will continue to accrete.

heavy metals (Douglas, 1987; Dorn and Dragovich, 1990; Robinson and Williams, 1992; Mottershead and Pye, 1994; Villa et al., 1995). These coatings formed because transport pathways brought the necessary constituents, and because barriers to further transport fixed these constituents on fracture sides, in regolith, or on rock fragments in soils.
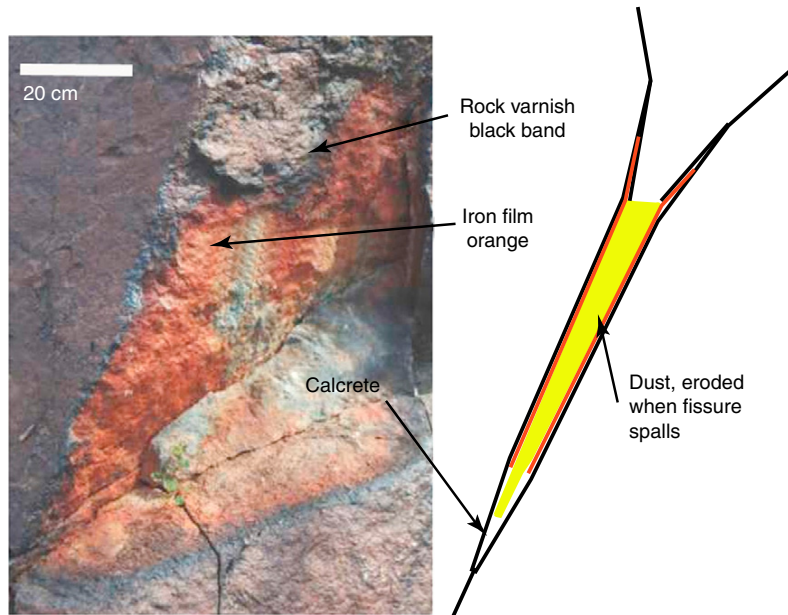
Figure 4 Rock-coating sequence occurring on the walls of desert rock fractures. This fissure once hosted dust and weathered rock fragments. Carbonate leached from desert dust reprecipitates as laminar calcrete skins deeper in the rock fracture. An orange, iron-rich coating forms where dust is in constant contact with fissure sides. A centimeter-scale band of black rock varnish rims the outer edge of the fracture where the dust has been washed away.
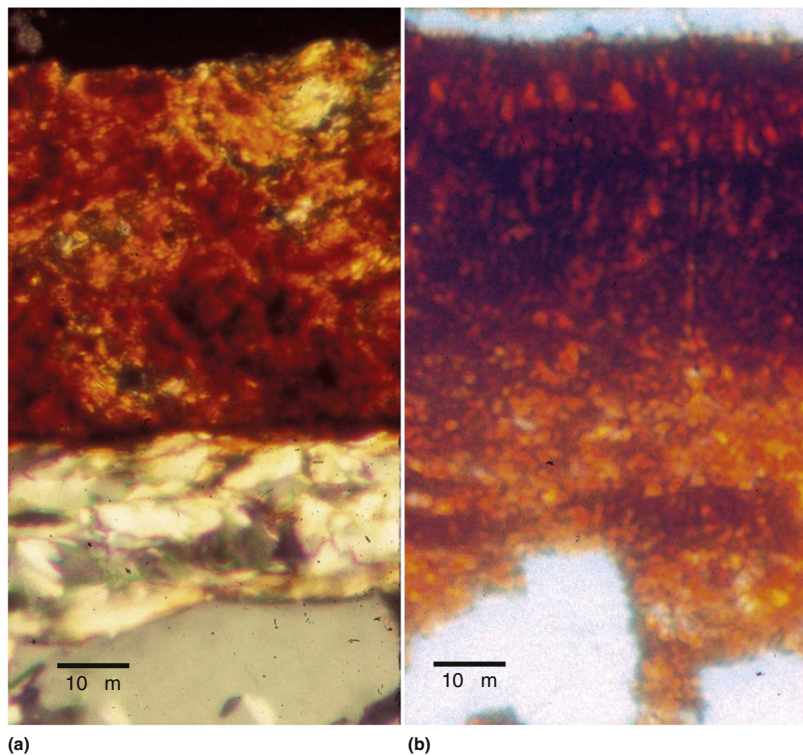

Figure 5 Optical thin sections show how changes in landscape geochemistry alter rock coatings originally formed in desert fissures (cf. **Figure 4**). (a) White calcrete first formed a coat over the gray quartz. Then, when the fissure opened wide enough to accumulate dust and weathered fragments, this dust fostered the formation of the orange film on top of the calcrete. (b) First, an iron film formed in the crevice. Then, the rock fracture opened wide enough to wash the accumulated dust away from the rock surface. This allowed the formation of a black rock varnish.
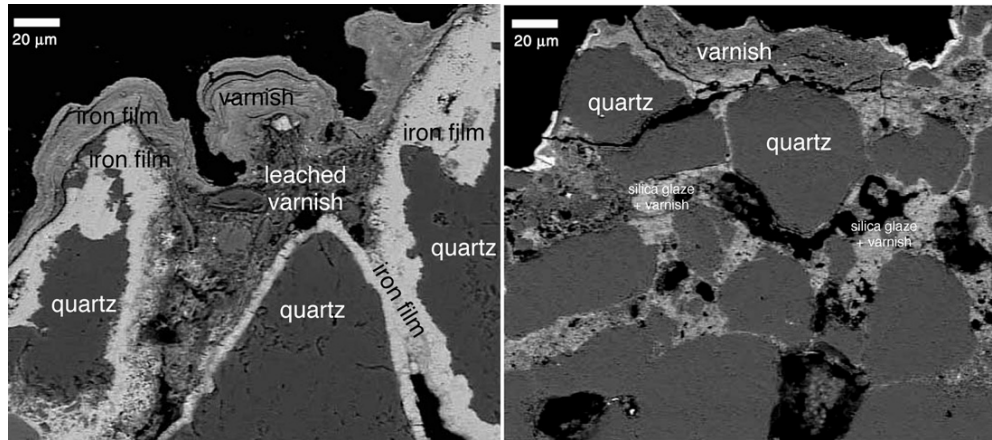
Figure 6 Spalling of sandstone in Whoopup Canyon in Wyoming exposes the silica glaze that coats fractures. The change from subsurface fracture to subaerial surface enables rock varnish to accrete on top of the silica glaze. The left BSE image shows case hardening by Fe (and some Mn) leached from the varnish. The right BSE image presents Mn and Fe combining with silica glaze in pore spaces, forming a different type of case hardening.
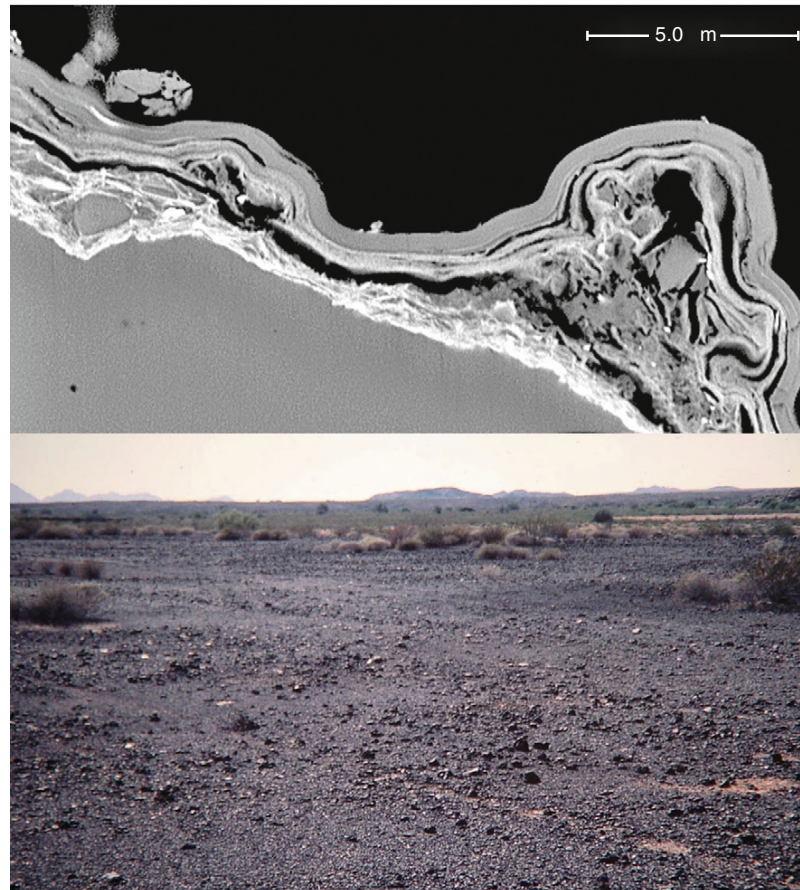

Figure 7 Cobbles in desert pavements can develop a very shiny appearance. Some of this sheen, seen in the lower image from the Sierra Pinacate, Mexico, comes from silica glaze. In the upper BSE image, an iron film (brighter material) first formed on top of quartz on the sidewalls of a fissure. Then, dust accumulated in the fissure (fragments of gray material), and the dust was trapped by formation of more iron film. Then, the rock spalled and this former fissure was embedded in a desert pavement. A micron-thick layer of silica glaze then formed over the prior rock coatings at the ground-line band of the desert pavement cobble. This silica glaze allows some of the color of the underlying iron film to show through a very shiny appearance.

Figure 8 Carbonate crusts form on the underside of large boulders in Bk horizons in desert and semi-arid soils. Construction of a prehistoric rock cairn in the Panamint Valley, California (upper image) and 2010 debris flow in metropolitan Phoenix, Arizona (lower image), both expose pedogenically formed carbonate crusts (arrows).

The landscape geochemistry setting of a rock-coating changes when mass wasting exposes a former fracture coating, when a gully exposes regolith coatings, or when scouring brings a soil clast to the surface. Subsurface coatings brought into the subaerial environment through rock or soil erosion are extremely common. A critique of many rock coatings articles is that they do not even consider a subsurface origin for the coating under study. The unstated assumption of much research is that just because a coating occurs exposed to the atmosphere, it originated in that location.

Upon exposure in the subaerial environment, what were once subsurface coatings can experience several possible futures, diagrammed in **Figure 3**. Consider, for example, rock coatings that are ubiquitous in fractures occurring in warm deserts (**Figure 4**). A laminar calcrete skin precipitates where the fissures are most narrow; as the fissures open up, orange iron films accrete; a centimeter-wide band of black rock varnish grows where the fissures are close enough to the surface for precipitation to seep in and wash dust from fissure sides.

This colorful sequence of rock coatings found on the sides of rock fissures in warm and dusty deserts (**Figure 4**) is modified as the landscape geochemical environment changes. As the fissure gradually opens wider, dust is washed from the walls of the fissure by precipitation, and this change allows the formation of manganese-rich rock varnish (**Figure 5(b)**). With spalling, carbonic acid dissolves the laminar calcrete skins that are exposed, except where the iron film has already formed a protective covering (**Figure 5(a)**). Spalling also promotes the formation of black manganese rock varnish over the orange surface, because the removal of the alkaline dust no longer inhibits microbial enhancement and fixation of manganese.

Joints or fractures in rocks in semi-arid environments commonly accumulate silica glaze that helps start the process
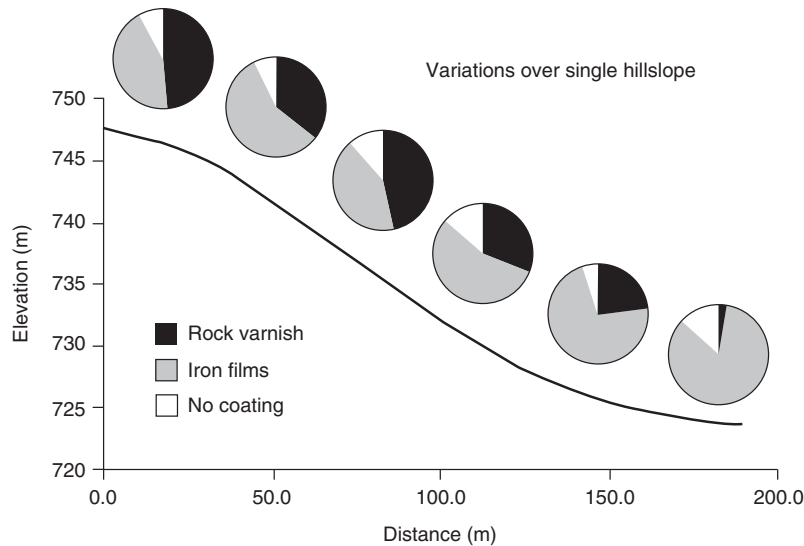

Figure 9 A rock coating catena (Palmer, 2002) exemplifying how three different types of rock coatings change down a basalt hillslope in the Mojave Desert. The hillcrest has less soil erosion, and hence rock varnish dominates. More and more iron films occur further down the slope, reflecting greater soil erosion exposing the iron films that originally formed in the subsurface.

of case-hardening joint faces (Dorn, 1998). With erosion exposing joint faces to the subaerial environment, changes typically ensue. **Figure 6** documents two types of postexposure changes seen in the semi-arid western USA. Both changes involve the accumulation of rock varnish, followed by leaching of manganese and iron dissolved from the varnish – which then infiltrates into the underlying pores. Sometimes, the iron (with some manganese) infills pore spaces (left image in **Figure 6**). In other cases, the manganese and iron combine with the silica glaze in the pore spaces and further contribute to case hardening the rock surface (right image in **Figure 6**).

Another example of the influence of erosion altering the landscape geochemistry of subsurface-formed rock coatings comes from the spalling of a cobble in a Sonoran Desert pavement (**Figure 7**). An iron film originally formed inside a rock fissure in a desert pavement cobble. Dust particles then adhered to the iron film, and iron film helped cement dust to the fissure side walls. Then, the rock split open, changing the landscape geochemical setting from a fissure to exposure at the soil line in a desert pavement. Desert pavement cobbles often develop a very shiny line at the soil line called a ground-line band (Engel and Sharp, 1958; Dorn and Oberlander, 1982). Ground-line bands are shiny, in part, because they develop coatings of silica glaze. **Figure 7** exemplifies that even a micron-thick layer of silica glaze can impart this sheen.

Erosional processes in deserts, both anthropogenic and natural, can expose carbonate crusts that become temporary subaerial coatings (**Figure 8**). Originally formed in the Bk horizon of soils, the carbonate is slowly dissolved through interaction with carbonic acid in precipitation. A landscape geochemistry interpretation is that the geochemical barrier present in the soil no longer exists in the subaerial environment. Changes in the position of pedogenic carbonate crusts have been used to analyze prehistoric geoglyphs and other earthen features (Cerveny et al., 2006).

Figure 10 Examples of lithobionts in different stages of covering subaerial rock surfaces. Upper left: hillslope of welded tuff in central Arizona where light green lichens cover rock surfaces that have remained stable for a few hundred years. Lower left: lichens coating joint faces at a spring near Yunta, South Australia. Upper right: dark-colored fungi colonize the surface of a former joint face, while lichens grow inside of engravings, Kaho'olawe Island, Hawaii. Lower right: Whoopup Canyon, Wyoming, where lichens completely coat surfaces where the dark-colored heavy-metal case-hardened joint face has spalled away.

Desert cobbles and small boulders in undisturbed settings host black manganese-rich rock varnish in a subaerial position, with an orange iron film forming where the clast remains in contact with the underlying alkaline soil (Cerveny et al., 2006). Rock coatings can offer a visually distinctive clue that modern soil erosion has been active, because seeing an abundance of orange iron films mean that clasts with the black rock varnish have been eroded. A study of variability in rock coatings along a single hillslope (Palmer, 2002) found greater amounts of soil erosion in the steepest portion and at the bottom of the disturbed hillslope in the Mojave Desert, resulting in the exposure of orange iron films at the surface (**Figure 9**). Eventually, if erosion ceases or slows tremendously, black rock varnish will reform. However, **Figure 9** illustrates that the second order of control, erosion, plays a key role in determining the type of rock coating that is seen in disturbed settings.

4.5.2.3 Third-Order Control: Competition from Lithobionts

Lithobiontic coatings are organisms that live on the surface (epiliths), bore tubes into rocks (euendoliths), occupy fissures in rocks (chasmoendoliths), or live within the pore spaces of weathering rinds (cyptoendoliths) (Golubic et al., 1981). Lithobiontic coatings thinner than a millimeter are classified as biofilms; those between 1 and 5 mm are biorinds; and
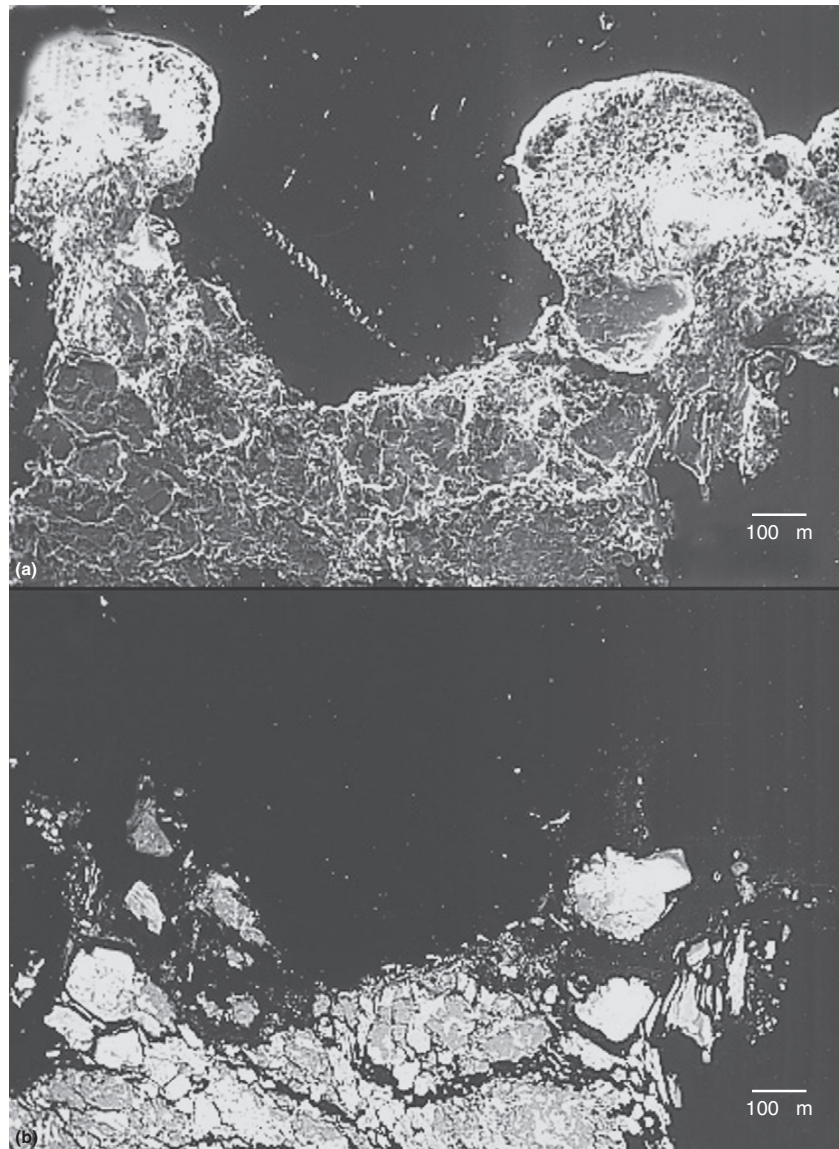

Figure 11 Granodiorite inselberg surfaces at Garden Butte, Papago Park, central Arizona, are dominated by lichens rather than rock varnish. Images (a) and (b) compare secondary electrons (a) to back-scattered (BSE) electrons (b). Note how the lichens seen with secondary electrons (a) penetrate into the rock along mineral boundaries and appear to enhance the spacings between minerals, either mechanically or through chemical weathering.

coatings greater than 5 mm are called biocrusts (Viles, 1995; Gorbushina, 2007).

Lichens, fungi, and algae lithobiontic coatings grow much faster than most inorganic rock coatings such as rock varnish, iron films, or silica glaze (Friedmann and Galun, 1974; Rundel, 1978; Golubic et al., 1981; Dragovich, 1987; Viles, 1995; Souza-Egipsy et al., 2004; Bhatnagar and Bhatnagar, 2005; Loso and Doak, 2006). As a result, these subaerial organisms commonly dominate rock faces (**Figure 10**). The third order of control, thus, involves conditions that control the growth of fast-growing lithobionts, where biofilm communities can grow in decades to hundreds of years (Viles, 2001).

One way that lithobionts take possession of a rock surface is through enhancing the weathering and erosion of rock material (Paradise, 1997; Lee and Parsons, 1999). Lichens grow not only on the surface, but also in pore spaces between mineral grains (**Figure 11**). Increased spacing between mineral grains destabilizes the rock surface and spalling takes place. Part of the process involves enhanced dissolution of minerals under lichens (Aghamiri and Schwartzman, 2002; Gordon

Figure 12 Lithobionts commonly secrete acids that dissolve inorganic rock coatings. The left image shows basalt talus in the Mojave Desert, California with inset photo of a petroglyph that was sampled for electron microscopy. The right image is a secondary electron microscope image from this inset showing a euendolith (tube boring) microcolonial fungi that is dissolving rock varnish.
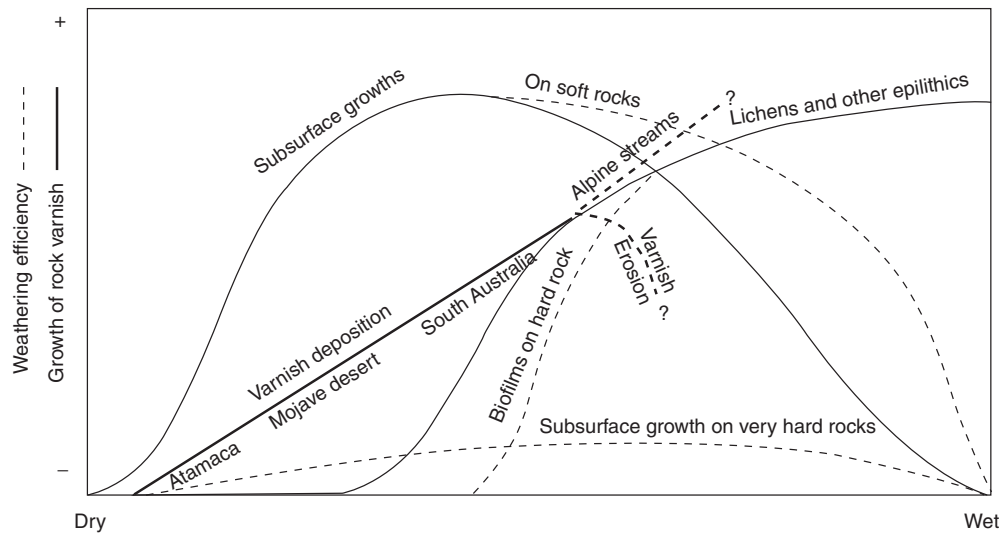

Figure 13 A landscape geochemical conceptualization of how lithobionts and rock varnish interact together. Moisture plays a vital role in the growth of rock varnish and in the weathering efficiency of lithobionts. Secondary factors presented in this model are competition from lithobionts for rock varnish and rock hardness for lithobionts. Adapted from Viles (1995) and Dorn and Oberlander (1982).
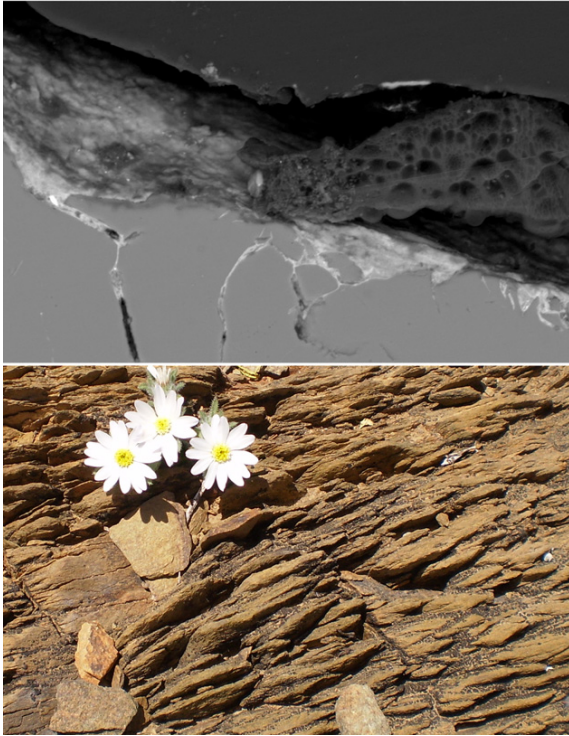
Figure 14 Varnish and biofilms of fungi and lichens grow on schist (lower image, where flower width is 2 cm). At the present time, biofilms appear to be dissolving varnish, as illustrated in the BSE image (image width is ∼100 μm; the epoxy has separated from the fungi and dissolved varnish). The dissolving varnish is then reprecipitating inside fractures, promoting case hardening with iron and manganese heavy metals. This example corresponds with the location of 'varnish erosion' in **Figure 13**, where biofilms are growing on hard rocks.

and Dorn, 2005a). Lichens are then able to recolonize these spalled surfaces much faster than inorganic coatings such as rock varnish or iron films. Another way that lithobionts replace other rock coatings is by biochemically dissolving (Dragovich, 1987) the preexisting coating (**Figure 12**).

An example of the third order of control on rock coatings compares the behavior of lithobionts and another rock coating to the external forcing of moisture. Viles (1995: 32) diagrammed lithobiont weathering as a function of moisture and hardness of the host rock. Dorn and Oberlander (1982) argued that the growth of rock varnish is influenced by moisture and competition from lithobionts. These two conceptualizations are combined in **Figure 13**, linked through a common focus on moisture. Lichens are most common in moist settings, whereas much drier environments foster endoliths. Rock varnish survives best and grows the slowest in drier environments, but as moisture increases lithobionts biochemically dissolve more rapidly forming varnish (e.g., **Figure 12**).

Moisture conditions as diagrammed in **Figure 13**, however, are not static. A site moves to the right and left on the diagram with microclimatic oscillations. A slight shift to wetter conditions can foster the colonization of lithobionts and result in varnish erosion. Considered from the perspective of **Figure 13**, a site near the peak of varnish growth can shift into varnish erosion where acid-producing fungi have colonized rock varnish. The effect of such a change is seen in **Figure 14**. Although lithobionts do chemically dissolve and erode preexisting rock coatings and prevent the formation of many inorganic accretions, it is important to note that lithobionts can also stabilize rock surfaces by holding weathered fragments in place (Gehrmann et al., 1988; Kurtz and Netoff, 2001; Viles and Goudie, 2004). Lithobionts can also generate protective
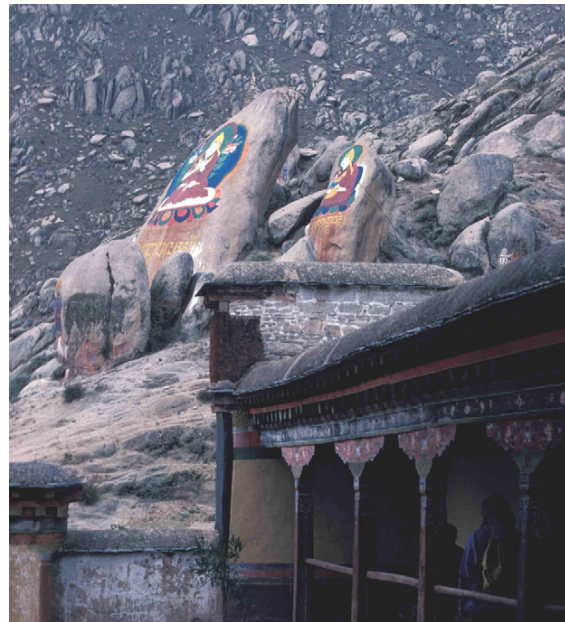

Figure 15 Anthropogenic paint balls transported and applied to rock surfaces at South Mountain Park, Arizona.

Figure 16 Anthropogenic pigments applied next to the DeBrung Monastery, Tibet.

coatings of silica glaze (Lee and Parsons, 1999) and oxalate crusts (Souza-Egipsy et al., 2004).

4.5.2.4 Fourth-Order Control: Transport Pathways

Rock coatings require a sufficient abundance of constituent elements and those elements are transported to accretion sites.

Sometimes, the constituents are fairly ubiquitous – such as silica, clay minerals, and iron. For other rock coatings, the concentrations transported to a coating site are quite low and enhancement is required – such as with the manganese in rock varnish or iron in heavy metal skins. In other cases, although the overall abundance of material such as oxalate minerals might be low on a rock face, locally strong geochemical
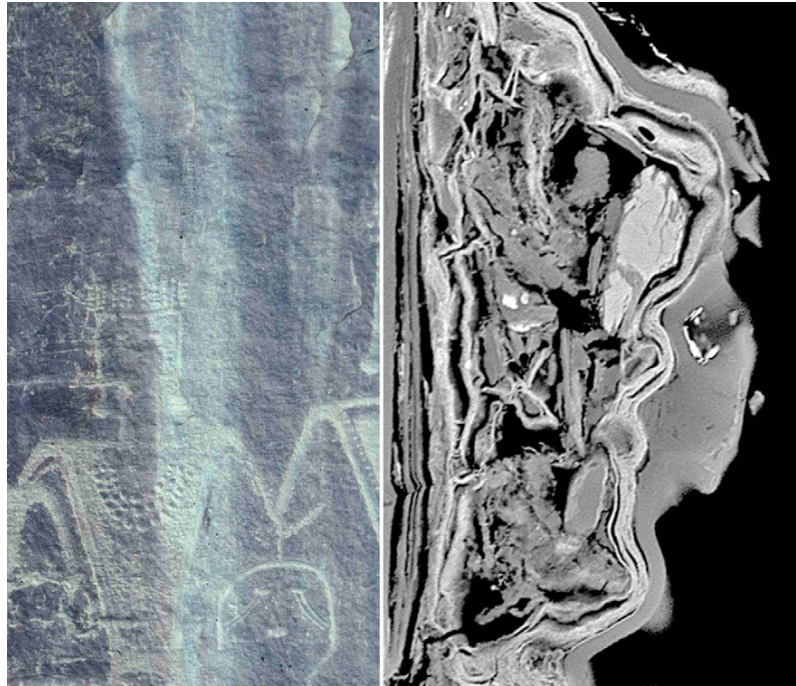

Figure 17 Streak of silica glaze formed over a petroglyph panel at McKonkey Ranch, Utah. The white streak was sampled above the engraving on a natural joint face. The BSE image shows three types of rock coatings, where the host rock is on the left side of the electron micrograph. On top of gray quartz is a thin layer of rock varnish (bright material) formed. Then, on top of that varnish is dust film loosely cemented with iron and manganese. On top of this rests the water-streak silica glaze. The source of the water-mobilized and transported silica appears to be a rock spall that redirected overland flow. The photograph is about 2 m in length, and the BSE image width is 10 μm.
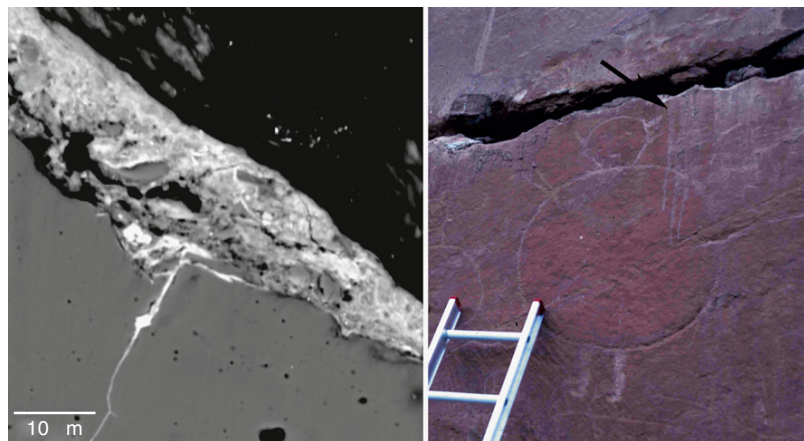

Figure 18 A sandstone face at Medicine Lodge Creek, Wyoming, has a fracture occupied by birds. Droppings are mobilized and drip down the rock art panel. The back-scatter electron microscope image shows phosphate mixing with detrital rock fragments, perhaps transported by water flow.

gradients might exist near a source of calcium oxalate such as lichens. The fourth general control on the occurrence of rock coatings is the requirement that the constituents of a coating have a pathway of transport to a rock-surface site.

Some transport pathways are obvious. Pigments are applied to rock surfaces (Li et al., 2001; Hortola, 2005; Simionescu et al., 2009) through anthropogenic transport (e.g., **Figures 15** and **16**). Streaks of oxalate crust flowing down from oxalate-producing lichens at Stone Mountain (e.g., **Figure 1**) reveal a visual trace of a transport pathway. A white streak formed over a Utah petroglyph panel corresponds with a thin coating of silica glaze (**Figure 17**). Transport pathways can be dozens of kilometers for the dust that composes dust films and rock varnish, or very short in the case of iron and manganese mobilized from rock vanish and transported into pores to case harden the underlying rock (**Figures 6** and **14**).

Transport of raw mineral ingredients involves two general preconditions. The constituents must be present and they must migrate to the rock face. Bird droppings (Arocena and Hall, 2003) or microorganisms (Konhauser et al., 1994), for example, generate the requisite material for a phosphate skin. Then, phosphates are mobilized and reprecipitated (**Figure 18**). In another example, the formation of silica glazes on granite-building stones in Rio de Janeiro first requires dust deposition, then silica is mobilized from the dust to reprecipitate as silica glaze (Smith et al., 2007). Deposited dust, in general, appears to be a key agent in the formation of pollution-related coatings in urban settings where the first general step is dust deposition, followed by complex interactions that result in the net migration of elements from the dust into a rock coating (McAlister et al., 2006).

Salt crust formation exemplifies how multiple transport steps can involve very different processes (Oguchi et al., 2002).

The salt crust seen on weathered surfaces such as Mushroom Rock in Death Valley, for example, was first transported by wind from the salt playa to the soil adjacent to the talus boulder. Then, salt was dissolved in precipitation and moved by capillary action up the side of the boulder to precipitate as salt crusts (**Figure 19**).

Multiple transport pathways are key to the formation of black crusts occurring on marble tombstones and limestone buildings in humid regions undergoing anthropogenic pollution. Sulfate and oxalate crusts both occur on such surfaces as shown in **Figure 19**. Sulfur from carbon fuel combustion interacts with the host carbonate to produce gypsum sulfate crusts (Potgieter-Vermaak et al., 2004). Then, this

Figure 20 Sulfate crust on marble tombstone in the Old Fellowship Cemetery in Atlanta, Georgia, USA.

Figure 19 Barium sulfate, sodium chloride, calcium sulfate, and strontium sulfate weathers Mushroom Rock in Death Valley, California. The BSE micrographs on the right show a barium sulfate crust as the brighter material both fragmenting the basalt and covering mineral surfaces. The bright white in these images are barite and darker crystals are weathered basalt silicate minerals.
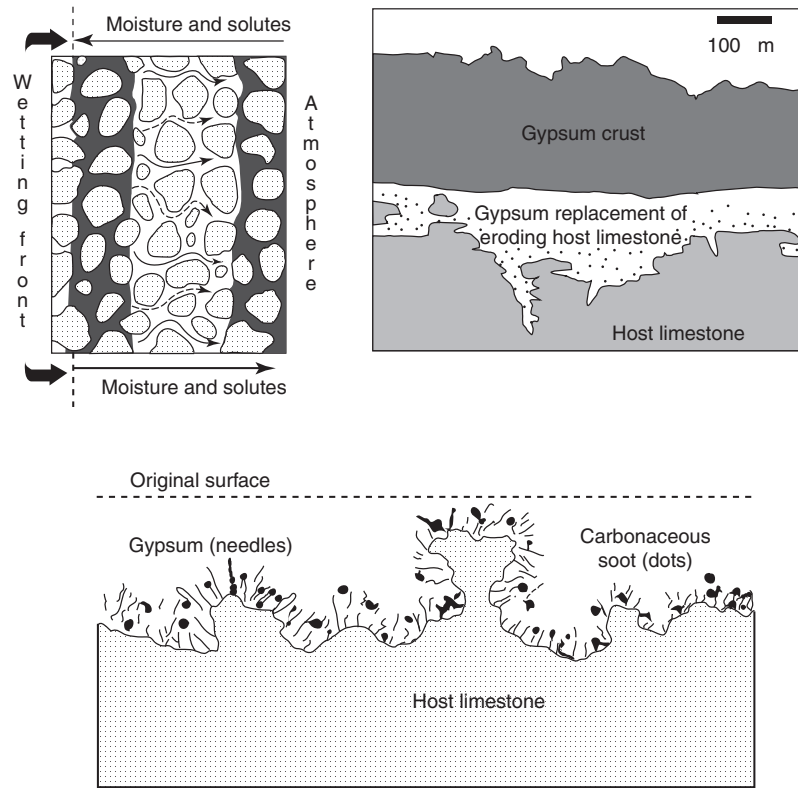
Figure 21 Pollution-generated gypsum crusts can replace the host limestone through flow of sulfate-rich solutions migrating inward from the surface or outward from the rock, and they can exist as needles over a dissolving surface.
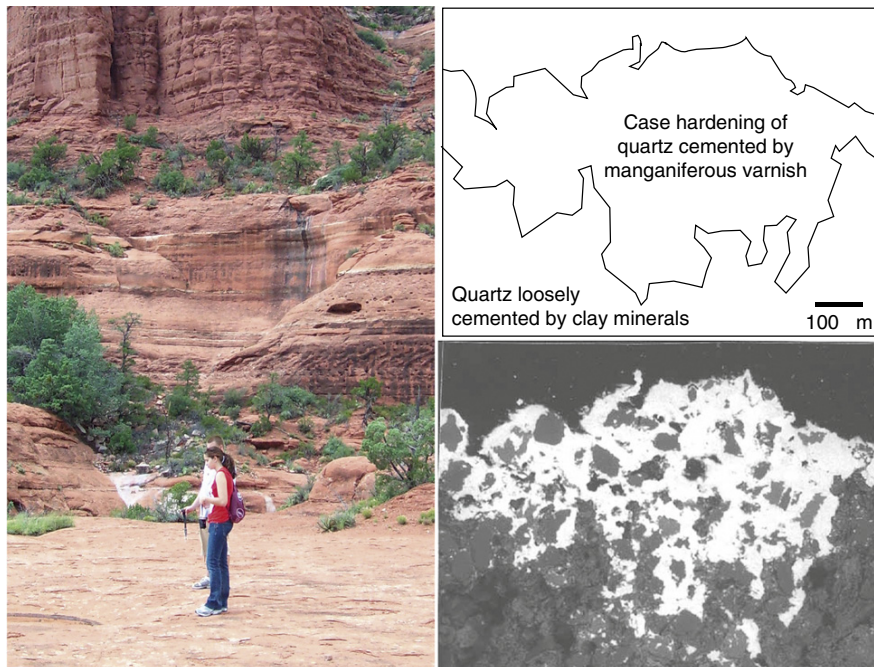

Figure 22 Waterflow streaks can sometimes be fungi, lichens, heavy metal skins, and sometimes rock varnish. In this case, streaks are heavy metal skins that impregnate the sandstone of Sedona, at Schnebly Hill Road, Arizona.

gypsum is then transported by capillary water microns to millimeters on the rock surface to contribute to the development of biofilms of cyanobacteria (Ortega-Calvo et al., 1994) (**Figure 20**).

The deposition of sulfate crust occurs in tandem with dissolution of the limestone, but the style of the accretion can vary (**Figure 21**). In some cases, a thicker crust of several hundred micrometers forms as the gypsum replaces the limestone (Vergès-Belmin et al., 1993) through a process by which sulfate-rich solutions migrate outward from the rock in the early stages of surface desiccation (Smith, 1994). In other cases, the sulfate crust manifests itself as a mix of gypsum needles and soot over karren (Camuffo et al., 1983).

Sometimes, the lack of a transport pathway for a key ingredient can determine what type of rock coating accretes. This is especially true for rock varnish. Black streaks across sandstone surfaces of the Colorado Plateau are almost always attributed to rock varnish, but this is generally incorrect. These water-flow deposits commonly lack clay minerals. As clays are vital to the formation of rock varnish (Potter and Rossman, 1977; Krinsley et al., 1995; Krinsley, 1998; Dorn, 2007), the manganese and iron deposited without the clays results in a heavy metal skin (**Figure 22**). Another example comes from Hawaii. Silica glaze forms on the rainshadow side of the island of Hawaii (**Figure 1**), in part because of the paucity of clay mineral transport to basalt flow surfaces.

4.5.2.5   Fifth-Order Control: Barriers to Transport

Physical, chemical, and biological barriers halting the transport of elements results in the accretion of rock coatings. This fifth order of control is not ranked higher, because the other controls can prevent the occurrence of a coating, even if a barrier to transport exists. For example, even though dust is ubiquitous in warm deserts (Goudie, 1978) and coatings occur where electrostatic or physical forces hold dust particles together (Jordan, 1954; Bishop et al., 2002; Ganor et al., 2009), the lack of bare rock surfaces (first order), the exposure of a subsurface coating (second order), the growth of lithobionts (third order), or the transport of other materials by water or wind (fourth order) can all interfere with the occurrence of a dust coating (**Figure 23**).

Physical and chemical barriers commonly work in tandem to generate inorganic rock coatings, as it the case for silica glaze. Dorn (1998) proposed that silica glaze formation starts
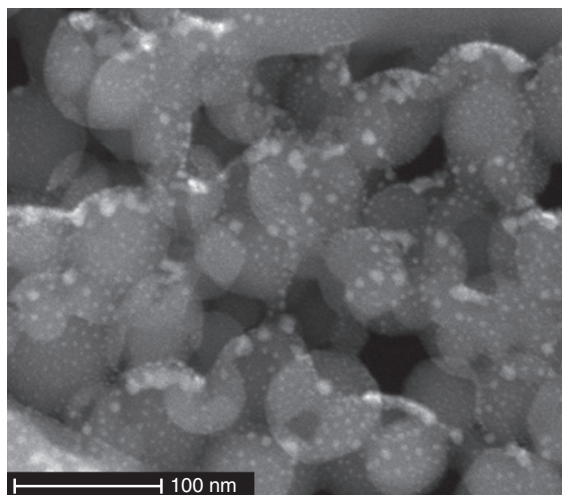

Figure 24   HRTEM image of silica glaze spheroids in a sample from the Ashikule Basin, Tibetan Plateau. The bright dots are artifacts.
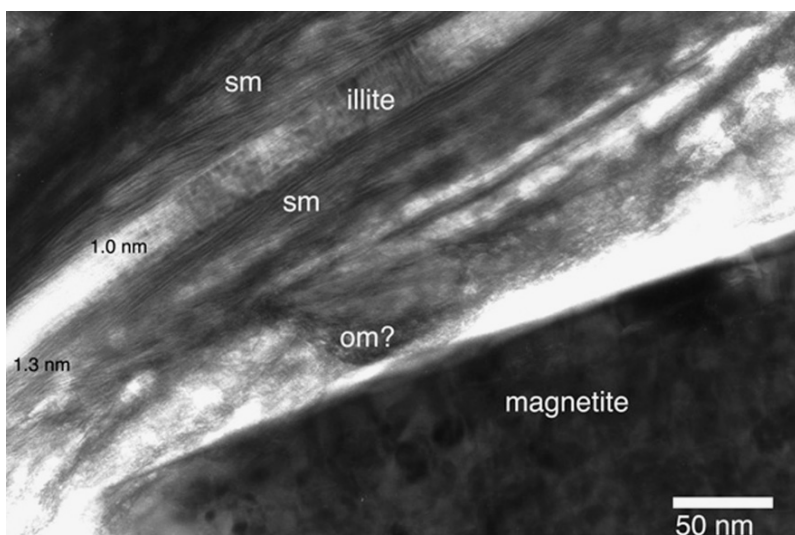

Figure 23   High-resolution transmission electron microscope image of a dust film that has been preserved inside a partially opened rock crevice. Its position protects the coating from being washed away by incident precipitation. The sample was collected from a granodiorite surface, South Mountain, central Arizona. The nature of the clays in this dust film shows an orientation parallel to magnetite surface. A mixture of illite and smectite (sm) occurs. The illite has a spacing of 1.0 nm. The darker portions of the smectite are too thick for spacing measurement, but the thinner portions show spacings of 1.3 nm. There may also be organic matter (OM?) as a part of the dust film.

Physical barrier: van der Walls
force promotes dust
accumulation, providing
raw ingredients of clays

5 m
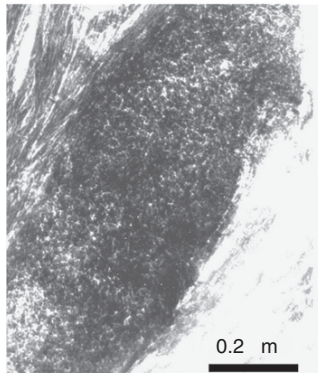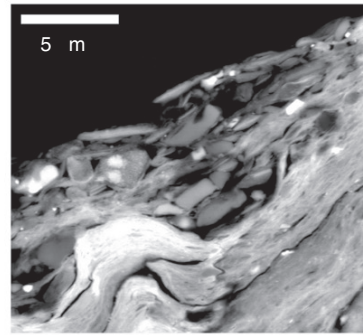
Biological barrier: Mn and Fe fixation in bacteria sheaths

1 m

Si
Al   Varnish
              K Ca
                      Mn Fe
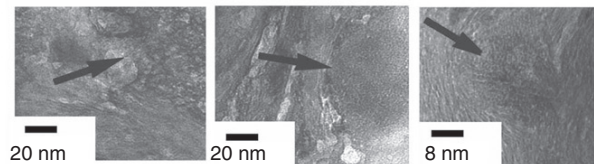
                          Mn
Si
Al   K Ca
           Ti   Fe
                    Spot on bacteria

0.2 m
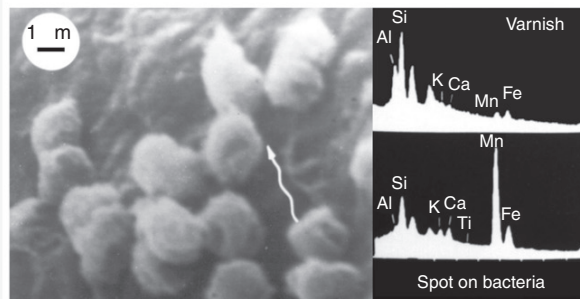
Dissolution from
cell wall (granular
fragments)

20 nm   20 nm   8 nm

and

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

10 nm   10 nm

20 nm   20 nm
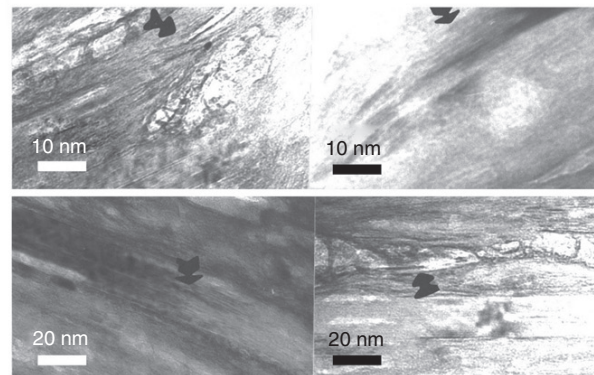
Figure 25 Different barriers to transport are involved in the accretion of rock varnish. The top BSE image illustrates dust that has accumulated on top of rock varnish from the Ashikule Basin, Tibet. HRTEM and secondary electron microscopy images of cocci bacterial forms from Antarctic varnish, and energy-dispersive electron microscopy shows that the bacteria are concentrating manganese and iron in their sheaths. HRTEM of samples from Peru, Death Valley, and Antarctica illustrate instability and then barriers at the nanometer scale where oxides are dissolved from bacterial sheath fragments, transported a few nanometers, and then fixed into mixed-layered illite–montmorillonite clays.

with soluble Al–Si complexes $[Al(OSi(OH)^3)^{2+}]$ that are common at the water–rock interface (Browne and Driscoll, 1992). Dew or frost deposition supplies sufficient moisture to mobilize Al–Si complexes, where the transition between complete and partial wetting on silica surfaces is about 20–70 nm (Zorin et al., 1992; Churaev, 2003). Crossing this physical transition would result in the deposition of silica with particles in the size range of 20–70 nm. High-resolution transmission electron microscopy (HRTEM) finds evidence of spheroids in this size range in silica glaze (**Figure 24**), an observation consistent with this model of silica glaze formation (Langworthy et al., 2010).

A sequence of physical, biological, and physiochemical barriers are needed for the formation of rock varnish (**Figure 25**). Varnishing begins with physical barriers of electrostatic or physical forces holding dust particles together on subaerial surfaces (Jordan, 1954; Bishop et al., 2002; Ganor et al., 2009). Then, the biological action of bacteria concentrate manganese and iron (Dorn and Oberlander, 1981; Hungate et al., 1987; Dorn, 2007; Northup et al., 2010). Some of the bacterial sheaths become microfossils (Dorn and Meek, 1995; Dorn, 1998; Krinsley, 1998) that then dissolve. Decay of the Mn–Fe casts mobilizes nanometer fragments. Physiochemical fixation takes place only a few nanometers away when the oxides are fixed
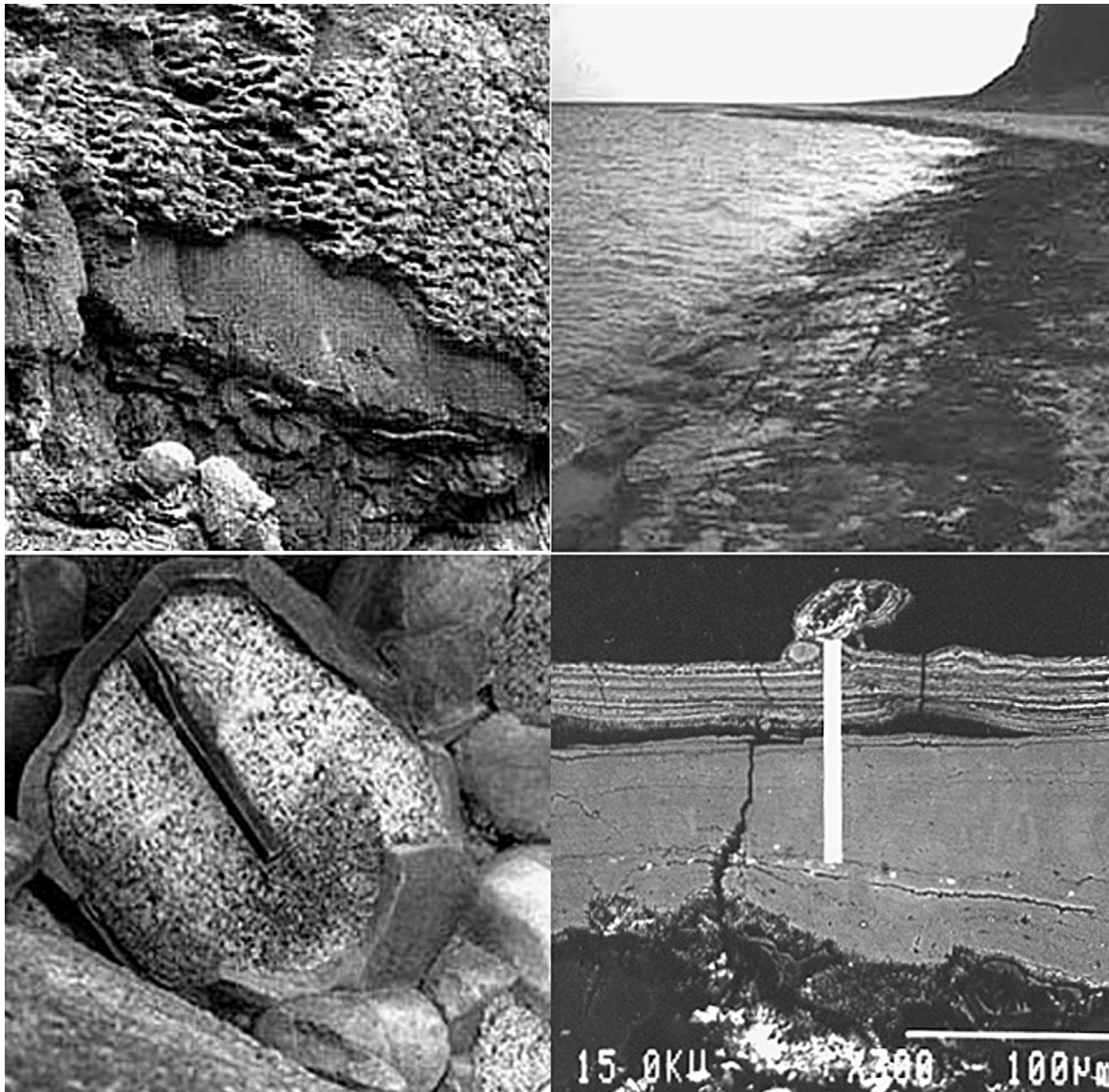
Figure 26 Carbonate crusts formation in different environments. The two left images show tufa formed in a lacustrine environment at Pyramid Lake, Nevada, generating centimeter-scale crusts over rock surfaces. The upper right image illustrates a biogenic carbonate crust of beachrock tens of centimeters thick along the northeastern shore of the Sinai Peninsular. The lower right BSE image shows carbonate crust formed as a result of sprinkler water evaporating on a tombstone in Phoenix, Arizona.

into mixed-layered clays (Potter, 1979). HRTEM imagery (e.g., **Figure 25**) shows Mn and Fe inserted into mixed-layered clays. Potter (1979: 174–175) hypothesized:

> "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…"

Rock varnish formation, then, appears to be the result of a sequence of barriers and nanometer-scale transport: first, physical barriers to the migration of first dust that supplies clay minerals; second, biological barriers that enhance manganese and iron; third, Mn and Fe are transported nanometers to adjacent clay minerals; and fourth, the physiochemical processes cement clay minerals to the rock and to prior varnish. This is the polygenetic model of rock varnish formation (Dorn, 1998).

Although carbonate crusts do not necessarily require a complex sequence, they can form from physical, chemical, or biological barriers to transport of carbonate (**Figure 26**). Tufas and other types of carbonate crusts are known to form from both biotic and chemical processes that create barriers to further transport (Pentecost, 1985; Pedley, 1990; Viles and Goudie, 1990; Benson, 1994; Arp et al., 1999; Carter et al., 2003; Yoshikawa et al., 2006). Marine carbonate cementing rock surfaces in coastal areas appear to be related to activity of algae and cyanobacteria (Krumbein, 1979; Kendall et al., 1994). The physical barrier of evaporation can also form carbonate crusts (Schlesinger, 1985).

Barriers to elemental migration can shift, resulting in very different types of rock coatings, even over scales of tens of nanometers (**Figure 27**). In a sample from the dusty and alkaline Ashikule Basin, Tibet, layered varnish rests on top of and underneath silica glaze composed of spheroids. In this HRTEM image, varnish rests distinctly on the underlying rock and silica glaze spheroids makes a distinct contact with the varnish both underneath and above the silica. Energy-dispersive X-ray spectroscopy analysis of the middle zone reveals that the spheroids are composed of Si and O, similar to **Figure 24**. The shifting geochemical barrier could have been something as subtle deposition of alkaline dust changing the pH from near-neutral conditions favoring rock varnish formation to higher pH conditions favoring silica glaze formation, and then back again to near-neutral pH values.

Geochemical barriers can shift over short or long time-scales, ranging from hours to thousands of years. Temporary rock coatings of ice can melt within a day (Hetu et al., 1994). Organic coatings on andesite volcanic blocks form during the final stages of the solidification of a lava flow, resulting in the coalification of plant material (Donoghue et al., 2009). Acid-fog generates coatings that mix silica glaze and jarosite, formed from evaporative processes (Shiffman et al., 2006). Iron films transform from ferrihydrite to goethite (Raiswell et al., 2009) under glaciers and ice sheets over periods of less than 100 years. Silica glazes can form within a few decades (Gordon and Dorn, 2005b) and can alter lava flow appearances dramatically within centuries to millennia (**Figure 1**). Rock varnishes
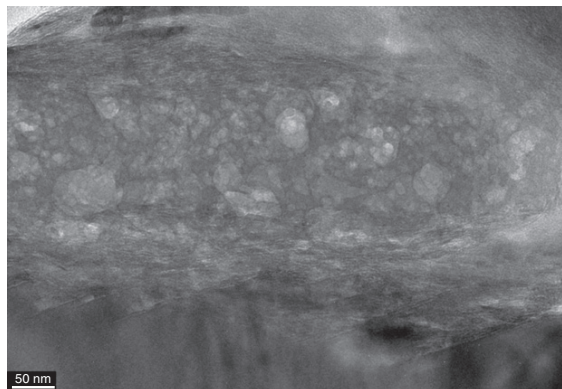

Figure 27 HRTEM image of silica glaze interdigitating with rock varnish. The dark material at the bottom of the image is the underlying rock. Layered rock varnish forms a 50-nm thick deposit on the underlying rock. The barrier to transport changed, resulting in silica glaze spheroids deposited in a layer about 200-nm thick. Then, layered rock varnish deposited on top of the silica spheroids.

accrete evidence of millennial-scale climatic change through shifting geochemical barriers (**Figure 28**); time periods with stronger manganese barriers record wet intervals (Liu and Broecker, 2000, 2007; Broecker and Liu, 2001).

The creation of one geochemical barrier can generate another barrier. Manganese and iron oxides enhanced in rock varnish (**Figure 28**) scavenge heavy metals (Jenne, 1968; Thiagarajan and Lee, 2004; Wayne et al., 2006). Modern aerosols are generally much higher in such heavy metals such as lead from the use of leaded gasoline (Ganor et al., 2009). The upper micron in rock varnish, thus is greatly enhanced in lead, because iron and manganese scavenges this pollutant and fixes it (**Figure 28**).

Rock coatings are rarely stable for more than a few thousand years. In a few cases, the layering pattern of varnish microlaminations reveals that stable rock surfaces can host coatings for a few hundred thousand years (Liu and Broecker, 2008b; Liu, 2010). Along the coast of southern Peru, meters of salt crust have coated bedrock of a marine isotope stage 5e marine terrace over the last 10^5 years (**Figure 29**), and sulfate crusts formed in Victoria Land, Antarctica may be as old as the last time a locus was glaciated (Giorgetti and Baroni, 2007). Burial can preserve rock coatings in Antarctica (Marchant et al., 1996). In one locale, geochemical barriers remained intact after burial, preserving rock varnishes for 10^7 years (**Figure 30**) (Dorn and Dickinson, 1989).

An issue that should not be neglected is the role of nucleation sites as important barriers for migration. This is the case for bacteria that concentrate manganese and iron in rock varnish (**Figure 25**) (Dorn and Oberlander, 1981; Hungate et al., 1987; Dorn, 2007; Northup et al., 2010). Nucleation sites can also be important in the formation of some sulfate crusts (**Figure 31**). Carbon particles are known to serve as sites of gypsum precipitation in urban polluted contexts (Del Monte and Sabbioni, 1984; Del Monte et al., 1984).

In summary, landscape geochemistry theory interprets the presence of rock coatings as reflecting physical, biological, or chemical barriers to the transport of elements. However, the presence of inorganic rock coatings can only occur where there is limited competition from lithobionts such as lichens that
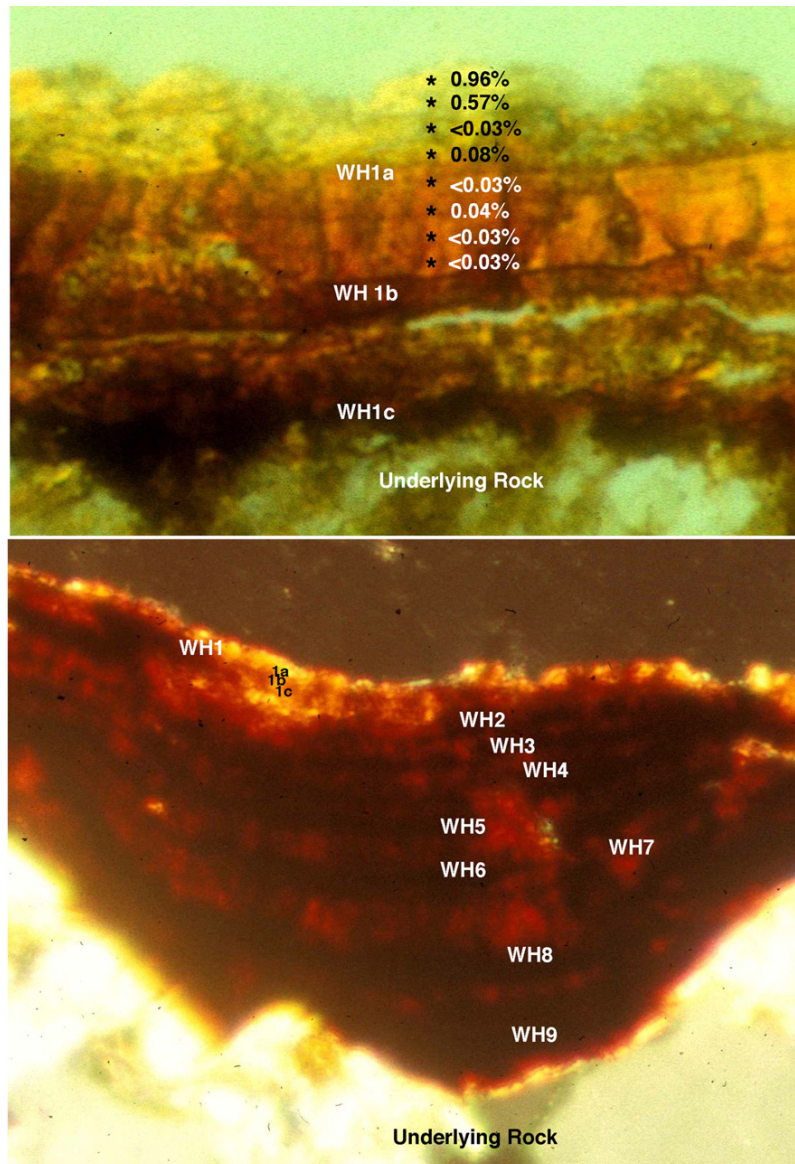
Figure 28 Microlaminations in rock varnish reflect shifting geochemical barriers. Wetter environments enhance barriers to Mn migration and result in the accretion of dark Mn-rich layers. These ultra-thin sections are of rock varnishes collected from the Ma Ha Tuak Range, Phoenix, Arizona. Wetter microenvironments increase rates of varnishing and can preserve relatively fine paleoclimatic information. The upper section (thickness ∼28 μm) shows all three wet phases of the Little Ice Age WH1 signal (Liu and Broecker, 2007): WH1a, WH1b, and WH1c. Also annotated on this section are wavelength-dispersive electron microprobe analyses of PbO; these analyses show the typical pattern of lead contamination of the uppermost microns in varnish from twentieth-century automobile pollution. The values are in PbO weight percent, and the approximate distance between the probe spots are 2 μm. Note how PbO drops down close to or below minimum detection limits underneath this twentieth-century varnish. The bottom image was collected from a drier microenvironment, and this drier setting slows the rate of varnishing to the point where only the major wet Holocene (WH) periods (Liu and Broecker, 2007) are recorded (thickness ∼40 μm).

can grow much faster. These barriers to transport can be widespread, leading to extensive coatings of rock varnish. These barriers can be linear, resulting in streaks of silica glaze or oxalate crusts. Barriers can also be discrete places, such as carbonate crusts accumulating on the undersides of desert boulders. The geographical expression of such barriers leads to the amazing variety of rock coatings occurring in terrestrial weathering environment.

4.5.3   Importance of Rock Coatings in Geomorphology

Rock coatings influence landforms in a variety of ways. At the most general level, the esthetic and dramatic bare rock landforms that motivate the general public, students, and professionals alike are colored by ubiquitous rock coatings. The appearance of favored icons of geomorphology, such as Uluru

Figure 29 Marine Terrace, southern Peru, where up to 4 m of sodium chloride salt crust covers bedrock.

being coated with iron films (Dorn and Dragovich, 1990) or the spectacular alluvial fans of Death Valley darkened by rock varnish (Dorn, 1988), cannot be separated from landforms. Personal satisfaction associated with field work is, thus, inseparably linked with scenic aspects imposed by rock coatings (e.g., **Figure 1**).

Rock coatings are also relevant to geomorphological studies, because they can help stabilize landform surfaces through case hardening. Case hardening commonly derives from the mobilization and reprecipitation of rock-coating materials inside pore spaces in the weathering rind (Conca and Rossman, 1982). Calcite is a common mineral that case-hardens surfaces (Mellor et al., 1997). Heavy metals also case harden by infilling of pore spaces in a weathering rind, for example, sandstone at Petra, Jordan (**Figure 1**) and Sedona, Arizona (**Figure 22**). **Figure 32** illustrates stabilization of delicate weathering features through reprecipitation of rock varnish or silica glaze. In addition to the migration of single types of coating material into the weathering rinds, different types of mobilized rock coatings are commonly mixed together inside the weathering rind (**Figure 6**).

The rock-coating material reprecipitated into weathering rinds does more than physically protect through case hardening. In general, chemical weathering rates decrease over time in large part because of the role of clay-coated mineral surfaces (Meunier et al., 2007). Some types of rock coatings, such as silica glaze, can slow the rate of chemical weathering (Gordon and Dorn, 2005b). In a study of basalt surfaces of known age in Hawaii, chemical dissolution of plagiocase under silica glaze was much lower than plagioclase not covered by silica glaze (**Table 2**).

Other types of rock coatings can, in contradistinction, accelerate the physical weathering of rocks. The calcrete crust and dust films that precipitate and accumulate inside rock fissures (**Figure 4**) wedge open those fractures (Coudé-Gaussen et al., 1984; Villa et al., 1995; Cerveny et al., 2006; Dorn et al., 2008). Analysis of 20 classic bedrock desert landforms in the Southwestern USA reveals minimum rates of rock spalling from dirt cracking to be between 0.3% and 1.5% per 1000 years. Thus, the precipitation of calcrete crusts and the expansion and contraction of dust films inside fissures can

complete resurface a desert landform within a timescale in the range of 66 000–400 000 years.

The study of rock coatings includes an extensive effort to use characteristics of these coatings to determine exposure age. In particular, rock varnish has seen decades of study in order to determine if different characteristics could be used to assess when varnish started to form. Knowing the approximate starting time for varnishing would, therefore, provide insight into the age of a glacial moraine, alluvial-fan deposit, stream terrace, landslide, or other feature. **Table 3** presents the various strategies used to estimate the start of varnishing.

Out of these different dating methods, the most advanced approach is the result of two decades of research by Tanzhuo Liu of Columbia University (Dorn, 2009). Scholarly research into rock coating initiated with the field and laboratory studies of rock varnish by Alexander von Humboldt (von Humboldt, 1812). Rock-coating studies over the past two centuries have typically focused on a handful of samples. By contrast, Dr. Liu has analyzed more than 10 000 microstratigraphic sequences of rock varnishes obtained from millimeter-scale rock depressions (e.g., **Figure 33**). His painstaking analysis of varnishes, based on the study of three orders of magnitude more samples than analyzed in a typical publication, has led to a revolution in our understanding of how climatic changes are recorded by varnish microlaminations (Liu and Broecker, 2007, 2008a, 2008b; Liu, 2010). The geomorphological implications of Dr. Liu's research are profound, offering desert geomorphologists a tool to study in tandem chronometry and the influence of climatic change (Dorn, 2009).

Rock coatings have significance in extraterrestrial contexts, such as the ubiquitous dust coatings on lunar surfaces (Gaier, 2005). Although it is possible that rock varnish might exist on Mars inside rock fractures (Krinsley et al., 2009) and perhaps in other settings (DiGregorio, 2010), most research on Mars rock coatings view accretionary coatings and weathering rinds as occurring together, perhaps in some type of mixture (McAdam et al., 2002; Haskin et al., 2005).

Dorn (1998) predicted that silica glazes should be found on Mars, and silica glazes in terrestrial volcanic settings have been investigated as potential analogs (Minitti et al., 2005, 2007; Chemtob et al., 2010). An analysis of chemical-weathering conditions on Mars (Kraft et al., 2004) suggests that four steps might be involved in the formation of silica glazes on Mars: (1) a fresh rock surface is exposed; (2) dust is deposited on rock surfaces; (3) thin films of liquid water form between dust grains along the dust-rock interface leading to (4) silica glaze deposition (Kraft et al., 2004, p. 2).

There is another possibility to explain the possible occurrence of silica glaze on Mars and Earth that has not yet been considered: water vapor. An unsolved problem on the geography of terrestrial rock coatings concerns why rock varnish is so common in subtropical deserts, but silica glaze is ubiquitous on basalt surfaces in rainshadows of Hawaiian volcanoes Haleakala, Mauna Loa, Mauna Kea, and Hualalai. One possible explanation is that the paucity of dust inhibits varnish formation that is dependent on clay minerals (**Figure 25**). However, the abundance of water vapor in this tropical context could not be ruled out. Thus, a 20-year laboratory experiment exposed basalt rock chips to 80% and 90% levels
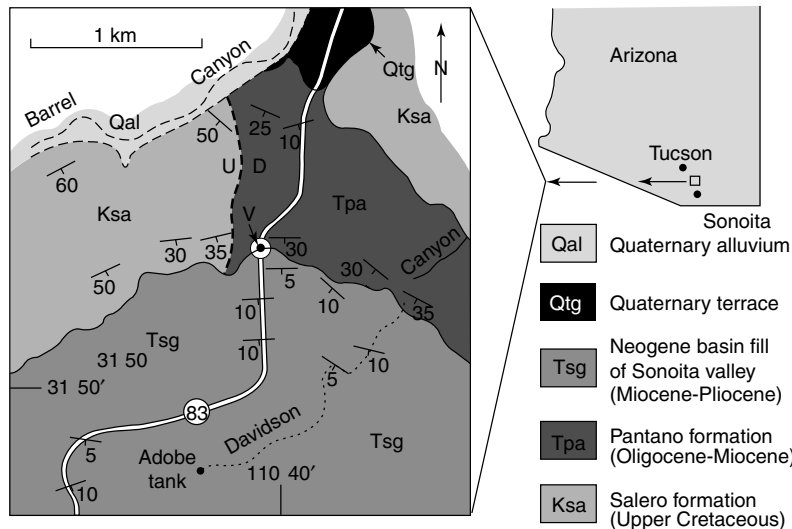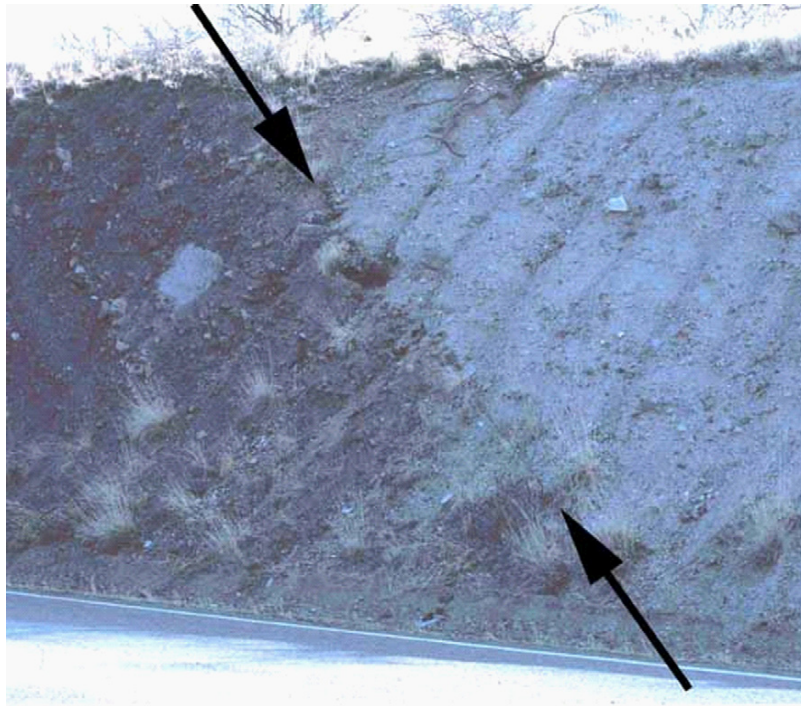
Figure 30   Rock varnish formed originally on colluvium on a Miocene hillslope of the Pantano Formation has been preserved at Davidson Canyon, southern Arizona. Arrows indicate the varnished colluvial horizon that is overlain depositionally by sandy gravels – part of Neogene basin fill. The composition of this varnish is similar to modern semi-arid varnishes (Dorn and Dickinson, 1989).

of relative humidity. No liquid water was involved. This experiment found that water vapor alone can generate silica glaze and may be an important factor in explaining why silica glaze is the dominant rock coating in humid warm drylands (Figure 34). Although water vapor concentrations on Mars are extremely small, the length of time for mineral–water vapor interactions on Mars make it possible that coatings amorphous silica occurring on Mars could be a product of billions of years of nanoscale water vapor interaction.

4.5.4   Conclusion

Fourteen general types of coatings cover rocks in the terrestrial weathering environment. Some coatings are always found separately, whereas others blend together creating an almost infinite variety. The only general theory that has been proposed to understand rock coatings is the paradigm of landscape geochemistry, originally developed by Soviet geographers. This framework focuses on the spatial aspects of
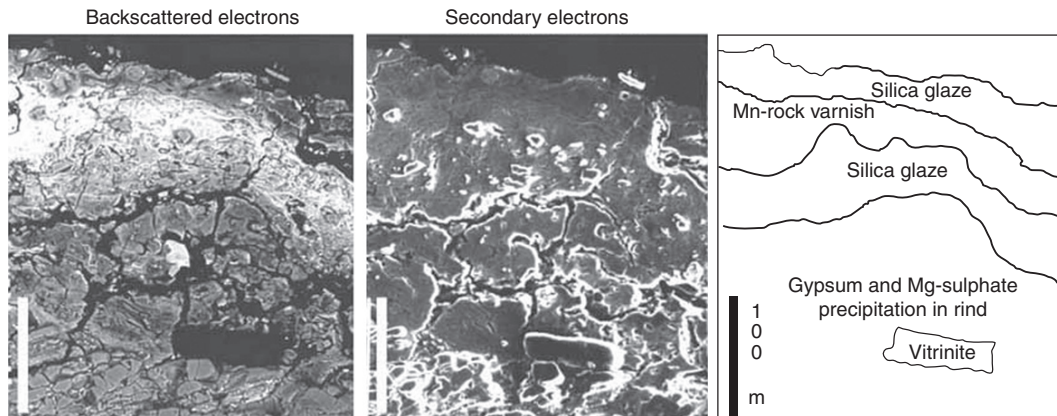
Figure 31 A particle of vitrinite serves as a nucleation site for sulfate crust precipitation at Karolta, South Australia. The vitrinite is seen topographically in secondary electrons, but its low atomic number makes it appear dark in back-scattered electrons. After the sulfate crust precipitated around the carbonaceous particle, the landscape geochemistry environment oscillated between favoring silica glaze and rock varnish formation.
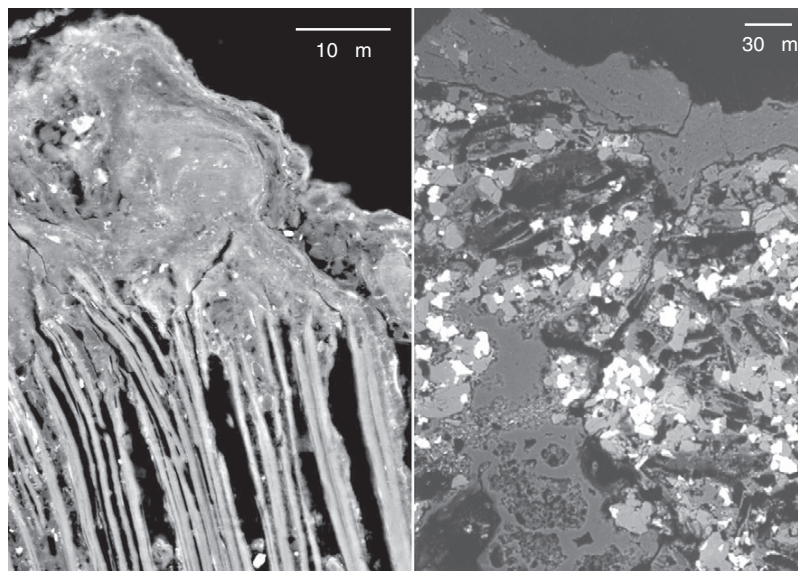

Figure 32 BSE imagery showing that case hardening occurs from the remobilization of rock coatings into pores in the underlying rock. Left: rock varnish has dissolved and reprecipitated in the underlying mica, as weathering has gradually opened the mineral (left), from the Ashikule Basin, Tibet. Right: silica glaze reprecipitated into pore spaces in the weathering rind of basalt, Kaho'olawe Island, Hawaii. In both cases, the weathered fragments of the host rock are held together by the reprecipitated rock coatings.

biogeochemistry and interprets rock coatings in terms of element abundance, element migration, geochemical flows, geochemical gradients, and geochemical barriers. These components of understanding rock coatings are reorganized here in a hierarchy of five orders of control to explain what types of rock coatings develop:

- *First order.* Bare rock faces must be exposed by erosional processes for rock coatings to be seen.
- *Second order.* Coatings originally formed in the subsurface can be exposed by erosional processes and are inherited from a different landscape geochemistry environment.
- *Third order.* Lithobionts such as lichens dominate rock surfaces in conditions where they grow much faster than inorganic rock coatings.
- *Fourth order.* The elements of rock coatings must be transported to bare rock surfaces.
- *Fifth order.* Barriers to the further transport of constituents result in the accumulation of rock coatings.

Rock coatings are important to the broader field of geomorphology in several different ways. They alter the appearance of bedrock landforms. Coatings can promote surface stability through case hardening; this first involves the mobilization of constituents from rock coatings and

Table 2   Weathering of plagioclase[a] grains of Hawaiian basalt surfaces exposed for different lengths of time, underneath silica glaze and not under silica glaze

Surface	Not under silica glaze		Under silica glaze	
	Grain area[b]	Porosity[c]	Grain area[b]	Porosity[c]
Mauna Ulu-a (1974 AD)	217 500	0.071 ± 0.018	160 500	0.009 ± 0.018
Mauna Ulu-b (1974 AD)	216 000	0.058 ± 0.014	216 500	0.008 ± 0.011
Mauna Ulu-c (1974 AD)	202 500	0.007 ± 0.004	247 000	0.010 ± 0.022
flow f7d h7.9 ($\sim$700 BP)	238 500	0.94 ± 0.17	183 500	0.13 ± 0.19
flow f5d c8.2 ($\sim$2000 BP)	303 000	1.63 ± 0.15	160 500	0.39 ± 0.23
flow f5d p3.5 ($\sim$3150 BP)	141 000	2.90 ± 0.25	185 500	0.54 ± 0.33
Mauna Kea Glacial Polish ($\sim$14 000 BP)	201 500	26.20 ± 10.33	154 000	15.71 ± 5.82

[a]Representative composition in oxide weight percent of analyzed plagiocalse minerals: 3.22% Na_2O, 0.22% MgO, 29.12% Al_2O_3, 48.22% SiO_2, 18.10% CaO, 0.12% TiO_2, 0.40% MnO, and 0.54% FeO.
[b]Grain area is measured in square micrometers as a total for all mineral grains analyzed.
[c]Each value indicates the average and standard deviation of the porosity measurements.

Table 3   Different methods that have been used to assess rock varnish chronometry

| Method	Synopsis of method
Accumulation of Mn and Fe	As more varnish accumulates, the mass of manganese and iron gradually increases. Occasionally this old idea is resurrected (Lytle et al., 2002), but it has long ago been demonstrated to yield inaccurate results in tests against independent control (Bard, 1979; Dorn, 2001).
Appearance	The appearance of a surface darkens over time as varnish thickens and increases in coverage. However, much of this darkening has to do with exposure of inherited coatings, and with the nature of the underlying weathering rinds, that do not permit accurate or precise assignment of ages based on visual appearance. There is no known method that yields reliable results.
Cation-ratio dating	Rock varnish contains elements that are leached (washed out) rapidly (Dorn and Krinsley, 1991; Krinsley, 1998). Over time, a ratio of leached to immobile elements decline over time (Dorn, 2001). If the correct type of varnish is used, the method performs well in blind tests (Loendorf, 1991). This method also has seen use in places such as China (Zhang et al., 1990), Israel (Patyk-Kara et al., 1997), South Africa (Whitley and Annegarn, 1994), Yemen (Harrington, 1986), and elsewhere.
Foreign material analysis	Rock carvings made historically may have used steel. The presence of steel remains embedded in a carving would invalidate claims of antiquity, whereas presence of such material as quartz would be consistent with prehistoric antiquity (Whitley et al., 1999).
Lead profiles	Twentieth-century lead and other metal pollution is recorded in rock varnish, because the iron and manganese in varnish scavenges lead and other metals. This leads to a 'spike' in the very surface micron from twentieth-century pollution. Confidence is reasonably high, because the method (Dorn, 1998: 139) has been replicated (Fleisher et al., 1999; Thiagarajan and Lee, 2004; Hodge et al., 2005) with no publications yet critical of the technique that can discriminate twentieth century from pre-twentieth-century surfaces.
Organic carbon ratio	Organic carbon exists in an open system in the rock varnish that covers petroglyphs. This method compares the more mobile carbon and the more stable carbon. The method is best used in soil settings (Harrison and Frink, 2000), but it has been applied experimentally to rock varnish in desert pavements (Dorn et al., 2001).
[14]C carbonate	Calcium carbonate sometimes forms over varnish, and can be radiocarbon dated, providing a minimum age for such features as rock art. The method has been used in Australia (Dragovich, 1986) and eastern California (Smith and Turner, 1975; Cerveny et al., 2006).
[14]C organic	The hope is that carbon trapped by coating provides minimum age for the petroglyph. First developed in 1986, two independent investigators working in a blind test (Dorn, 1997; Watchman, 1997) both found organic carbon that pre- and post-dates the exposure of the rock surface. The only person who still uses organic carbon of unknown residues in radiocarbon dating (Watchman, 2000; Huyge et al., 2001), Watchman now admits that he has not tested results against independent controls (Watchman, 2002; Whitley and Simon, 2002a, 2002b).
[14]C oxalate	The inorganic mineral oxalate (e.g., whewellite: $CaC_2O_4 \cdot H_2O$) sometimes deposits on top of or underneath rock varnish (Watchman et al., 2000). Because this mineral contains datable carbon, the radiocarbon age can provide a minimum age for the underlying or overlying varnish. The most reliable research on radiocarbon dating of oxalates in rock surface contexts has been conducted in west Texas (Rowe, 2001; Spades and Russ, 2005) and in a rock art shelter (Watchman et al., 2005).
Uranium-series dating	As radionuclides are enhanced in varnish (Marshall, 1962), uranium-series isotopes show potential (Knauss and Ku, 1980). Complications surround acquiring the necessary amount of material from the basal layers and concerns over accounting for the abundant thorium that derives from clay detritus instead of radioactive decay.
Varnish microlaminations (VML)	Climate fluctuations change the pattern of varnish microlaminations (VML). The confidence level is high, because the method (Liu, 2003; Liu and Broecker, 2006) has been replicated in a rigorous blind test (Marston, 2003), and the method is based on analyses of over 10 000 rock microbasins.
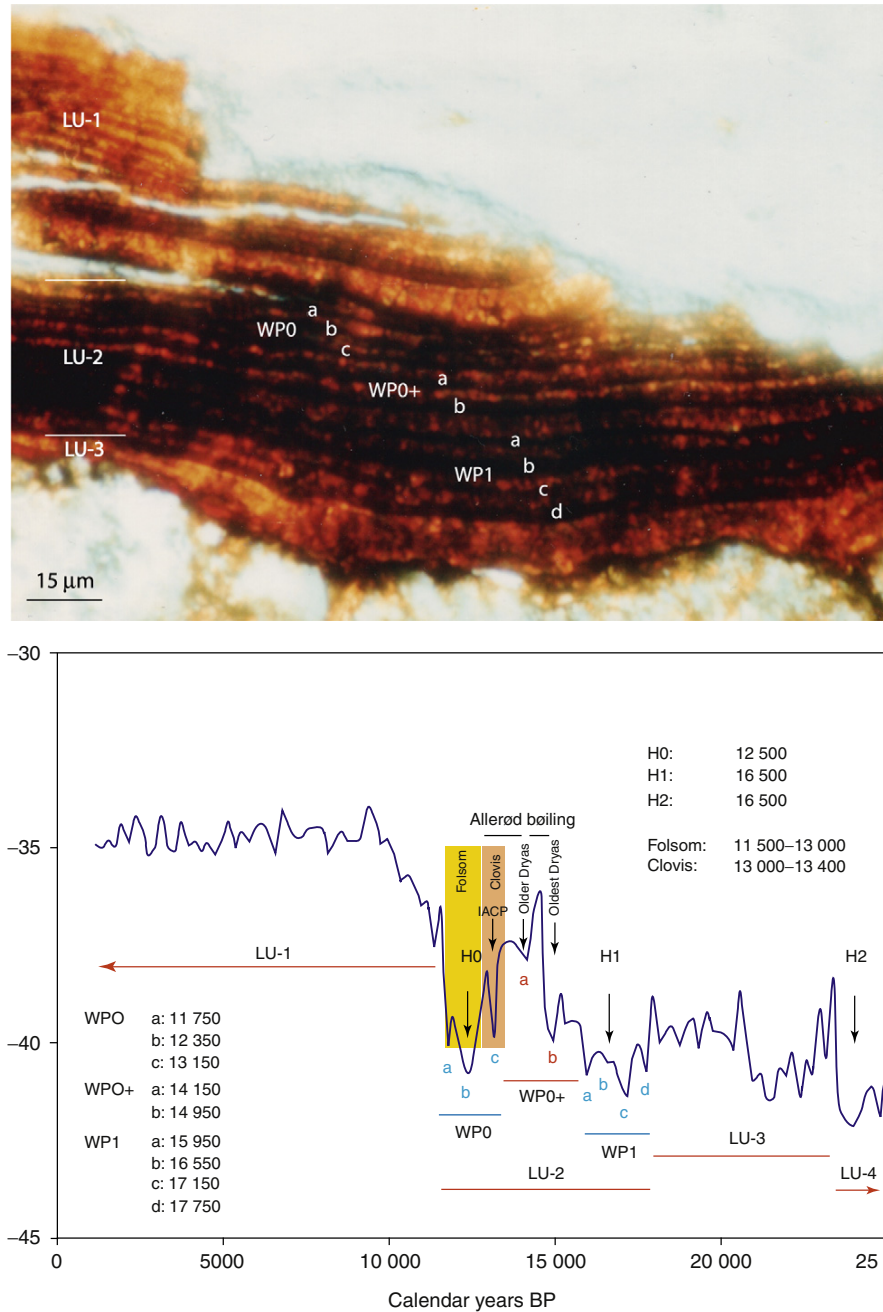
Figure 33 A varnish ultra-thin section from Galena Canyon fan in Death Valley (with the upper layers irregularly polished off during thin section production) exemplifies how different terminal Pleistocene varnish microlamination patterns. The age correlation presented here comes from independent numerical age control and from the Greenland ice core record. For the sake of temporal recognition, the well-known Folsom and Clovis lithic technologies are placed in this high-resolution sequence. The nomenclature of layering units (LU), Heinrich Events (e.g., H0, H1, H2), wet periods in the late Pleistocene (WP) identified by black varnish layers follows previous research (Liu and Broecker, 2007, 2008a, 2008b; Liu, 2010).

then reprecipitation within the pore spaces of the underlying weathering rind. By contrast, rock coatings formed in rock fissures in dusty warm deserts can accelerate physical-weathering rates substantially through wedging rocks apart.

Rock coatings likely occur as silica glaze on Mars. One of the most significant aspects of rock coatings in geomorphology rests with the revolutionary research by Tanzhuo Liu, where two decades of painstaking analysis of over 10 000
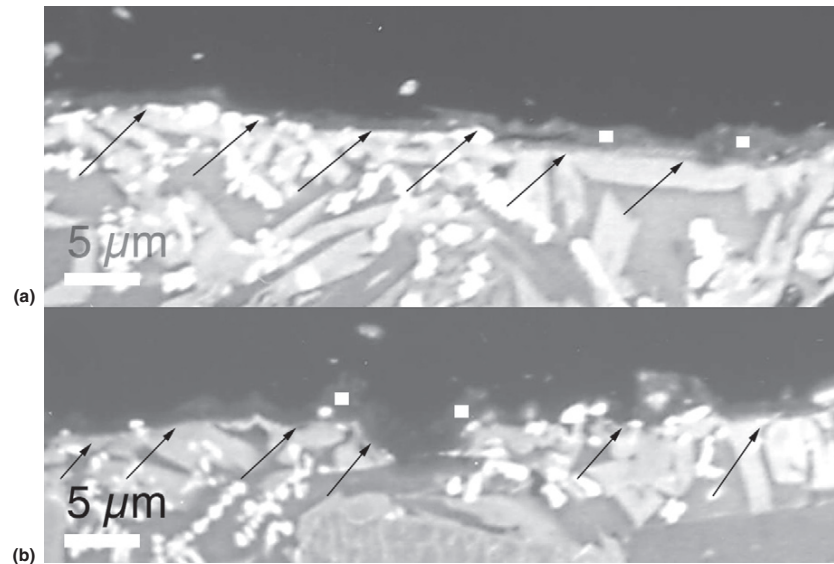
Figure 34   BSE images of silica glaze formed on basalt rock chips after exposure to only air with a relative humidity of (a) 90% and (b) 80% at 18 °C in a 20-year-long laboratory experiment. Arrows show contacts between the silica glaze and the underlying basalt. The white dots indicate the positions of focused beam electron microprobe measurements. A typical water vapor-formed silica glaze composition is MgO 0.06%, Al_2O_3 0.57%, 80.22% SiO_2, 0.04% K_2O, 0.22% CaO, 0.08% TiO_2, 0.06% Fe_2O_3 with abundant porosity.

microsedimentary basins exemplifies how rock coatings can be used to analyze paleoclimatic changes and also provide minimum ages to understand landform evolution.

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