

## Chapter 7

# Desert Rock Coatings

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### Introduction

Desert landforms are characterized by an abundance of 'bare' rock and mineral surfaces. Mountains host widespread exposures of bedrock. Gravel desert pavements cap alluvial terraces and fans. Even sand dunes are themselves composed of rock fragments exposed to the atmosphere without substantive plant cover. This chapter focuses on an irony, that the supposed fundamental bare-rock nature of desert landforms stretches the truth.

In reality, rock coatings, even those thinner than 10  $\mu\text{m}$  (0.010 mm) substantially alter the appearance of almost all of the rock surfaces found in deserts (Fig. 7.1). Consider just a few of the icons of desert geomorphology. The main Petra tourist attraction of the Al-Khazneh Tomb façade is coated with a black manganese-rich varnish, allowing the carved portions of the elaborate burial chamber to stand out. The almost white colour of Ayers Rock is coated by mostly iron-clay orange accretions, facilitating photogenic displays. Dramatic sandstone escarpment faces of the Colorado Plateau in such places as Monument Valley are frequently coated by a reddish-brown silica glaze formed inside the unopened joint fracture and then exposed by block wasting.

The systematic study of rock coatings started tens of millennia ago, as prehistoric peoples targeted very specific rock coatings for petroglyph manufacturing

as well as application of artificial rock coatings to create paintings (Whitley, 2001; Whitley, 2005). The scientific study of rock coatings started in 1799 (von Humboldt, 1812), when major differences in manganese composition between coatings and the underlying rock led to recognition of rock varnish's accretionary nature.

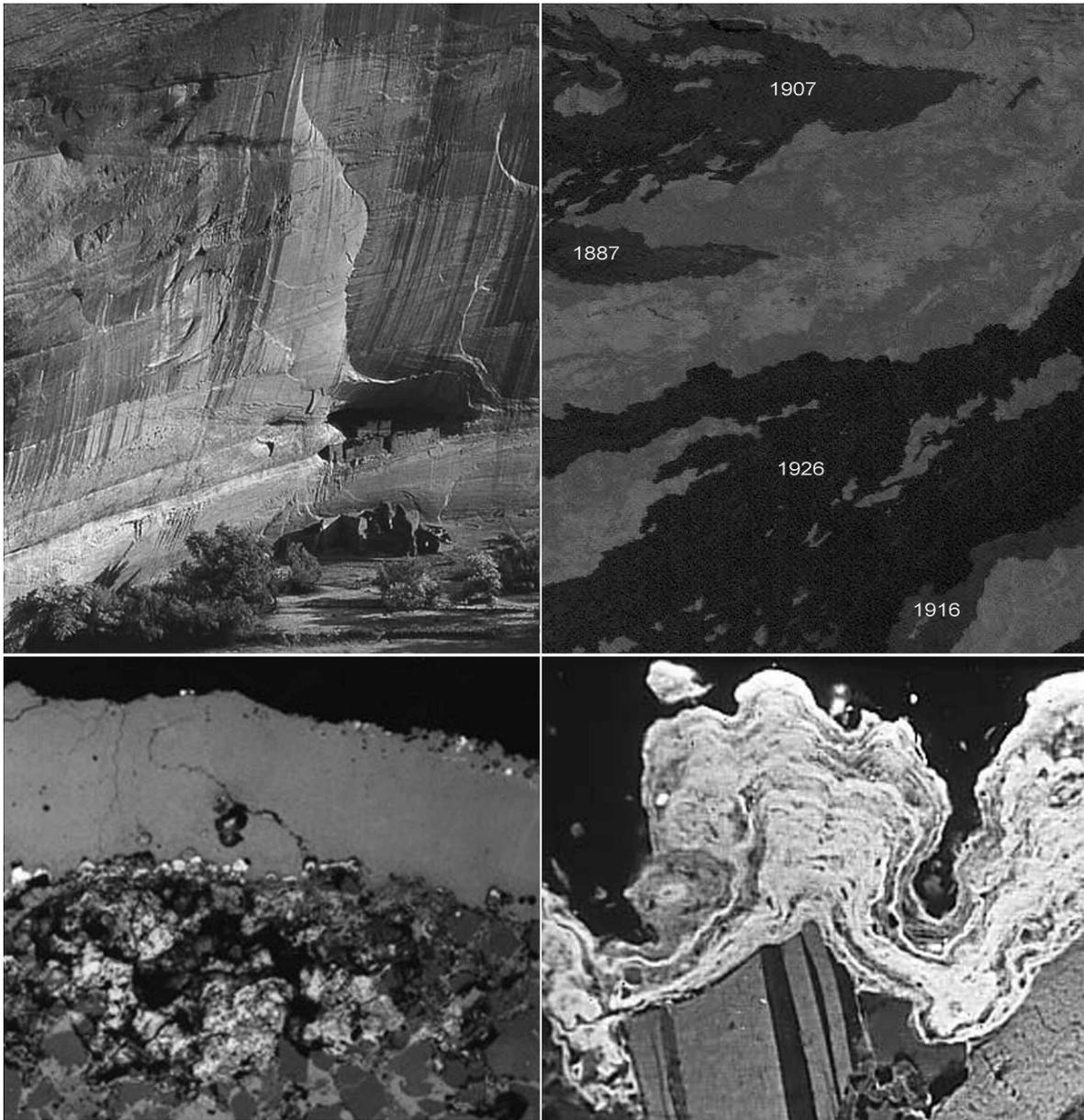
There are over a dozen different types of rock coatings (Table 7.1). Within each type, tremendous variety exists at spatial scales from kilometres to micrometres. For example, there are at least six different types of silica glazes (Dorn, 1998: 294–312). Interdigitation also exists between different types of rock coatings, resulting in complex microstratigraphic sequences. For example, lava flows in the arid Ashikule Basin of Tibet host carbonate skins, dust films, lithobiontic coatings, oxalate crusts, phosphate skins, rock varnish, silica glazes, and sulfate crusts. In another example, lithobionts like lichens are normally associated with rock weathering, but they can also play key roles in generating silica glazes (Lee and Parsons, 1999) and oxalate crusts (Beazley et al., 2002). Given the variety and complexity of rock coatings, it should be of no surprise that researchers not infrequently confuse different types of coatings in their data collection and analysis.

This chapter introduces the field of desert rock coatings. After introducing the paradigm perspective of landscape geochemistry that drives an overall conceptual understanding of rock coatings, I present current hypotheses of how different rock coatings form, followed by a summary of their use in desert geomorphology. This chapter ends by identifying future research needs.

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**Fig. 7.1** Rock coatings change the appearance of bare rock landforms. *Upper Left:* A vertical face at Canyon de Chelly, Arizona, is streaked with heavy metal skins, iron films, lithobiont coatings, oxalate crusts, rock varnish, and silica glaze. *Upper Right:* Lava flows in the arid regions of Mauna Loa show a distinct color change within decades as a direct result of accumulation of silica glaze. The true color image, courtesy of NASA, has a length

of 3.6 km with west at the top. The electron microscope images (backscatter detector) demonstrate that rock coatings are external accretions, exemplified by an oxalate crust from the arid Olary Province in South Australia in the *lower left* image that is about 500  $\mu\text{m}$  thick. Rock varnish on the *lower right* from Kitt Peak in the Sonoran Desert is about 100  $\mu\text{m}$  thick

**Table 7.1** Major categories of rock coatings

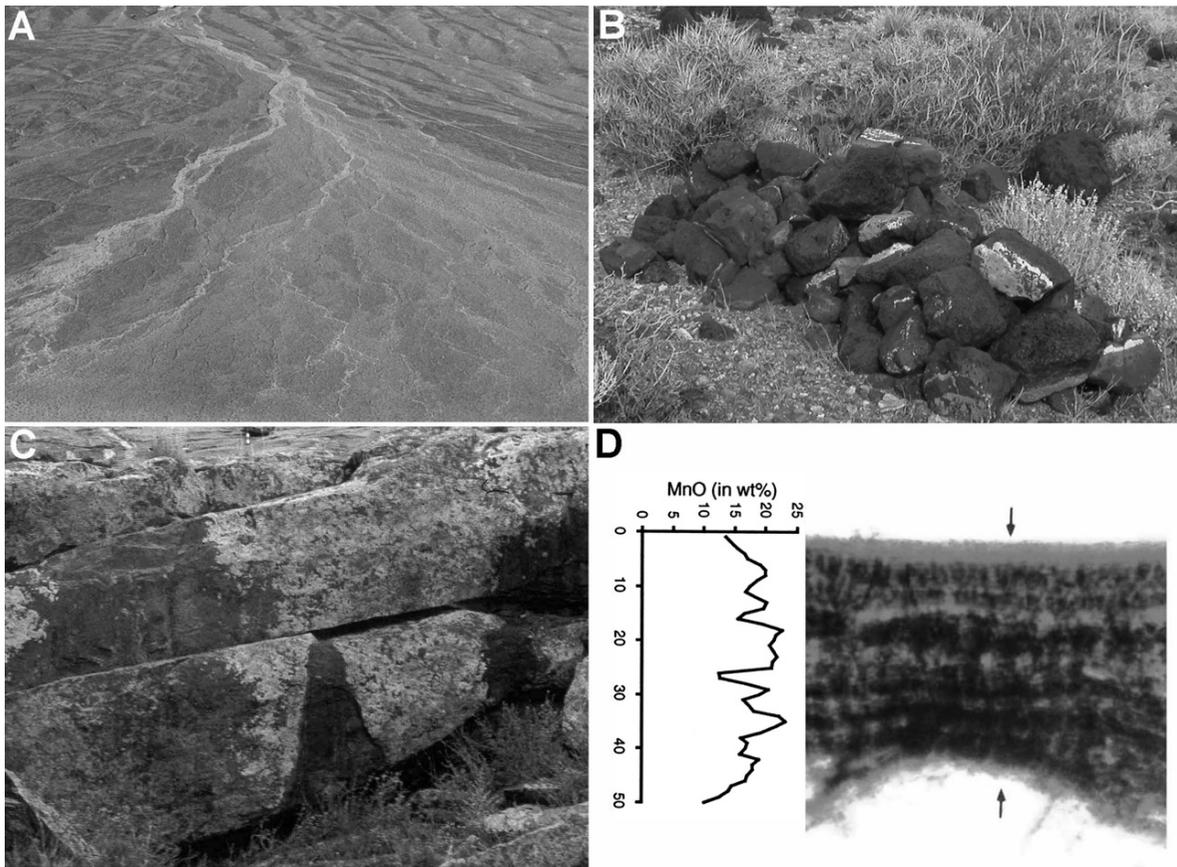
Coating	Description	Related terms
Carbonate Skin	Composed primarily of carbonate, usually $\text{CaCO}_3$ , but sometimes $\text{MgCO}_3$	Calcrete, travertine
Case Hardening	Addition of cementing agent to rock matrix material; the agent may be manganese, sulfate, carbonate, silica, iron, oxalate, organisms, 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.	Sometimes described by chemical composition
Iron Film	Composed primarily of iron oxides or oxyhydroxides; unlike orange rock varnish some films do not have clay as a major constituent.	Ferric oxide red staining, 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.	Saltpeper; 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
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 lustre, 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

## Landscape Geochemistry Model of Rock Coating Development

Landscape geochemistry, as developed in Soviet geography (Polynov, 1937; Perel'man, 1961, 1966; Glazovskaya, 1968; Glazovskaya, 1973) and brought into the English literature (Fortescue, 1980), integrates studies of element abundance, element migration, geochemical flows, geochemical gradients, and geochemical barriers with the classification, interpretation, and spatial laws pertaining to geochemical landscapes. No other conceptual framework of looking at rock coatings explains the quantity or diversity of data, is as relevant to a variety of disciplines, or provides such a

clear framework to analyze rock coatings (Dorn, 1998: 20–27). Furthermore, there is no alternative; landscape geochemistry currently provides the only larger theoretical framework for the study of desert rock coatings.

Viewed from the spectacles of landscape geochemistry, rock coatings occur where geochemical, biological, or physical barriers exist to the flow of coating constituents, so long as a rock surface is stable long enough to allow coatings to accrete. The geographical expression of these barriers can be extensive in area, such as the overall alkaline nature of desert rock surfaces facilitating the stability of iron (Fe) and manganese (Mn) in rock varnish (Fig. 7.2A). There



**Fig. 7.2** Desert rock coatings accumulate at different types of geochemical barriers. (A) In southern Death Valley, California, the geochemical environment is alkaline enough to permit the accumulation of Fe and Mn on alluvial-fan cobbles. (B) The undersides of buried boulders on Panamint Valley shorelines, California, have accumulated carbonate, but in the case of this prehistoric cairn, the carbonate slowly dissolves from exposure

to rain. (C) Lichen growth at Yunta Springs, South Australia, has dissolved most of previous iron film, rock varnish and silica glaze. (D) Rock varnish microlaminations of black Mn-rich layers record wetter climates, while orange Mn-low layers record drier conditions in the Zunggar Desert, western China (Zhou et al., 2000). The image is courtesy of Tanzhuo Liu (Liu, 2008)

are also linear barriers at chemical discontinuities, allowing such coatings as carbonate skins to accumulate on the undersides of desert boulders (Fig. 7.2B). These barriers shift in space and on timescales of  $10^{-3}$  to  $10^3$  years, causing temporary coatings of ice to melt within a day (Hetu et al., 1994), silica glazes to form within decades (Fig. 7.1) carbonate skins to dissolve within centuries (Fig. 7.2C), or rock varnishes to accrete evidence of millennial-scale climatic change (Liu, 2003; Liu, 2008; Liu and Broecker, 2007; Liu and Broecker, 2008a, 2008b) (Fig. 7.2D).

Desert rock coatings can be interpreted by following a five-order hierarchical sequence of landscape geochemical controls (Dorn, 1998: 324–344).

### **First-Order Process: Geomorphic Controls**

An obvious first control rests in the need for processes that generate the bare rock on which coatings accrete. Deserts are dominated by rock coatings, because deserts are weathering-limited landscapes where detachment and transport exceeds weathering (Gilbert, 1877). Rock coatings also dominate desert landforms because host rock surfaces remain stable long enough to accumulate coatings. Some surfaces can remain stable for  $10^5$  years (Nishiizumi et al., 1993; Liu and Broecker, 2000; Liu, 2003), although most rock surfaces do erode more rapidly

(Gordon and Dorn, 2005a). For example, biotite weathering promotes granite grussification that limits the development of rock coatings on granitic surfaces (Fig. 7.3A).

### ***Second-Order Process: Inheritance from the Subsurface***

Rock coatings can and do originate in soil (Engel and Sharp, 1958; Ha-mung, 1968; Hayden, 1976; Robinson and Williams, 1992) and in rock fissures (Dorn and Dragovich, 1990; Douglas et al., 1994; Mottershead and Pye, 1994; Frazier and Graham, 2000; Cerveny et al., 2006; Kim et al., 2006). Subaerial exposure occurs from soil erosion (Hunt and Wu, 2004) or spalling of the overlying block (Villa et al., 1995). These inherited rock coatings are extremely common, even though very few investigators note the possibility that the samples they collected may have originated underground. This general lack of appreciation may be because there are many possible trajectories for what happens to inherited coatings after exposure. The more common post-exposure sequences are: continued erosion exposes even more subsurface coatings; the rock under the inherited coatings erodes — effectively removing weathering rind and coating; inherited coatings erode, only to be replaced by a different subaerial coating; lithobionts grow on inherited coatings (Fig. 7.3B); or a similar or different coating grows on top of the inherited coating (Fig. 7.3C).

### ***Third Order Process: Habitability for Lithobionts***

Faster growing coatings such as lichens dominate over slower-growing accretions. Unless they are overcome by anthropogenic application of pigments (Lee et al., 1996; Wang and Hua, 1998; Saiz-Jimenez and Hermosin, 1999; Li et al., 2001), lithobiontic (Golubic et al., 1981) coatings such as lichens and fungi (Urzi et al., 1992; Souza-Egipsy et al., 2004) grow much faster than most natural inorganic coatings, effectively ‘taking out’ the competition (Fig. 7.3B). Some have even speculated that bacteria precipitate black Mn-rich coatings like rock varnish just to heat up

desert surfaces in order to reduce surface habitability for lichens. The latest research reveals that desert rock surfaces host an incredible variety of adventitious extreme organisms (Benzerara et al., 2006; Fajardo-Cavazos and Nicholson, 2006; Kuhlman et al., 2006). The speedy ones take possession of the surface.

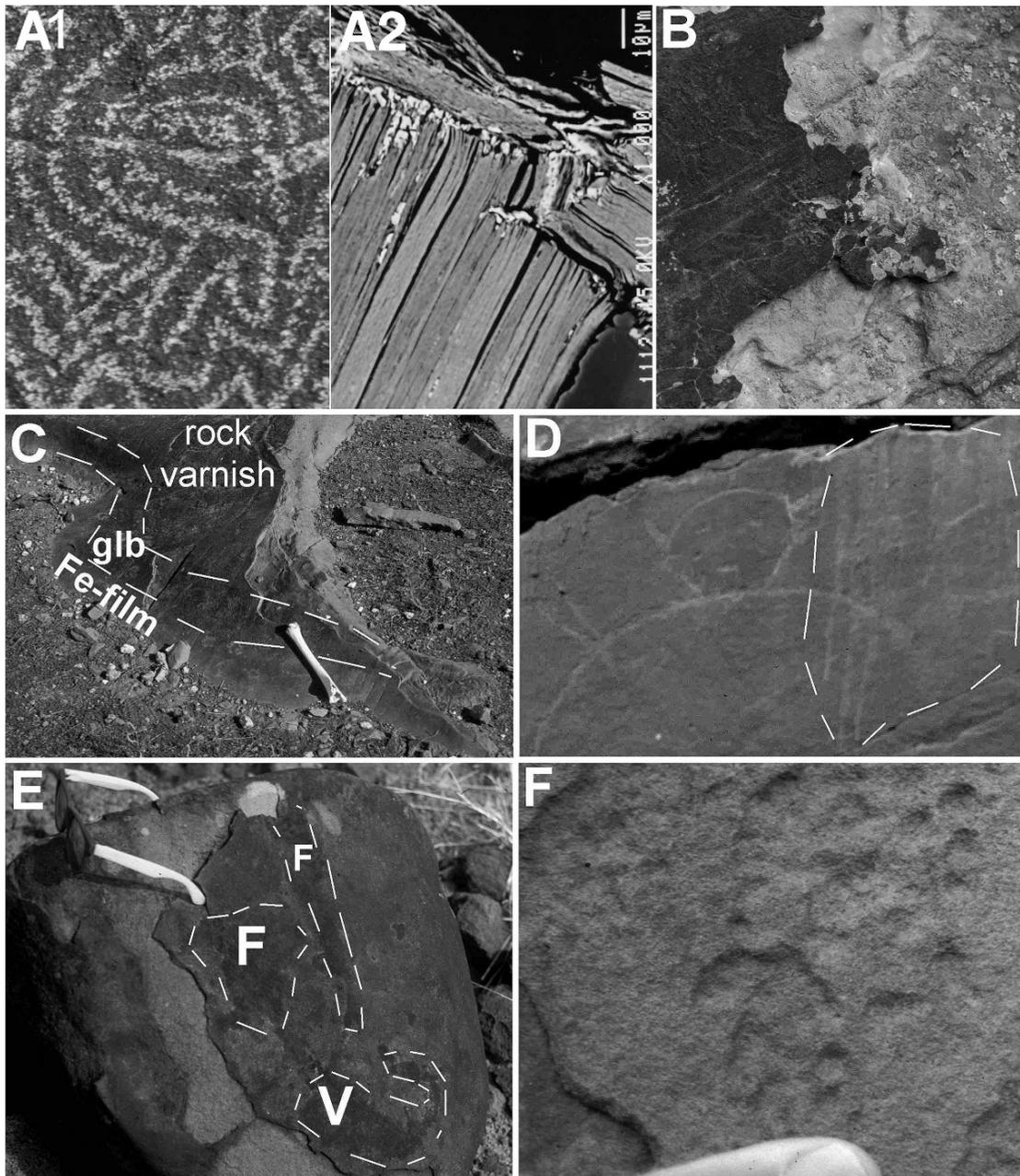
Fourth- and fifth-order processes — typically the starting point for rock coating research — involve movement of coating constituents and their fixation on rock surfaces. However, these processes only influence the nature of desert rock coatings when: (1) rock faces are exposed by erosion; (2) exposed rock faces are stable enough to support rock coatings; and (3) lithobionts do not outcompete other coatings.

### ***Fourth-Order Process: Transport Pathways***

Transport of raw mineral ingredients involves two steps. 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 that is then mobilized and re-precipitated (Fig. 7.3D). Many oxalate-rich crusts found in deserts similarly rely on lithobionts to manufacture the oxalate that is then transported by water flow over rock surfaces (Beazley et al., 2002). Constituent availability alone, however, can be a factor in determining what type of rock coating grows. For example, water flows over sandstone cliff faces have an abundance of Mn and Fe precipitation, but these water-flow deposits often lack clay minerals; since clays are vital to the formation of rock varnish (Potter and Rossman, 1977; Potter, 1979), the net result is often the formation of a heavy metal skin (Dorn, 1998: ch 8) instead of a rock varnish. Similarly, the basalt flows of semi-arid Hawai’i lack the overwhelming aeolian deposition of clay minerals found in continental deserts, resulting in the dominance of silica glazes (Dorn, 1998: ch 13) over relatively rare Hawaiian rock varnish (Fig. 7.3E).

### ***Fifth-Order Process: Barriers to Transport***

Physical, geochemical, and biological barriers come into play only after all of above processes do not



**Fig. 7.3** Landscape geochemistry influences coating development. **A.** Petroglyph carved into varnished granodiorite, south-central Arizona (A1), where biotite oxidation and hydration from this site (A2) limits the accretion of rock varnish to the length of time it takes to erode a *grus* grain. **B.** Lichens, cyanobacteria, and fungi (*right side* of image) have almost completely eroded silica glaze from a sandstone joint face, Wyoming. The new lithobiont community now plays a key role in case hardening the surface, as has been found elsewhere (Viles and Goudie, 2004). **C.** Slow soil erosion at Karolta, South Australia, exposes two rock coatings. Erosion first exposed the ground-line band (glb), a very thin and shiny accretion of silica glaze and manganese that orig-

inally forms at the soil-rock-atmosphere interface (Engel and Sharp, 1958). Then, continued erosion exposed iron film. Sub-aerial rock varnish then started to grow over both of these former subsurface coatings. **D.** Phosphate skin over sandstone, eastern Wyoming, where a bird droppings were mobilized then and precipitated (inside *dashed area*) over mostly silica glaze. **E.** Basalt boulder on the rainshadow side of Kaho'olawe Island, Hawai'i, is mostly coated by silica glaze, but pockets of rock varnish (v) and fungi (f) also grow. **F.** Dust film deposited over sandstone in a Colorado Plateau alcove that is protected from rainsplash and water flow

rule out coating accretion. Dust coatings (Fig. 7.3F), for example, form at locales (Johnson et al., 2002) where the physical barrier of Van der Waals forces are *not* overcome by shear stresses imposed by water flow. Iron films, carbonate skins, and natural heavy metal skins are examples of coatings that may accrete at either geochemical (Krauskopf, 1957; Collins and Buol, 1970; Scheidegger et al., 1993; Huguen et al., 2001; Nanson et al., 2005) or biological barriers (Ha-mung, 1968; Chukhrov et al., 1973; Mustoe, 1981; Robbins et al., 1992; Robbins and Blackwelder, 1992). These geochemical barriers, in turn, can trap additional elements; for example, rock varnish forms at a barrier to Mn and Fe mobility where the Mn-Fe oxides in turn capture dozens of trace and rare elements (Wayne et al., 2006).

## Formation

The processes by which different desert rock coatings form are best organized through the hierarchy discussed in the previous section. Since the first-order processes of exposing bare rock and the fourth-order processes of constituent transport do not in and of themselves produce accretions, the examples presented below focus on key steps making some of the more common desert rock coatings.

### **Second-Order Process: Fissuresol Coatings**

A common cause of desert rock spalling is the gradual growth of fissuresols (Fig. 7.4A). Fissuresols are formed by the accumulation of rock coatings and sediment fill inside joints (Coudé-Gaussen et al., 1984; Villa et al., 1995; Frazier and Graham, 2000). As coatings and fill accrete, the fissure opens slowly until detachment occurs, exposing coatings originating inside of the crevice. Exposed fissuresols might only be a few centimetres across (Fig. 7.4B), or they might run completely through a 3-metre-diameter boulder (Fig. 7.4F).

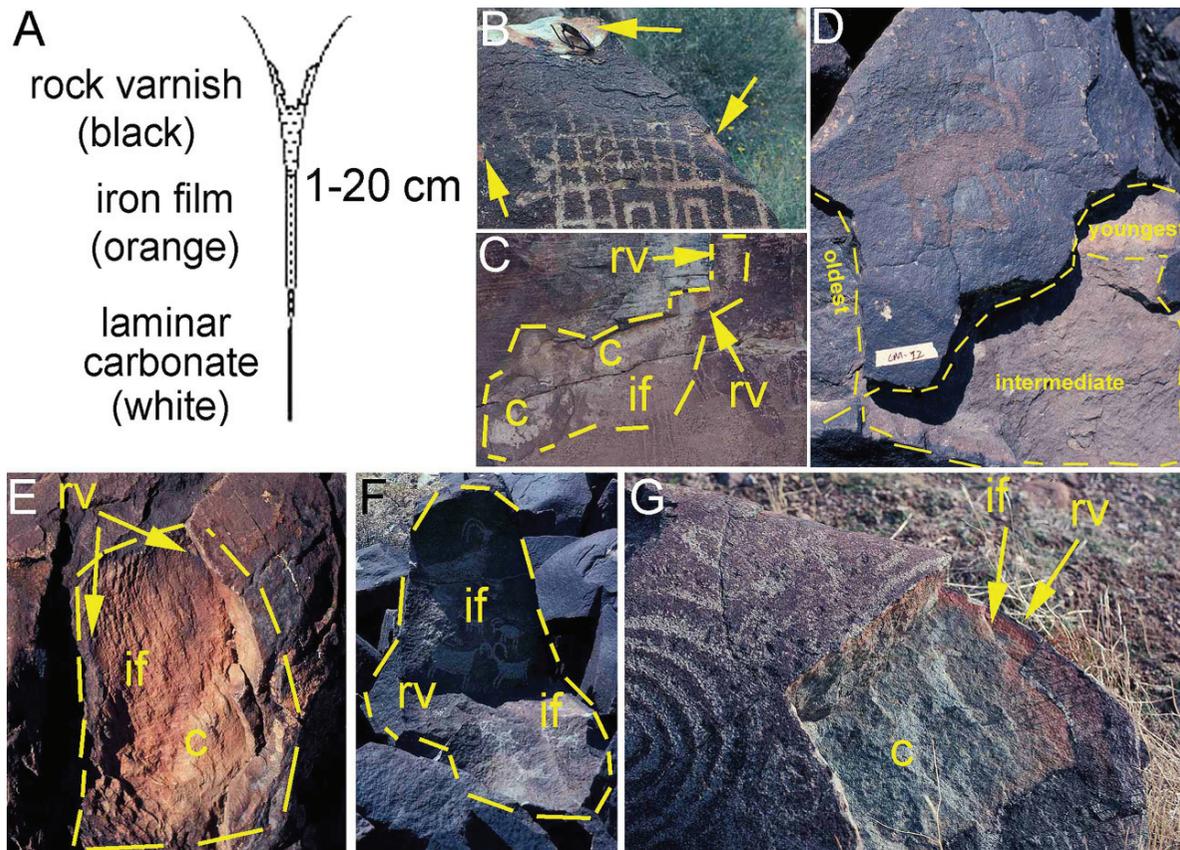
Three types of rock coatings form inside fissures in drier deserts, and all three are exposed by rock spalling. Carbonate skins form in the deepest parts of the fracture (Fig. 7.4C, E, G), but this carbonate coating is not

long-lived since it dissolves from exposure to carbonic acid in precipitation. The perimeter of a fracture develops a distinct zonation of an inner wider band of orange iron film and a narrow outer band of black rock varnish (Fig. 7.4B, E, F, G). These are not the Mn-Fe coatings found in saprolite fractures (Weaver, 1978). Rather, the iron films are clay-iron accretions similar to the orange coating found on the underside of desert pavement cobbles, and black coatings are manganese-rich rock varnish.

After exposure, if conditions are too xeric for fast-growing lithobionts (cf. Fig. 7.3B), then subaerial rock varnish grows on top of the fissuresol coatings (cf. Fig. 7.4D). The darkest rock varnishes seen on any given landform are usually those that start as a fissuresol, because there is foundation of a fairly complete coverage on the host rock. In contrast, those varnishes that start out on abraded clasts are not as dark and not as well coated. On rock surfaces exposed by abrasion processes (e.g., fluvial, glacial, littoral action), the rock varnish must first accumulate in nucleation sites in isolated microtopographic basins. Then, only after taking millennia to get this foothold does rock varnish grow together horizontally to form a complete coating. In contrast, the fissuresol acts like a paint primer that covers the whole surface, helping the black subaerial varnish to accrete a darker and more complete cover. This is why the sample selection criteria used by researchers (Harrington and Raymond, 1989; McFadden et al., 1989; Reneau, 1993) is based on an incomplete understanding of rock coating formation.

Fissuresol sequences (Fig. 7.4A) are the most common type of inherited rock coatings in drier deserts, but fractures in rocks in semi-arid environments typically contain silica glaze (Fig. 7.5D, E) that can be dense (Fig. 7.5F–H) or can be a more porous clay-rich fracture coating (Graham and Franco-Vicaino, 1992; Thoma et al., 1992; Frazier and Graham, 2000).

Silica glaze in fractures is just the start. In the semi-arid sandstone *cuestas* of the Colorado Plateau and Wyoming basins, joint faces often accumulate black rock varnish after faces are exposed by erosion. Then, some of the iron and manganese in the varnish is leached (Dorn and Krinsley, 1991) to mix with silica glaze. The net effect is a case hardening of sandstone surfaces through a mixture of inherited silica glaze and iron and manganese leached out of varnish and washed into the rock (Fig. 7.5A, B, C).



**Fig. 7.4** Rock coatings formed within fractures in drier deserts. **A:** Generalized sequence of rock coatings found inside a still-closed desert rock fracture. **B–G:** Fissuresol sequences occur in all deserts and all rock types such as: **B,** granodiorite, southern Nevada; **C,** sandstone, southern Utah; **D** and **F,** basalt,

eastern California; **E,** silicified dolomite, South Australia; **G,** hornfels, Sonoran Desert, Arizona. rv = rock varnish; if = iron film; c = carbonate skin. Horizontal photo dimensions are 0.7 m (B), 1.3 m (C), 0.4 m (D), 0.6 m (D), 2.5 m (F), and 0.6 m (G)

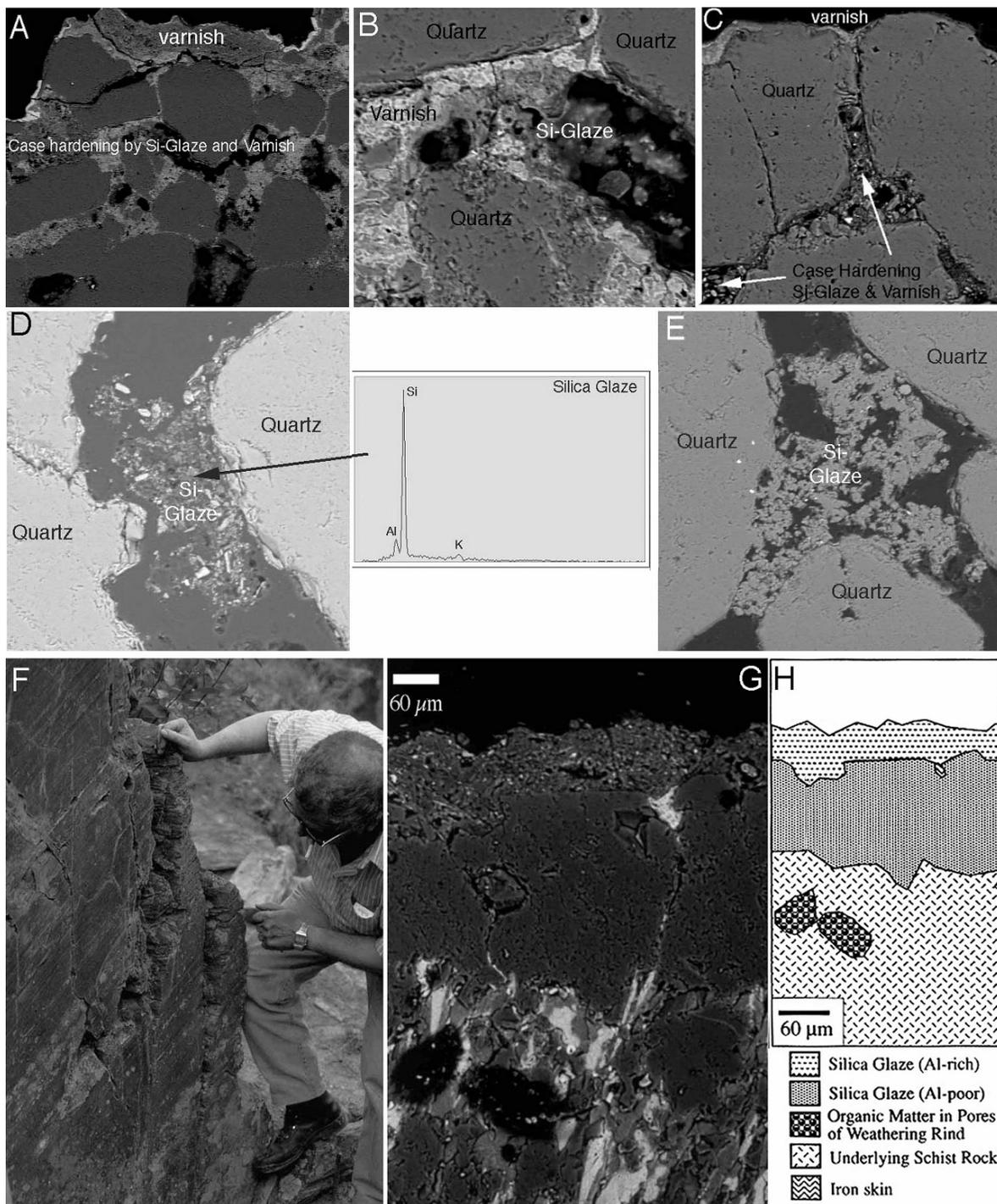
### Third-Order Process: Lithobionts

Life coatings on rocks (lithobionts) include epiliths that live on the surface, euendoliths that bore tubes, chasmoendoliths occupying fissures, and cryptoendoliths that live in weathering-rind pores (Golubic et al., 1981). Lithobionts can also be grouped into  $\leq 1$  mm biofilms,  $\sim 1$ –5 mm biorinds, and  $> 5$  mm biocrusts (Viles, 1995) that may be composed of bacteria, cyanobacteria, fungi, algae, and lichens. Although the general consensus in the past was that desert lithobiontic communities had low diversity, new methods reveal an astounding variety of organisms living on rock surfaces (Kuhlman et al., 2005; Benzerara et al., 2006; Fajardo-Cavazos and Nicholson, 2006). A single gram of rock varnish, for example, contains  $10^8$

microorganisms of *Proteobacteria*, *Actinobacteria*, eukaryota, and *Archaea* (Benzerara et al., 2006; Kuhlman et al., 2006).

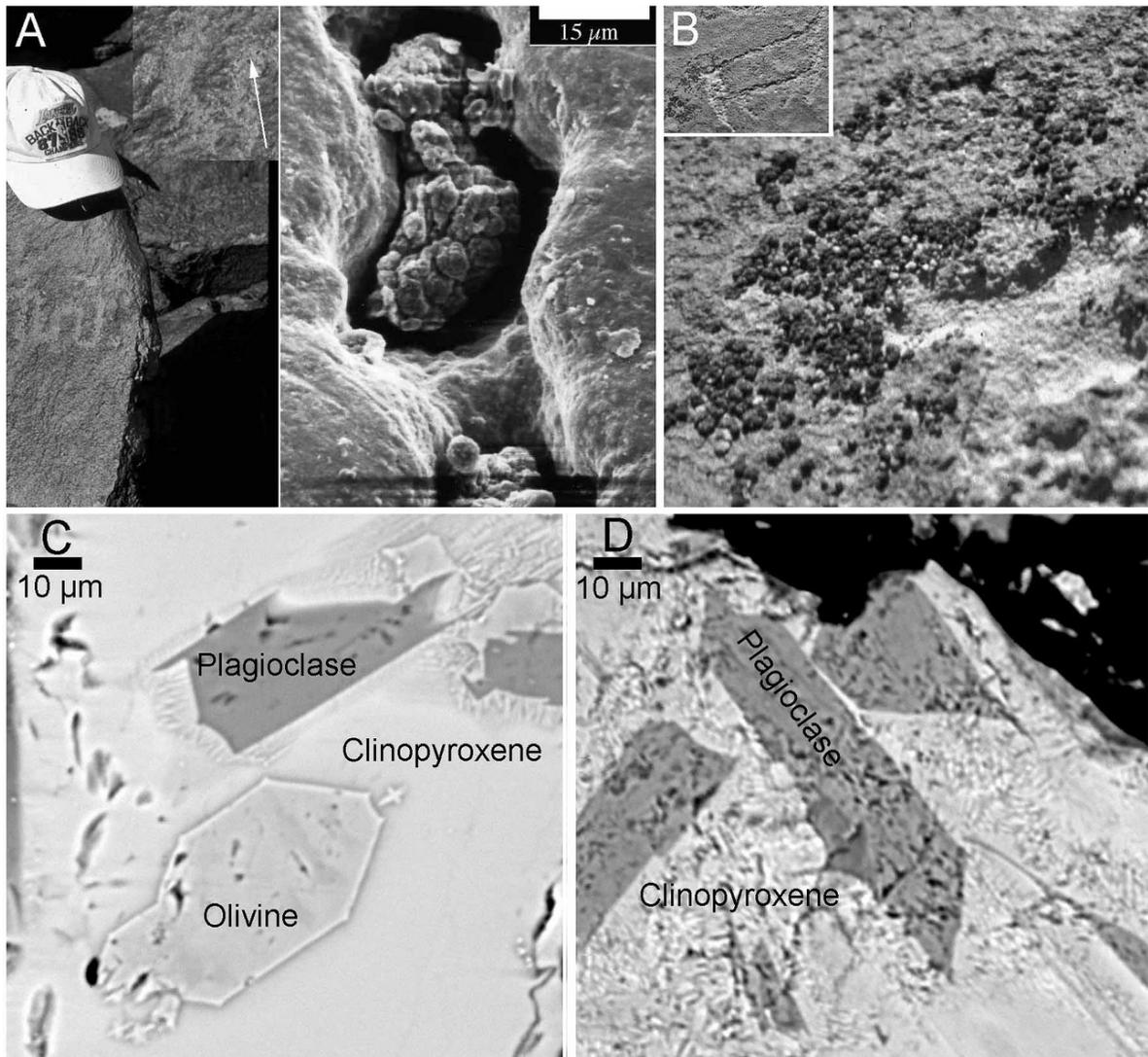
A critical aspect of fast-growing lithobionts such as fungi and lichens is their capability of weathering inorganic rock coatings (Fig. 7.6A, B), as well as the underlying rock (Fig. 7.6B, C, D). By eroding the rock coating or its underlying substrate, lithobionts obtain possession of the surface.

Viles (1995: 32) modelled the weathering activity of lithobionts in conditions of varying moisture and rock hardness. A similar graphical presentation for rock varnish had considered growth also in terms of two simple factors, moisture and competition from lithobionts (Dorn and Oberlander, 1982). While these authors all acknowledge the simplicity of two variable perspectives, the interplay of lithobiont weathering



**Fig. 7.5** Silica glaze rock coatings formed within fractures in semi-arid environments. Images A–E come from Wyoming sandstone cuestas and F–G from Portugal schist. Images A–C show how Mn and Fe leached from a very surface layer of rock varnish migrates into the sandstone, mixing with the pre-existing silica glaze to case harden the outer millimetres. Images D and E present silica glaze from an unopened joint face, collected

~40 cm up into a joint covered by an overlying sandstone block, but opened for sampling. A schist joint face in northern Portugal (F) hosts a fairly uniform layer of mostly silica under a clay-rich silica glaze (G–H). Images A–E and G are backscattered electron micrographs with image widths of: A (1800 µm); B (140 µm); C (140 µm); D (210 µm); E (260 µm)



**Fig. 7.6** Weathering activity of lithobionts. **A.** Varnished basalt boulder in the Mojave Desert with inset photo of petroglyph and showing location of the electron microscope image of a euendolith (tube boring) microcolony fungi that is effectively dissolving rock varnish. **B.** Both silica glaze and rock varnish are being weathered and eroded by lichen growing on sandstone at Legend Rock, Wyoming. When the lichen is removed, the rock

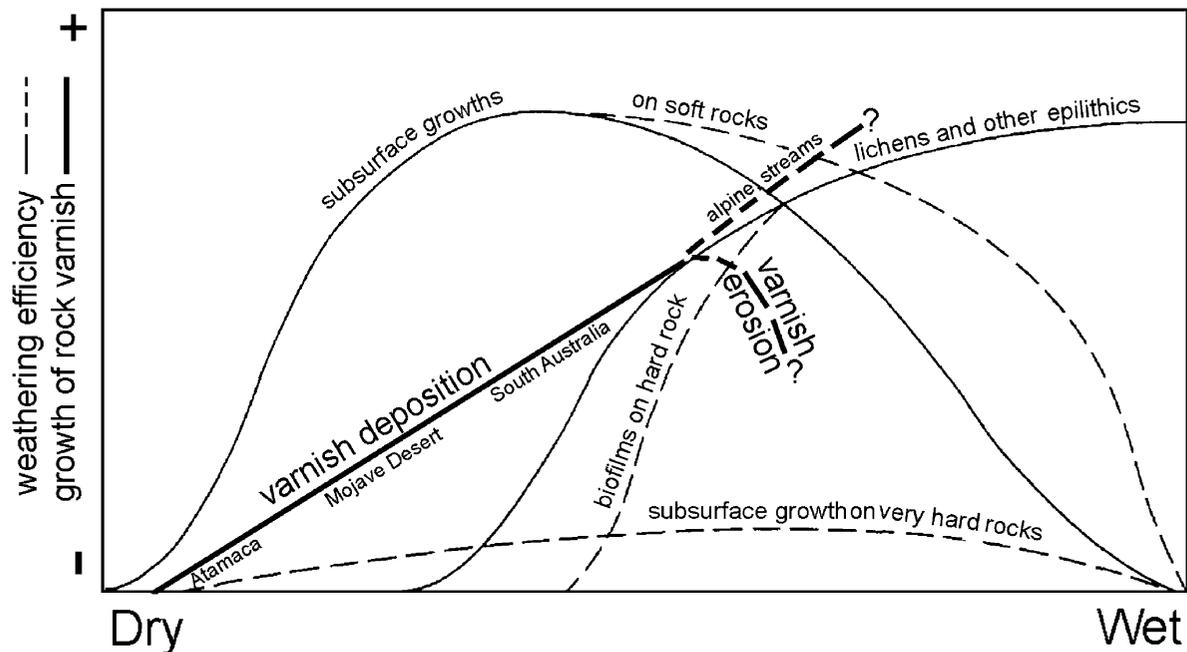
easily erodes, because the sandstone had become a silty powder under the lichen cover. **C** and **D** present backscattered electron microscopy imagery of weathering of lava flow f7dh7.9 on the desert side of Hualalai Volcano, Hawai'i. The less weathered sample (**C**) was collected away from lichens, and the sample with more porosity (dark 'holes' in **D**) was collected directly beneath *Stereocaulon vulcani* (image **D**)

and rock varnish growth can be understood at a general level by combining these two conceptualizations (Fig. 7.7).

Consider first the rock varnish perspective, viewed as the varnish rate deposition line in Fig. 7.7. In the drier deserts, varnish grows slowly, but subsurface lithobionts offer little competition. In conditions

wetter than semi-arid South Australia, lichens and other epilithics reach a point that varnish erosion from the secretion of acids is faster than varnish formation.

Then, consider impact of lithobiont activity on rock varnish. The thinner lines in Fig. 7.7 represent the potential euendoliths that bore holes in varnish (Fig. 7.6A), biofilms of fungi, cyanobacteria, and



**Fig. 7.7** Graphical conceptualization of how lithobionts and rock varnish interact together, adapted from Viles (1995) and Dorn and Oberlander (1982). The graph is a generalization of how moisture impacts the growth of rock varnish and the weathering efficiency of lithobionts.

In the case of rock varnish, a second key factor other than moisture is competition from lithobionts. In the case of lithobionts, a second key factor is the hardness of the rock

algae that prevent varnish from growing, and lichen biorinds that secrete enough acid to completely dissolve away varnish (Figs. 7.3B and 7.6B). The efficiency of lithobionts in weathering both rock and varnish is highest on the wettest side of the graph, where varnishes are not found except under special conditions. The only circumstances where rock varnish can form in wetter environments are where epilithics have not yet colonized subglacial features, moraines and stream-side surfaces (Klute and Krasser, 1940; Whalley et al., 1990; Dorn, 1998).

Finally, examine the lithobiont's weathering efficiency in Fig. 7.7. Organisms impose three major 'styles' of biological weathering in their possession of rock surfaces: (1) epilithic biofilms and lichen-dominated surfaces; (2) endolithic-dominated; and (3) mixed biorinds (Viles, 1995). Epilithic biofilms and lichens dominate in the most mesic locales. Endolithic lithobionts can survive in extremely xeric settings. In the middle ground epilithic biofilms, epilithic lichens, and endolithic communities all mix together with varnish growth and varnish erosion. The hardness

or softness of the rock comes into play as a way of modelling how another factor can make life harder or easier on a lithobiont.

An important point must be made for those concerned about the impact of lithobionts on preservation of cultural resources such as rock art and stone monuments. The vast majority of the literature reveals overwhelming evidence of the weathering power of lithobionts (Jones and Wilson, 1985; Dragovich, 1986b; Cooks and Fourie, 1990; Viles, 1995; Banfield et al., 1999; Viles, 2001; Stretch and Viles, 2002; Souza-Egipsy et al., 2004; Gordon and Dorn, 2005b), and some may be tempted to remove this erosive force. However, it is often far better to leave lithobionts alone because of their ability to hold rock fragments in place (Gehrmann et al., 1988; Bjelland and Thorseth, 2002). Simply killing the lithobionts can end up 'releasing sediment behind a dam', allowing millimetres to centimetres of weathered fragments to erode in a short time (e.g. Fig. 7.6B). Another reason to why it is often better to leave lithobionts alone is because some have an ability

to case harden surfaces (Viles and Goudie, 2004); others can help generate a protective coating of silica glaze, (Lee and Parsons, 1999); and still others help generate a protective coating of oxalate crust (Beazley et al., 2002; Souza-Egipsy et al., 2004). Thus, while it would be better for the stability of inorganic rock coatings and stone surfaces if lithobionts had never colonized, it is often far worse to intervene and use chemical or mechanical means to remove firmly-established lithobionts.

### ***Fifth-Order Process: Rock Varnish***

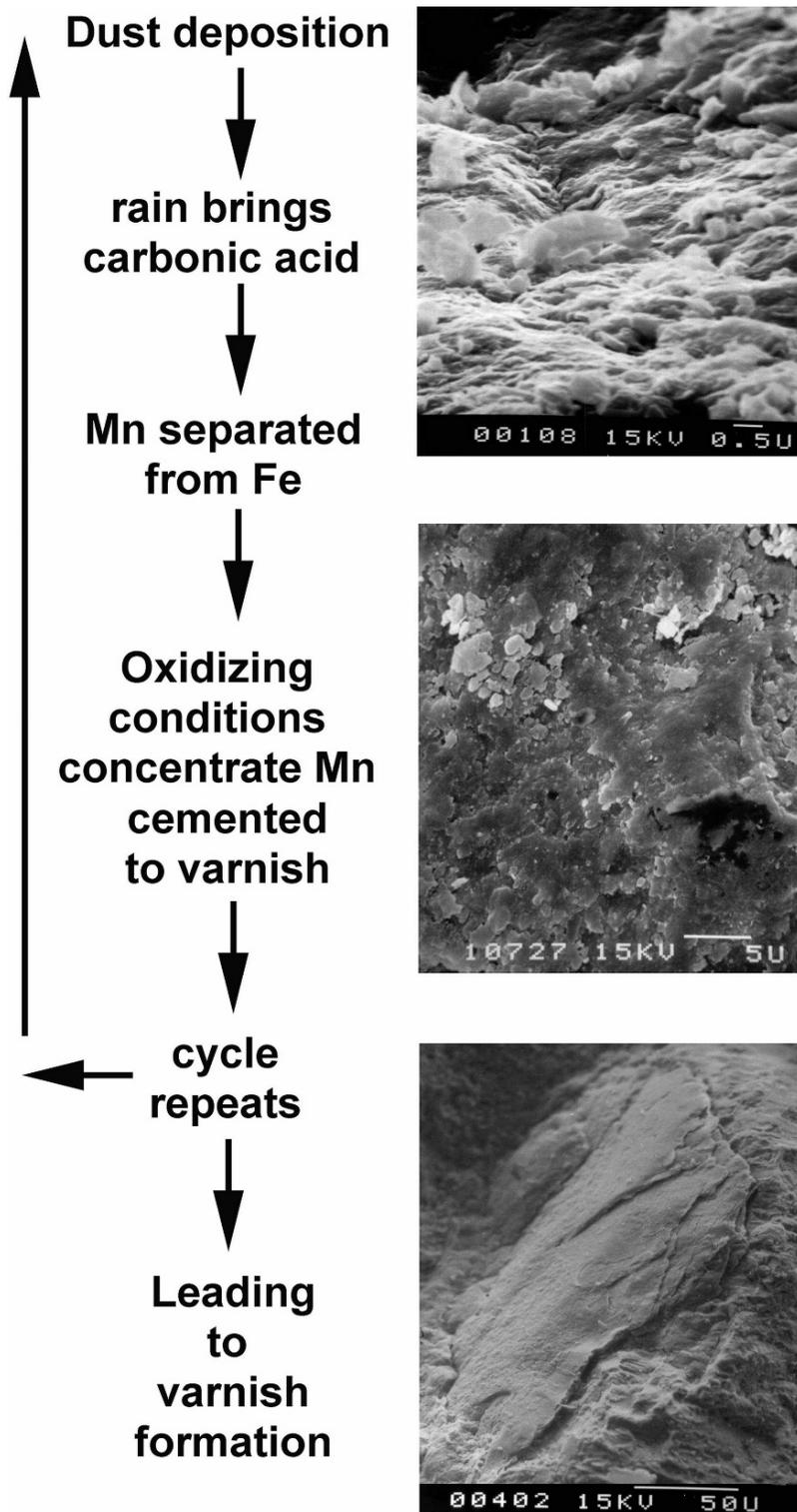
The most important aspect of understanding rock varnish formation was recognized more than two centuries ago, when the great enhancement of manganese (Mn) over iron (Fe) was first identified by Alexander von Humboldt. Mn is typically enhanced over Fe more than a factor of fifty above potential source materials such as dust, soils, water, and the underlying rock (von Humboldt, 1812; Lucas, 1905; Engel and Sharp, 1958; Dorn, 1998). The second most important varnish characteristic that must be explained is the dominance of clay minerals in rock varnish (Potter and Rossman, 1977; Potter and Rossman, 1979c; Dorn and Oberlander, 1982; Krinsley et al., 1990; Krinsley et al., 1995; Israel et al., 1997; Dorn, 1998; Krinsley, 1998; Diaz et al., 2002; Probst et al., 2002; Allen et al., 2004). Clay minerals make up about two-thirds of a typical subaerial varnish, Mn and Fe oxides a quarter, with several dozen minor and trace elements comprising the remainder of this black accretion that can grow to thicknesses exceeding 200  $\mu\text{m}$ .

The composition of rock varnish must be tied to and explained by processes that fix Mn and Fe. Even though clay minerals abound in desert dust that falls on varnished rocks, it is the fixation of clays by Mn-minerals (Potter and Rossman, 1977; Potter and Rossman, 1979a; Potter and Rossman, 1979c) that explains why the dust remains cemented onto rock surfaces for millennia. Although minor and trace elements arrive already adsorbed to the desert dust, many are enhanced by the scavenging properties of Mn-Fe oxyhydroxides (Forbes et al., 1976), redistributed by wetting (Thiagarajan and Lee, 2004). Thus, all of the major, minor, and trace components of varnish depend on the biogeochemical barrier that fixes Mn and Fe.

Four general conceptual models have been proposed to explain varnish formation. The first model that saw general acceptance for almost a century invokes abiotic geochemical processes (Linck, 1901; Engel and Sharp, 1958; Hooke et al., 1969; Moore and Elvidge, 1982; Smith and Whalley, 1988) to increase Mn:Fe ratios two to three orders of magnitude above concentrations found in dust and rock material. Small pH/Eh fluctuations to more acid conditions dissolve Mn but not Fe (Krauskopf, 1957). The Mn released by slightly acidic precipitation is then fixed in clays after water evaporation or an increase in pH, as idealized in Fig. 7.8.

Although an abiotic geochemical barrier to Mn has not yet been falsified, there are a number of varnish characteristics that are incompatible with this model. First, varnishes are found in environments simply too wet and acidic to oxidize Mn (Dorn, 1998). Second, rock varnish is not very common in environments, such as coastal fog deserts or the rainshadows of Mauna Loa in Hawai'i, where repeated pH fluctuations would be at their maximum. Third, there is no extreme rate-limiting step in the abiotic model. Multiple dust deposition and carbonic acid wetting iterations take place annually, even in drought years. A bit of Mn leached from dust with each wetting event would generate varnish accretion hundreds to tens of thousands times faster than rates seen in typical varnishes (Dorn, 1998; Liu and Broecker, 2000; Liu and Broecker, 2007). While abiotic processes are involved in clay cementation and in trace-element enhancement, and while some abiotic oxidation may prove to be important in some locales, these and other characteristics of rock varnish are incompatible with an abiotic geochemical barrier to Mn transport.

The second general model holds that lithobionts or their organic remains produce and bind the constituents of varnish, including Mn. Lichens (Laudermilk, 1931; Krumbein, 1971), cyanobacteria (Scheffer et al., 1963; Krumbein, 1969), microcolonial fungi (Staley et al., 1982), pollen (White, 1924), peptides (Linck, 1928), refractory organic fragments (Staley et al., 1991), gram-negative bacteria (Drake et al., 1993; Sterflinger et al., 1999), gram-positive bacteria (Hungate et al., 1987), amino acids from gram-positive chemo-organotrophic bacteria (Nagy et al., 1991; Perry et al., 2004), fatty acid methyl esters (Schelble et al., 2005), a host of gram-negative Proteobacteria groups and Actinobacteria



**Fig. 7.8** The abiotic model of varnish formation postulates that acid solutions separate divalent  $Mn^{2+}$  from dust or tiny rock fragments that come to rest on surfaces. Then, oxidiz-

ing conditions trap the  $Mn^{4+}$  in varnish. This cycle would then repeat thousands of times to produce a  $100\ \mu m$  thick varnish

(Kuhlman et al., 2005), and a variety of microbial forms (Jones, 1991; Allen et al., 2004; Benzerara et al., 2006) are found on, in, or under rock varnish.

The vast majority of these lithobionts do not play a role in the fixation of Mn or Fe, and many of them actively erode varnish (Figs. 7.6 and 7.7). Because there are so very many adventitious organisms and organic remains associated with varnish, and because Mn-oxidizing organisms cultured from rock varnish (Krumbein and Jens, 1981; Palmer et al., 1985; Hungate et al., 1987) may not necessarily be those that form varnish, the only reliable evidence for a biotic origin of varnish must come from *in situ* observations of microbial forms coated with enhanced Mn and Fe (Dorn and Oberlander, 1981, 1982; Dorn et al., 1992; Dorn and Meek, 1995; Dorn, 1998; Krinsley, 1998). Such forms resemble budding bacteria that grow very slowly.

The most recent proposal to explain varnish formation is silica binding (Perry and Kolb, 2003; Perry et al., 2005; Perry et al., 2006) where silica is dissolved from dust and other mineral matter. The silica then gels and condenses, 'baking black opal in the desert sun' (Perry et al., 2006). This process, however, cannot produce rock varnish formation, since no aspect of the silica binding model explains either Mn enhancement in varnish or the birnessite-family minerals observed in varnish (Potter, 1979; Potter and Rossman, 1979a; Potter and Rossman, 1979b; McKeown and Post, 2001; Probst et al., 2001). The silica binding model also fails to explain slow rates of varnish accretion, since silica precipitation in silica glaze forms in years to decades, not millennia required by varnish. Other problems with silica binding include: not being able to explain the dominance of clay minerals; not accommodating the geography of rock coatings, being unable to answer the simple question of why would silica glazes dominate on Hawaiian lava flows (Curtiss et al., 1985; Gordon and Dorn, 2005b), but not rock varnish; and the 'baking' requirement fails to explain varnishes that grow in cold and dark places (Anderson and Sollid, 1971; Douglas, 1987; Dorn and Dragovich, 1990; Whalley et al., 1990; Dorn et al., 1992; Douglas et al., 1994; Villa et al., 1995; Dorn, 1998).

At the present time, a polygenetic model (Fig. 7.9) is the only proposed hypothesis that explains existing criteria (Table 7.2). As the polygenetic name suggests, rock varnish formation derives a combination of processes, where slow-growing bacteria fix Mn and Fe that is then abiotically cemented by clay minerals. Simply

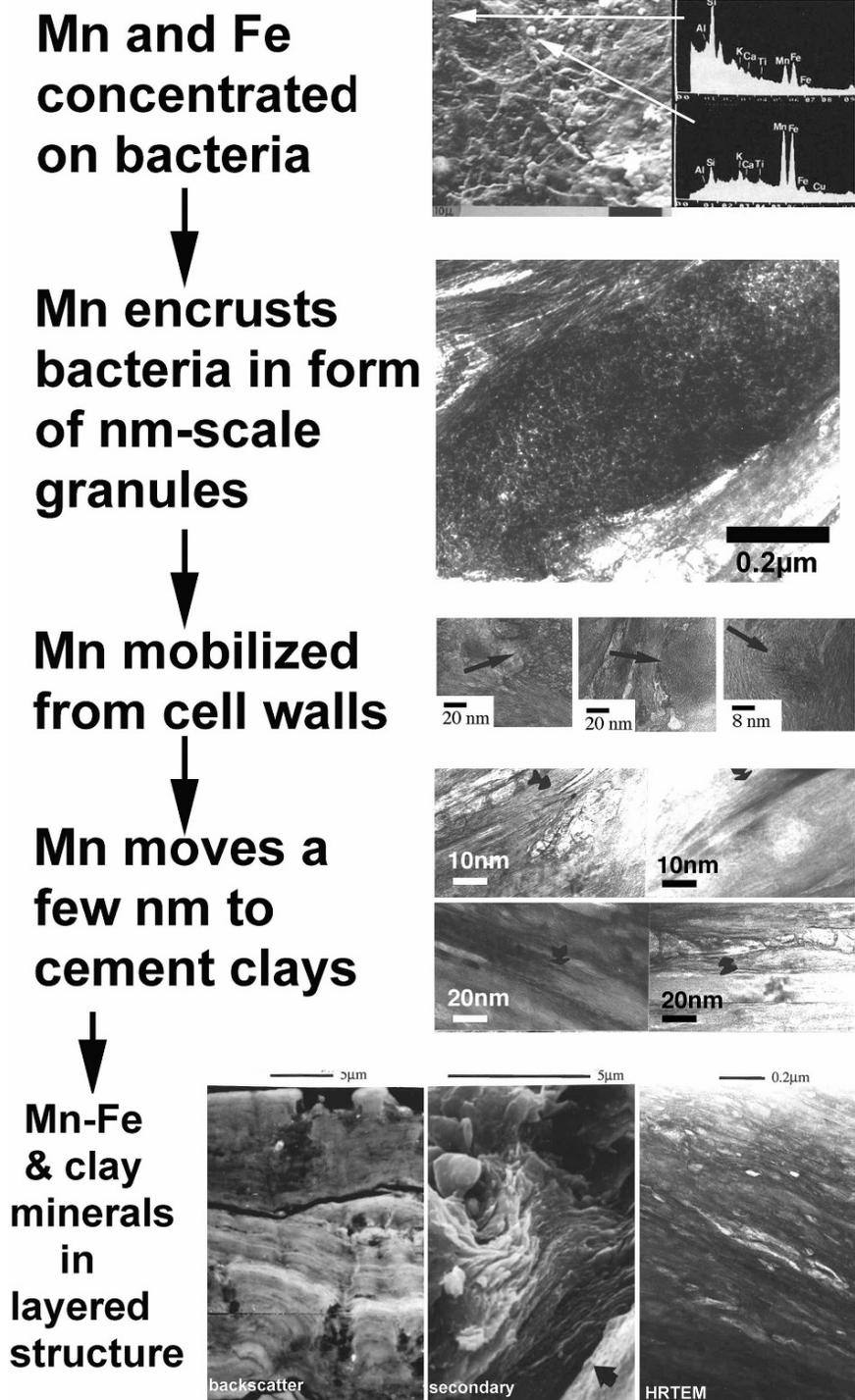
put, bacteria create the barrier to the movement of Mn. Bacteria concentrate Mn and Fe in fairly equal proportions in less alkaline times, but less Mn is enhanced in conditions of greater alkalinity. The geochemical barrier on bacterial casts breaks down over time, as acidic water slowly dissolves Mn and Fe. The resultant nanometre-scale granular fragments of Mn and Fe then move nanometres into the interstratified clay minerals deposited as dust on rock surfaces (Fig. 7.9). This process was predicted (Potter, 1979: 174–175) without benefit of the high resolution transmission electron microscopy imagery that showed the predicted steps of varnish formation (Dorn, 1998; Krinsley, 1998).

### **Fifth-Order Process: Silica Glaze**

Hydrated silica (opal) accretes on the surfaces of rocks in all deserts (Stevenson, 1881; Hobbs, 1917; Jessup, 1951; Fisk, 1971; Haberland, 1975; Butzer et al., 1979; Farr and Adams, 1984; Bourman and Milnes, 1985; Watchman, 1985; Zhu et al., 1985; Smith and Whalley, 1988; Fullagar, 1991; Weed and Norton, 1991; Smoot, 1995). The mineralogy of the silica is most often x-ray amorphous (Curtiss et al., 1985), but some have noted silica minerals such as mogonite (Perry et al., 2006).

The general appearance varies quite a bit, ranging from almost transparent to opaque, from a charcoal black to ivory (Fig. 7.10A), and from dull to highly shiny (Fig. 7.10D). Thicknesses range from microns (Fig. 7.10E, D) to almost a millimetre, even on the same sample (Fig. 7.10F). Controls on thickness are not well understood, but they include the type of silica glaze, moisture conditions, and whether or not the silica glaze had experienced recent spalling along intra-glaze fractures. Over time, a silica glaze slow rock dissolution (Gordon and Dorn, 2005b) and silica movement into the underlying rock can case harden a weathering rind (Figs. 7.10B and 7.5A–C).

Silica glazes fall into six general categories (Dorn, 1998: 294–312), based on the abundance of non-silica constituents of iron, aluminum, and micron-sized bits of mineral detritus. Type I accretes as a fairly homogeneous and texturally uniform deposit of amorphous silica (Fig. 7.10B, C2; bottom glaze in Fig. 7.5G, H). Type II hosts a large amount of mineral detritus, where the silica acts as a glue for



**Fig. 7.9** The polygenetic model of rock varnish formation (Dorn, 1998; Krinsley, 1998) combines bacterial enhancement of Mn and Fe with abiotic fixation of the Mn by clay minerals. The process starts with bacteria fixing Mn on sheaths. Wetting events dissolve Mn, creating a granular nanometre-scale texture. The desert dust supplies interstratified clay minerals, and the nanometre-sized fragments of Mn-oxides fit into the weath-

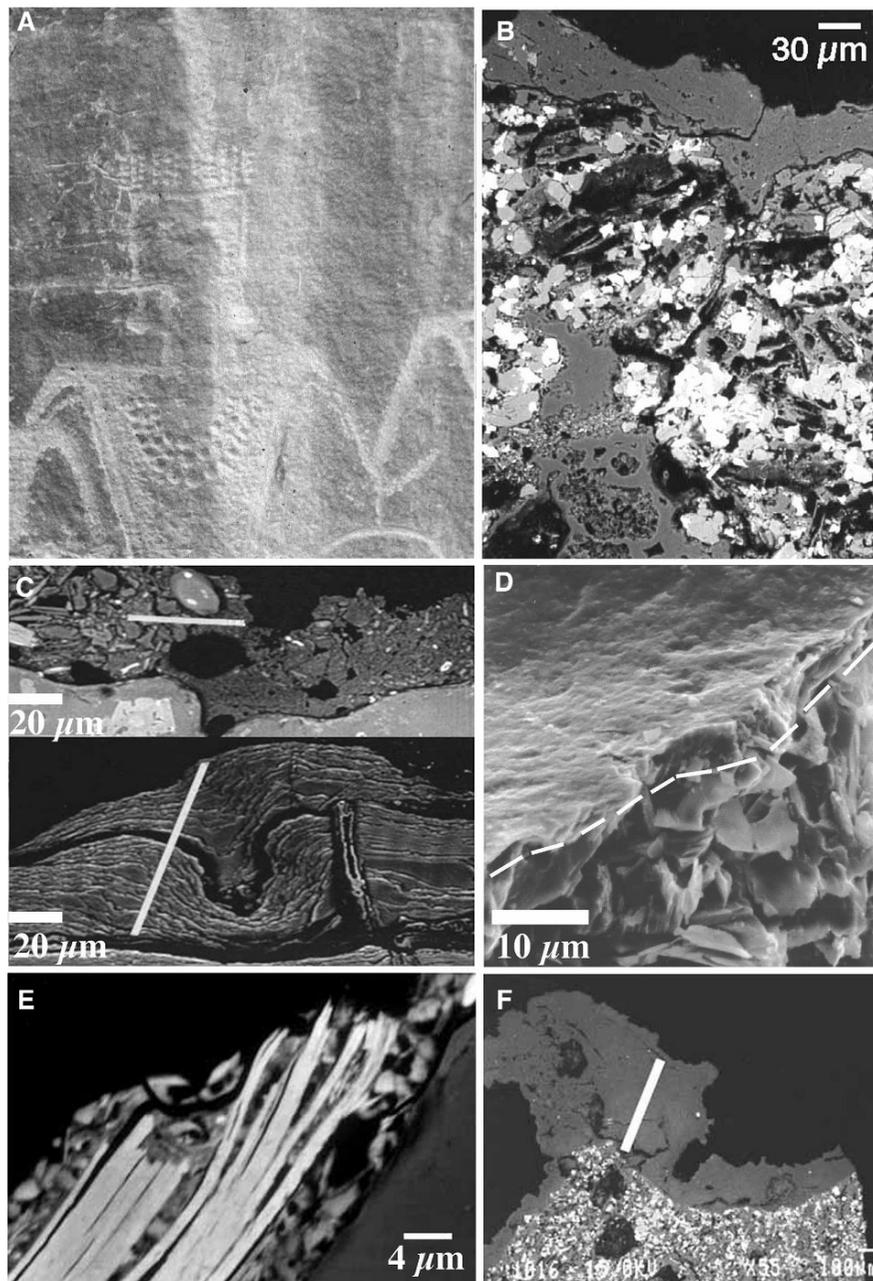
ered edges of these clay minerals, tightly cementing clays. The hexagonal arrangements of the oxygens in the tetrahedral or octahedral layers forms a template for the crystallization of layered birnessite, the Mn-mineral found most frequently in varnish. The net effect is highly layered texture at micrometre and nanometre scales imposed both by clay minerals and the cementing Mn-oxides

**Table 7.2** Key criteria of rock varnish formation explained by polygenetic model

Criteria	The polygenetic model explains . . .
Accretion Rate	. . . typical rates of accretion on the order of a 1-10 $\mu\text{m}$ per millennia (Dorn, 1998; Liu and Broecker, 2000). Although faster-growing varnishes occur (Dorn and Meek, 1995), varnish accretion rates based on studies of over $10^5$ microbasins (Liu, 2003; Liu, 2008; Liu and Broecker, 2007) demands the extreme rate-limiting step of budding bacteria concentrating Mn very slowly.
Clay Minerals	. . . the dominance of clay minerals in rock varnish (Potter and Rossman, 1977; Potter and Rossman, 1979c; Dorn and Oberlander, 1982; Krinsley et al., 1990; Krinsley et al., 1995; Israel et al., 1997; Dorn, 1998; Krinsley, 1998; Diaz et al., 2002; Probst et al., 2002; Allen et al., 2004), because the granular fragments of nanometre-Mn fragments from bacterial casts cement the clays to rock surfaces.
Fe behavior	. . . the differential enhancement of iron in different varnish layers (Liu et al., 2000; Broecker and Liu, 2001; Liu and Broecker, 2007) and different places (Adams et al., 1992; Dorn, 1998; Allen et al., 2004), because changes in alkalinity over time and space affect the ability of the bacteria to concentrate Mn.
Laboratory creation	. . . the creation of artificial varnish coatings by bacteria (Dorn and Oberlander, 1981; Krumbein and Jens, 1981; Dorn and Oberlander, 1982; Jones, 1991) may considered by some to be a vital criteria. However, given the extraordinary time scale jump between any laboratory experiment and natural varnish formation, and the extreme rate-limiting step involved in natural varnish formation, rigid application of this criteria may be problematic.
Lithobionts and organic remains	. . . the occurrence of different types of lithobionts and the nature of organic remains. The Mn-oxidizing bacteria actually making the varnish co-exist with these more abundant adventitious organisms, but the adventitious lithobionts are competitors.
Mn Enhancement	. . . the enhancement Mn typically more than a factor of fifty above potential source materials (von Humboldt, 1812; Lucas, 1905; Engel and Sharp, 1958), because the bacteria are seen <i>in situ</i> enhancing Mn.
Mn-mineralogy	. . . Mn-mineralogy characteristic of birnessite-family minerals (Potter, 1979; Potter and Rossman, 1979a; Potter and Rossman, 1979b; McKeown and Post, 2001; Probst et al., 2001), because the nanometre-scale fragments derived from bacteria fit well into the interstratified clays where they form layered phases such as birnessite.
Not just a few samples	. . . observations at sites around the world, because <i>in situ</i> enhancement of Mn-enhancing bacteria are seen globally (Dorn and Oberlander, 1982; Dorn et al., 1992; Dorn and Meek, 1995; Krinsley et al., 1995; Dorn, 1998; Krinsley, 1998; Spilde et al., 2002).
Paucity of microfossils	. . . the extremely infrequent occurrence of preserved microfossils, because the Mn-casts of bacteria are broken down by the varnish formation process Examination of $10^4$ sedimentary microbasins (Liu, 2003; Liu, 2008; Liu and Broecker, 2007), and decades of research has generated only a few observations of microfossils (Dorn and Meek, 1995; Dorn, 1998; Krinsley, 1998; Flood et al., 2003), just what would be expected from the polygenetic model.
Rock Coating Geography	. . . why rock varnish grows in one place and other rock coatings elsewhere. Over a dozen major types of coatings form on terrestrial rock surfaces, a plethora of varieties for each rock coating. The polygenetic model explains this geography (Dorn, 1998).
Varnish Geography	. . . why different types of rock varnishes occur where they occur (Dorn, 1998).
Laminations (VML)	. . . the revolution in varnish microlamination (VML) understanding. Over ten thousand sedimentary microbasins analyzed by Liu (Liu, 1994; Liu and Broecker, 2000; Liu et al., 2000; Broecker and Liu, 2001; Liu, 2003; Liu, 2008; Liu and Broecker, 2007), a method subject to blind testing (Marston, 2003), reveals clear late Pleistocene and Holocene patterns in abundance of major varnish constituents connected to climate change. The characteristics of this single largest varnish data set are explained by the polygenetic model by changes in wetness altering the alkalinity of desert surfaces (Dorn, 1990; Drake et al., 1993; Diaz et al., 2002; Lee and Bland, 2003).

all of the bits and pieces of rock fragments coming to rest on a rock surface (Fig. 7.10C1; upper glaze in Fig. 7.5G, H). Silica is still dominant in Type III, but iron and aluminum concentrations are substantive, ranging from 5–40 oxide weight percent for FeO and 5–30% for  $\text{Al}_2\text{O}_3$ . Type III often has a dirty brown appearance and is found extensively in Australia

(Watchman, 1992), in the Negev (Danin, 1985), in dryland Hawai'i (Curtiss et al., 1985), and in wetter climates (Matsukura et al., 1994; Mottershead and Pye, 1994). Types IV and V are about half silica, but aluminium is the only other dominant component in Type IV, while iron is the only other major constituent in Type V. Type VI glazes are dominated by  $\text{Al}_2\text{O}_3$



**Fig. 7.10** (continued)

that sometimes reaches more than 50% by weight (Fig. 7.10F). These aluminium glazes are not well documented in the literature, and the reasons for the major enhancement of aluminium is not well understood.

Unlike rock varnish that typically accumulates only a few microns over a millennium, silica glazes can

form very rapidly. Several different types have formed on historic lava flows in Hawai'i (Fig. 7.1) (Farr and Adams, 1984; Curtiss et al., 1985; Gordon and Dorn, 2005b). I have measured silica glaze formation within two years in the Owens Valley of eastern California (Fig. 7.10E) and within two decades on historic surfaces in the Mojave and Sonoran Deserts.

In addition to rapid formation rates, silica glaze also mechanically spalls along internal fractures. Thus, connecting thickness to age is extremely problematic.

Silica glazes form where there is a geochemical barrier to the migration of mobile silica. Since silica is ubiquitous in the host rock, dust, precipitation, groundwater seepage, and even opal phytoliths (Folk, 1978), there is no shortage of raw silica. Similarly, there is no great geochemical mystery in explaining silica movement to coated rock surfaces, since silica is easily dissolved in terrestrial weathering environments (Krauskopf, 1956).

Exactly how silica glaze is fixed to rock surfaces probably involves several different processes. The most common view is that monosilicic acid ( $\text{Si}(\text{OH})_4$ ) precipitates as a gel (Krauskopf, 1956; Williams and Robinson, 1989), and experiments indicate that dissolved silica does precipitate as amorphous silica (Paraguassu, 1972; Whalley, 1978). Others argue for the importance of evaporation (Merrill, 1906; Fisk, 1971; Watchman, 1992) and complexing with organic matter (Watchman, 1992; Perry and Kolb, 2003; Perry et al., 2006). Still others have made arguments that different lithobionts can play a role in forming silica glazes (Fyfe et al., 1989; Urrutia and Beveridge, 1994; Lee and Parsons, 1999).

The above mechanisms are not mutually exclusive, and the great variety of silica glaze types (Dorn, 1998: Ch13) do argue for different processes creating different geochemical barriers to silica migration. Precipitation of silicic acid gels certainly makes sense for Type I silica glazes, for example, since the uniform texture and chemistry of these homogeneous glazes would be consistent with this simple silica-precipitation process.

Type II through Type VI silica glazes, however, call for processes able to explain variable concentrations of aluminium and iron. The explanation for abundant aluminium probably rests with soluble aluminium silicate complexes ( $\text{Al}(\text{OSi}(\text{OH})_3)_2^+$ ). Soluble Al-Si complexes are ubiquitous at the water-rock interface (Lou and Huang, 1988; Browne and Driscoll, 1992), and they are easily released by weathering of phyllosilicate minerals (Robert and Tessier, 1992). The geochemical fixation of Al-Si complexes probably requires very gentle wetting events (Zorin et al., 1992) such as drizzle, as opposed to harsh convective storms. Once an initial silica glaze establishes itself, the silica acid or soluble Al-Si complex then more readily bonds to the pre-existing silica glaze (Casey et al., 1993). Other elements such as iron might be explained by strong adherence to silica surfaces through Fe-O-Si bonds (Scheidegger et al., 1993). The key to identifying processes responsible for the geochemical barrier rests in linking process to the type of silica glaze.

### ***Fifth-Order Process: Other Coatings***

The nature of this chapter does not permit a thorough explanation of the origin of every desert rock coating. Such information is presented in book form (Dorn, 1998). This section, however, summarizes explanations for the accumulation of four other desert rock coatings.

Iron films (Fig. 7.11A, D) are ubiquitous in and out of deserts, with at least three general categories. Type I iron films are mostly homogeneous iron with few other constituents (Fig. 7.11D). Type II iron films

**Fig. 7.10** Silica glaze in different desert settings. **A.** This central Utah petroglyph carved into sandstone is covered by light and dark stripes of silica glaze. **B.** Backscattered electron microscope image of silica glaze on the boulder presented in Fig. 7.3E, collected from the arid rainshadow of Kaho'lawe Island, Hawai'i. Its composition of more than 90% silica moved through pore spaces into the underlying rock, filling pores and fractures. The net effect of case hardening is seen in Fig. 7.3E. **C.** Two backscatter images of silica glaze on a lava flow in the arid Ashikule basin, West Kunlun Mountains, Tibetan Plateau. Image C1 illustrates loess cemented by silica where the line indicates electron microprobe measurements of 50–60%  $\text{SiO}_2$ , 5–15%  $\text{Al}_2\text{O}_3$ , and 1–6%  $\text{FeO}$  by weight. Image C2 shows the layer-by-layer deposition of 80–85%  $\text{SiO}_2$  with  $\text{Al}_2\text{O}_3$  only ~5%. **D.** This flat surface, seen by secondary electrons, illustrates an ex-

tremely shiny, dark silica glaze collected from a Nasca trapezoid geoglyph, Peru. Its sheen derives from a combination of the smooth surface and from ~3% Mn. Silica glaze and manganese rock varnish often combine in the shiny black ground-line band (Engel and Sharp, 1958) found on many desert pavement clasts. **E.** Silica glaze can form quite rapidly, in this case from the Owens Valley, eastern California within two years, freezing in place the weathered biotite mineral. **F.** This extremely thick accretion, collected from an opened joint face of Haleakala, Hawai'i, lava flow displays thicknesses ranging from <1  $\mu\text{m}$  to almost a millimetre. The line on this backscattered image indicates the location of an electron microprobe transect along which  $\text{Al}_2\text{O}_3$  values average 44%, but range from 19% all the way to 60% by weight (data table in Dorn, 1998: 311)

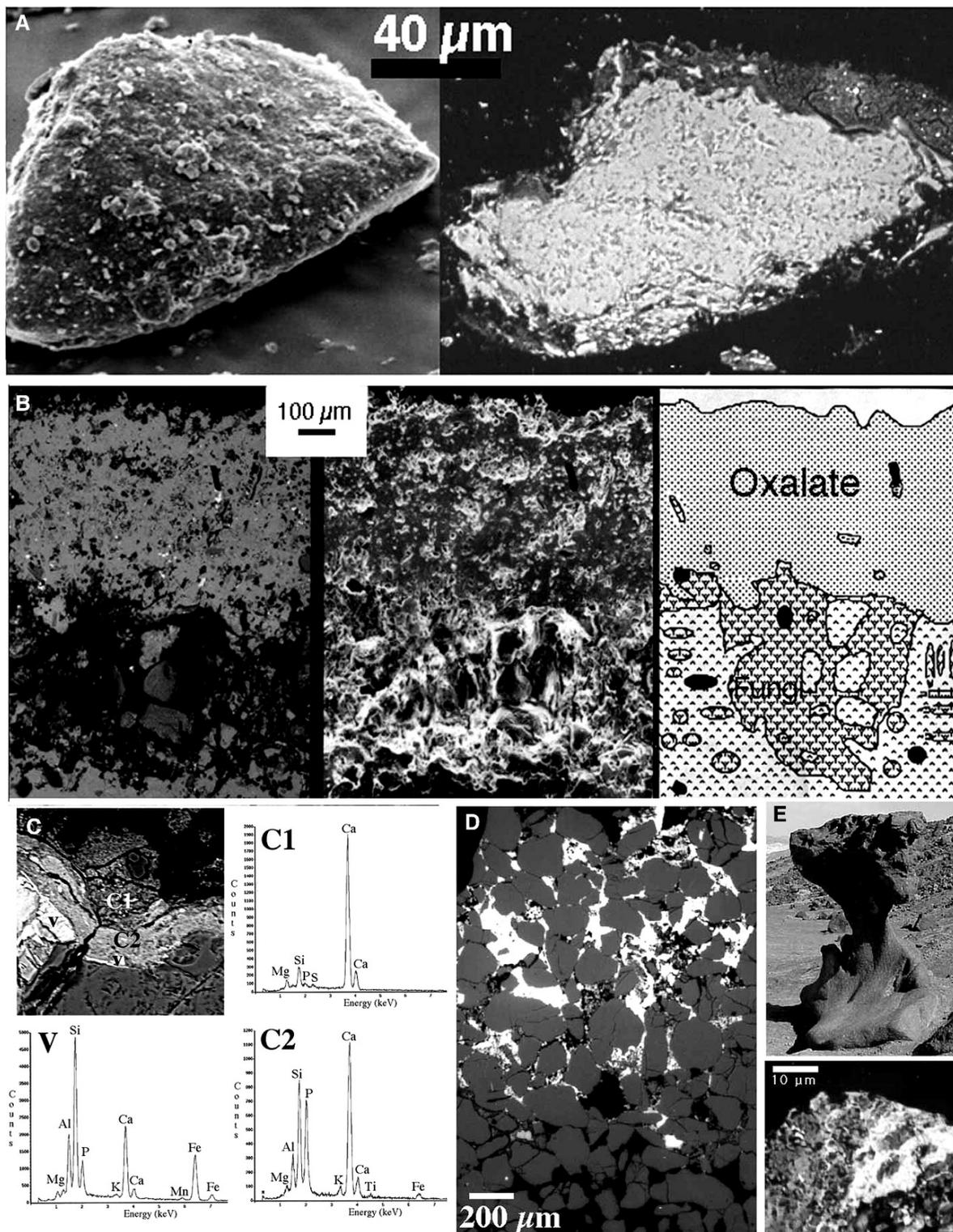


Fig. 7.11 (continued)

include aluminium and silicon as major elements, but still less abundant than iron. In Type III iron provides the orange to red coloration with concentrations of less than a third iron oxide by weight. The bulk of the coating comes from clay minerals (Fig. 7.11A).

The causes of iron films all involve biotic processes (Dorn and Oberlander, 1982; Adams et al., 1992; Konhauser et al., 1993; Schiavon, 1993; Konhauser et al., 1994; Dixon et al., 1995; Sterflinger et al., 1999; Fortin and Langley, 2005). Unlike rock varnish, however, no need exists for lithobionts to immobilize the iron. The barrier to iron movement on rock surfaces can simply be purely abiotic oxidation of iron, since the inorganic oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  is rapid above a pH of 5 (Collins and Buol, 1970; Marshall, 1977; Holland, 1978). Desert rock surfaces typically have pH values well above 5 (Dorn, 1990). However, the processes behind iron film fixation are probably far more complex, perhaps involving the formation of chemical Fe-O-Si bonds in Type II iron films (Hazel et al., 1949; Scheidegger et al., 1993), perhaps involving photooxidation (McKnight et al., 1988) in Type I iron films, and likely involving interaction with interstratified clays in Type III iron films much like rock varnish (cf. Fig. 7.9).

Oxalate crusts (Figs. 7.1 and 7.11B) are far less common than any of the aforementioned rock coatings, and they are more frequently found in wetter microenvironments such as locales of water flow. Oxalate minerals include carbon, oxygen and a divalent cation, such as magnesium, calcium, or manganese. Whewellite ( $\text{CaC}_2\text{O}_4 \bullet \text{H}_2\text{O}$ ) is the most common mineral. Oxalate crusts can vary considerably in appearance, including white, yellow, orange, red, red-brown, brown or black colours. Thickness also ranges considerably, from microns to a few millimetres. Al-

though the carbon can come from inorganic materials (Zák and Skála, 1993) and a host of plant and microbial sources (Lowenstam, 1981; Lapeyrie, 1988; Watchman, 1990; Cariati et al., 2000; Zhang et al., 2001), most of the oxalate found in deserts likely derives from the decay of lichens that synthesize the oxalate (Del Monte et al., 1987; Whitney and Arnott, 1987; Russ et al., 1996; Bjelland et al., 2002; Bjelland and Thorseth, 2002; Souza-Egipsy et al., 2004). After oxalate minerals crystallize, two additional steps are still required to form desert oxalate crusts. First, the oxalate must be mobilized away from the source, most typically by water flowing over a rock face away from lichens. Second, the oxalate must re-precipitate on desert rock surfaces; it is this last step that has eluded an explanation more detailed than evaporation.

Carbonate crusts (Figs. 7.2B and 7.11C) coat desert rocks in a variety of settings, including freshwater tufa, travertines and other carbonate deposits (Viles and Goudie, 1990; Carter et al., 2003), caves (Fyfe, 1996), lake shorelines (Benson, 1994), tropical beaches (Krumbein, 1979), subaerial rock faces mixed with clays and silica (Conca and Rossman, 1982; Conca, 1985; Dorn, 1998), and soils (Goudie, 1983). The mechanism of carbonate fixation varies greatly depending on environment, but both biotic (Krumbein, 1979; Viles and Goudie, 1990; Folk, 1993; Rodriguez-Navarro et al., 2003) and abiotic (Vardenoe, 1965; Gile et al., 1966; Bargar, 1978; Dandurand et al., 1982; Dunkerley, 1987; Benson, 1994) processes are invoked as key mechanisms in creating a geochemical barrier to carbonate movement.

Salt crusts (Fig. 7.11E) also appear as rock coatings in certain desert settings (Oberlander, 1988), but particularly associated with efflorescence (Goudie and Cooke, 1984) on porous rock surfaces (Smith, 1994;

**Fig. 7.11** Other types of rock coatings. **A.** Iron film illustrated by secondary (*left*) and backscatter (*right*) electron microscope images of an orthoclase feldspar sand grain from the bright orange Parker Dune Field, western Arizona. Clay particles are cemented to sand grains by iron oxides. **B.** Oxalate crust illustrated by backscattered (*left*) and secondary (*middle*) electron microscope images of a sandstone face in the semi-arid Black Hills, Wyoming. Small pockets of rock varnish also occur, and a fibrous fungal mat has grown in the weathering rind underneath the rock coating. **C.** Carbonate crust (C1 and C2) that formed on top of a rock varnish (v), but only after a boulder had been flipped to form a geoglyph at least  $8440 \pm 60$   $^{14}\text{C}$  years ago, according

to a radiocarbon age on the more silica-rich (C2) inner carbonate crust (Cervený et al., 2006). **D.** Iron film that impregnated sandstone at Petra, Jordan (Paradise, 2005). The iron film seen as bright white in this backscattered electron microscope image is a rock coating, but it also acts as a case hardening agent as the iron remobilizes and impregnates the host sandstone. **E.** At Mushroom Rock (E1), Death Valley, salt exists as efflorescent coatings seen on the surface, and as subflorescent deposits, as shown in the backscattered electron micrograph of barite (bright white) invading host basalt (mostly plagioclase) minerals (E1). Halite ( $\text{NaCl}$ ) and celestite ( $\text{SrSO}_4$ ) also coat surfaces on Mushroom Rock (Meek and Dorn, 2000)

Smith and Warke, 1996). Sulfates encrust desert surfaces (Goudie, 1972; Watson, 1988; Drake et al., 1993; White, 1993b). Nitrate can also coat rock surfaces (Mansfield and Boardman, 1932; Ericksen, 1981), as can phosphate skins (Trueman, 1965; Zanin, 1989; Konhauser et al., 1994; Arocena and Hall, 2003) (Fig. 7.3D).

## Use of Rock Coatings as a Chronometric Tool

Desert geomorphologists and geoarchaeologists have long used rock coatings as indicators of the antiquity of stone surfaces (Oberlander, 1994). Visual changes in such features as alluvial-fan sequences (Fig. 7.2B) (McFadden et al., 1989; Bull, 1991), the undersides of desert pavement clasts (Helms et al., 2003), inselberg debris slopes (Oberlander, 1989), glacial moraines (Staiger et al., 2006), and mass wasting (Moreiras, 2006) have all led to an intuitive belief that rock coatings can be used as way of obtaining minimum ages for erosive processes that ‘wiped clean’ prior rock coatings.

Very few investigators utilizing rock coatings as a chronometric tool, however, have written about the possibility that they may be including in their analyses ‘inherited’ rock coatings or that they may be sampling completely different types of coatings that look similar (McFadden et al., 1989; Harry et al., 1992; Reneau, 1993; Perry et al., 2006). I only present here chronometric tools that are clearly constrained by a landscape geochemistry perspective, grounded in hierarchical rock coating processes.

## Rock Varnish

Rock varnish has been studied more extensively than any other rock coating, including more than a century of exploration on its use as a possible method to date desert landforms (Dorn, 1998: Ch 10). Several different dating methods have been proposed (Table 7.3). Yet up until only the last few years, all such proposed techniques have been highly experimental — tried in only a few selected circumstances and only rarely subjected to blind testing (Loendorf, 1991; Marston, 2003). To

turn any dating method into a technique that can be practised widely requires the study of thousands of samples.

This level of extensive research has recently taken place only for the use of rock varnish microlaminations (VML) as a chronometric and palaeoclimatic research tool in desert geomorphology. The VML of orange (Mn-poor) and black (Mn-rich) layers accreted in subaerial varnishes (Perry and Adams, 1978; Dorn, 1990; Cremaschi, 1996; Leeder et al., 1998) can now be used with regularity and consistency. This revolution in varnish dating took detailed analyses of over ten thousand sedimentary microbasins studied through a decade of painstaking scholarship, laboratory work, and testing by Tanzhuo Liu (Liu, 1994; Liu and Dorn, 1996; Liu and Broecker, 2000; Liu et al., 2000; Zhou et al., 2000; Broecker and Liu, 2001; Liu, 2003; Marston, 2003; Liu, 2008; Liu and Broecker, 2007; Liu and Broecker, 2008a, 2008b). A complete discussion of the varnish microlaminations revolution for desert geomorphology is summarized in Chapter 21.

Some other rock varnish dating methods (Table 7.3) might also reach this stage of regular and consistent use. Yet, that next step would similarly require the level of funding and painstaking dedication achieved for the VML method.

## Carbonate

Carbonate crusts are used extensively as a chronometric tool in deserts. Tufa crusts are used to radiocarbon date palaeoshorelines (Benson et al., 1995). Pedogenic carbonate crusts, with an awareness of confounding factors, can inform on palaeoclimate (Monger and Buck, 1999) and can date soils through radiocarbon, uranium-series, and its gradual accumulation (Gile et al., 1966; Machette, 1985; Chen and Polach, 1986; Bell et al., 1991; Amundson et al., 1994). Pedogenic carbonate can also serve as a vessel for accumulating cosmogenic  $^{36}\text{Cl}$  (Liu et al., 1994).

The major difficulty in using carbonate crusts derives from uncertainties surrounding a vital assumption that the sampled carbonate deposit is ‘closed’ to post-depositional modification. Virtually all carbonate crust chronometric methods require that nothing happens to the carbonate minerals once they are deposited. Yet, because carbonate is extremely mobile in the terres-

**Table 7.3** 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 has also been used in such places as China (Zhang et al., 1990), Israel (Patyk-Kara et al., 1997), and 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	20th 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 20th 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; Wayne et al., 2006) with no publications yet critical of the technique that can discriminate 20th century from pre-20th 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).
<sup>14</sup> 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, 1986a) and eastern California (Smith and Turner, 1975; Cervený et al., 2006).
<sup>14</sup> 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-dates 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; Whitley and Simon, 2002b).
<sup>14</sup> C oxalate	The inorganic mineral oxalate (e.g., whewellite: CaC <sub>2</sub> O <sub>4</sub> · H <sub>2</sub> O) 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	Since 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.
Laminations (VML)	Climate fluctuations change the pattern of varnish microlaminations (VML). The confidence level is high, because the method (Liu, 2003; Liu, 2008; Liu and Broecker, 2007) has been replicated in a rigorous blind test (Marston, 2003), and the method is based on analyses of over ten thousand rock microbasins.

trial weathering environment, closed systems are rare (Stadelman, 1994). Some of the most stable components of carbonate crust are not actually carbonate, but silica associated with and sealing carbonate (Ludwig and Paces, 2002) and playing a role in generating laminations that are better for dating (Wang et al., 1996).

The great potential of carbonate crusts to serve as a geomorphic tool, depends on the identification of

those microsettings where silica helps generate a less open system. This is illustrated where carbonate crusts undergo a change in environment such that they actually interlayer with rock varnish. Radiocarbon dating carbonate superimposed over rock varnish (Smith and Turner, 1975; Dragovich, 1986a) was originally thought to be a very rare possibility. However, both anthropogenic and natural processes can flip boulders,

generating dating potential when the subaerial position of rock varnish and pedogenic position of carbonate crusts are inverted (Cervený et al., 2006). An example comes from rock cairns (cf. Fig. 7.2B) where carbonate crusts are exposed to the atmosphere and also where formerly varnished surfaces are thrust deep enough into the soil to form a carbonate crust (Fig. 7.11C). Dating the carbonate formed over the varnish provides a minimum age for the rotation, and the most reliable minimum ages for this flipping process derives from the silica-rich laminated carbonate crust (Fig. 7.11C2) (Cervený et al., 2006).

### **Oxalate**

Oxalate crusts (Fig. 7.11B) offer tremendous potential for geomorphic research, because oxalate is a carbon-bearing mineral. Both radiocarbon dating (Russ et al., 1990; Watchman et al., 2005) and stable carbon isotope palaeoclimatic analyses (Russ et al., 2000; Beazley et al., 2002) have yet to reveal the problems of an open system associated with carbonate. Although oxalate dating has yet to be used as a geomorphic tool, having been tried mostly on oxalate crusts formed over rock paintings,  $^{14}\text{C}$  dating provides opportunity to study such topics as mass wasting when an oxalate-streaked face topples and is buried by cliff retreat (cf. Fig. 7.1).

### **Lithobionts**

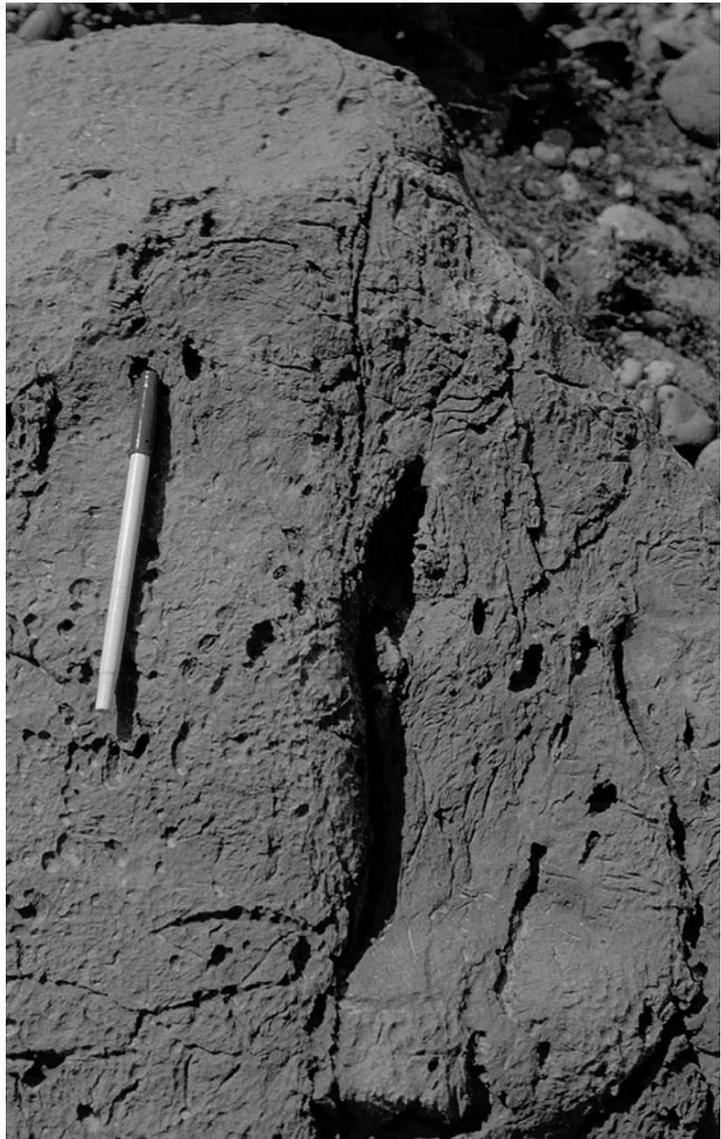
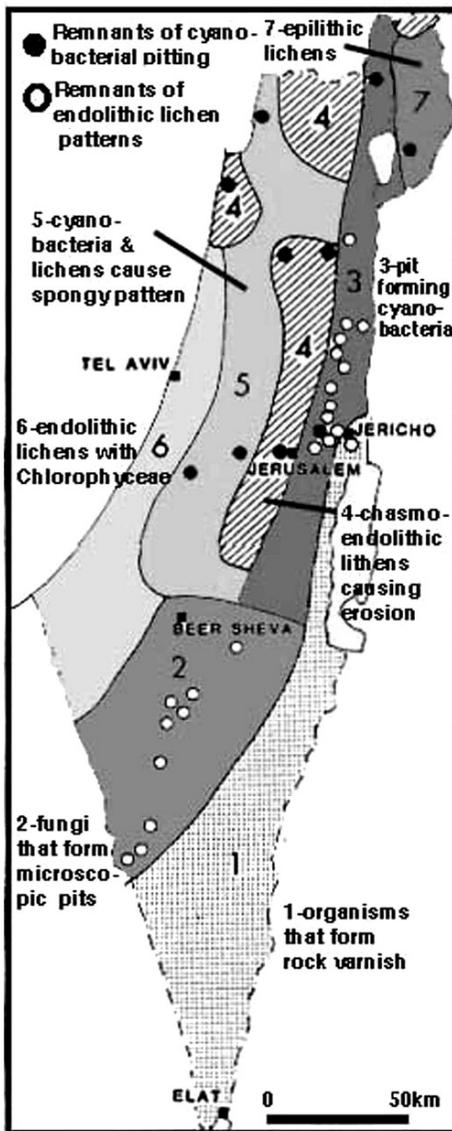
Measuring the progressive growth of lichens or lichenometry has been used extensively in Arctic and alpine settings (Lock et al., 1979; Matthews and Shakesby, 1983; Worsley, 1990). Most investigators focus on the largest lichen, assuming that its size indicates the age of colonization — and ideally substrate exposure. Comparing size against a dating curve yields a calibrated age. Although many lichenometry researchers interpret these dating curves in terms of an initial rapid juvenile growth, biologists believe that the ‘great growth’ is explained by a high mortality rate of early colonists (Loso and Doak, 2006). This difference in the interpretation of empirical curves does not deny the proven utility of this method in cool-wet regions where epilithic lichens thrive (Fig. 7.7).

Deserts lack moisture, placing a severe limitation on the activity of lichens (Fig. 7.7). Thus, lichenometry in drier regions has only seen speculative use, most often focused in archaeology (Joubert et al., 1983). Some work has been completed in semi-arid areas, such as basalt terraces in Lesotho, where methods were modified to study lichen cover on scarp faces (Grab et al., 2005). Lichen growth on rock falls in semi-arid eastern California has been used to infer past tectonic events (Bull, 1995). However, lichenometry has not seen substantive use in desert geomorphology.

Since moisture and rock hardness influence the weathering efficiency of lithobionts (Viles, 1995), it is a logical next step to infer that climatically distinct patterns of weathering might relate to particular climates — assuming that rock type can be controlled. Extensive research in Israel, controlling carbonate lithology, reveals distinctive weathering patterns generated by the different lithobionts of endolithic lichens, epilithic lichens, and cyanobacteria (Fig. 7.12) (Danin et al., 1982; Danin, 1983; Danin and Garty, 1983; Danin et al., 1983). Contemporary lithobiontic weathering in the driest parts of the Negev, for example, only creates small-scale pitting from microcolonial fungi and cyanobacteria, but there are also ‘puzzle pattern’ weathering features on these hyperarid carbonate rocks (Fig. 7.12). These puzzle patterns match forms produced by lichens that only grow in wetter parts of Israel. The conclusion reached was that a former wetter climates fostered the growth of and weathering efficiency of these more mesic lithobionts in the heart of the Negev (Danin, 1985; Danin, 1986). Thus, there exists substantive potential of weathering patterns to map out palaeoclimatic boundaries of desert weathering efficiencies.

### **Future Research Directions**

Academic roots have greatly influenced methods, conclusions and the overall agenda of previous desert rock coating research. For example, the geological focus of researchers in the late 19th and early 20th century on rocks led them to favour the incorrect hypothesis that coatings were ‘sweated’ out of the underlying rock and ‘baked’ on rock surfaces. It was not until electron microscopes showed incredibly distinct contacts



**Fig. 7.12** Generalized map of the distribution of dominant lithiobiontic weathering in Israel (modified from Danin 1986: 245). Rock varnish forming bacteria dominate in the driest parts of Israel, but as moisture increases so does the pattern of carbonate weathering — all the way to far northern Israel where epilithic lichens dominate. The photograph a southern Negev Desert car-

bonate boulder shows centimetre-scale pitting and 'puzzle pattern' weathering forms generated by long-dead and absent lithiobionts made under a wetter climate. Sub-millimetre pitting by microcolonial fungi and cyanobacteria is the contemporary lithiobiont weathering process slowly erasing the palaeoforms

between coating and rock (Potter and Rossman, 1977) that the almost universal accretionary nature of rock coatings came to be fully recognized (Dorn, 1998). Microbial ecologists, in contrast, have concentrated on culturing organisms and studying organic remains in association with rock coatings, with a concomitant

natural tendency to downplay mineralogically driven processes.

Funding has also influenced rock coating research. In an example of the tail of cash wagging the dog of research, NASA's agenda to search for life Mars has driven an explosion of interest in rock varnish

(DiGregorio, 2002; Gorbushina et al., 2002; Johnson et al., 2002; Mancinelli et al., 2002; Allen et al., 2004; Kuhlman et al., 2005; Spilde et al., 2005; Perry et al., 2006; Perry and Lynne, 2006). This is nothing new, since funding and sociological concerns have often driven ‘normal science’ (Fuller, 2000) between paradigm shifts.

It is most unlikely that the most significant rock coating research in the future will rest with targeted agency agendas or within a single disciplinary perspective. Thus, I list the top four interdisciplinary research agendas that I think would have the greatest potential impact on rock coatings research in desert.

- (1) *Use varnish microlaminations (VML) to answer the difficult desert geomorphology questions.* Tanzhuo Liu has just finished a decade of technique development that allows desert geomorphology researchers to date Holocene (Liu, 2008; Liu and Broecker, 2007) and late Quaternary (Liu and Broecker, 2008a, 2008b) landforms. In contrast to cosmogenic nuclides that suffer from high inherent costs and concerns over the ‘inheritance’ of nuclide build-up in any transported sediment (Robinson, 2002; Cockburn and Summerfield, 2004), VML can be used to tackle virtually any landform that hosts subaerial varnish. There are a host of classic and unsolved desert research questions ripe for answering through VML.
- (2) *The study of rock coatings in the context of priceless rock art.* There can be little doubt that anthropogenic factors and natural erosion continue to result in the destruction of countless numbers of rock art engraved or painted on desert rock surfaces (ICOMOS, 2000; Bertilsson, 2002; J.PaulGettyTrust, 2003; Varner, 2003; Keyser et al., 2005). Many laboratory scientists favour an interventionist strategy to preserve art by treatments such as organosilicone-polyurethanes (Puterman et al., 1998), acrylic copolymers (Brugnara et al., 2004), polymeric membranes (Drioli et al., 1995), *in situ* polymerization (Vicini et al., 2004), and intrapore precipitation of calcite (Tiano, 2004). Field scientists, in contrast, do not generally advocate active intervention by subtracting lithobionts or adding stabilizing agents (Dolanski, 1978; Pope, 2000; Zhang et al., 2001; Pope et al., 2002; DeAngelis et al., 2003; Tratebas et al., 2004). There is also a major perceptual difference between those studying building stones, who start with the premise that the host rock is unweathered stone from a quarry, and those studying natural rock art, who start with the premise that the host rock is already in a state of decay. Unfortunately, there is very little basic research on the role of rock coatings in the stabilization of or weathering of this priceless art. Much more research is needed, for example, on processes by which coatings stabilize stone surfaces by oxalate (Del Monte et al., 1987; Zhang et al., 2001), rock varnish (Gordon and Dorn, 2005a), heavy metals (Tratebas et al., 2004), silica glaze (Gordon and Dorn, 2005b), or simply understanding the spatial context of weathering and rock coatings (Barnett et al., 2005; Wasklewicz et al., 2005).
- (3) *Map the geography of rock coatings.* The normal strategy in rock coating research has been to utilize a microanalytical technique at a few sites, or even to bring to bear a suite of expensive tools at just a single site. Oberlander (1994: 118) emphasized that ‘researchers should be warned against generalizing too confidently from studies of single localities.’ Even though a spatial perspective on geochemistry helped prevent dead-ends in geochemical research (Perel’man, 1961, 1966, 1967; Fortescue, 1980; Perel’man, 1980), very few mapping studies of rock coatings have yet to be conducted (Danin, 1986; White, 1990; Christensen and Harrison, 1993; White, 1993a; Dorn, 1998; Palmer, 2002). Successful models for rock coating research must be able to explain simple geographical questions such as why, for example, rock varnish grows with iron films, silica glaze, phosphate skins, and oxalate crusts in the Khumbu of Nepal (Dorn, 1998: 360–361) and with dust films, carbonate crust, phosphate film, silica glaze, and oxalate crusts in Tibet (Dorn, 1998: 367–369). The recent paper entitled ‘baking black opal in the desert sun: the importance of silica in desert varnish’ postulated an untenable model for varnish formation simply by not considering the geography of varnish in locales with little or no light and heat (Anderson and Sollid, 1971; Douglas, 1987; Dorn and Dragovich, 1990; Whalley et al., 1990; Dorn et al., 1992; Douglas et al., 1994; Villa et al., 1995; Dorn, 1998).

(4) Falsify abiotic hypotheses, if possible. A general uncertainty envelopes research on the genesis of almost all rock coatings. There are often both abiotic and biotic processes capable of creating a geochemical barrier to fix manganese, iron, phosphate, carbonate and other coating constituents on rock surfaces. Even though the preponderance of evidence might favour a biotic mechanism, as is the case in rock varnish, the role of abiotic fixation simply cannot be ruled out at the present time. This uncertainty comes home as a giant problem if a rock coating is to be used as an indicator of ancient life on Earth (Crerar et al., 1980; Dorn and Dickinson, 1989), or on Mars (DiGregorio, 2002; Gorbushina et al., 2002; Mancinelli et al., 2002; Allen et al., 2004; Kuhlman et al., 2005; Spilde et al., 2005; Perry et al., 2006; Perry and Lynne, 2006). Just as the use of varnish as a bioindicator of ancient life on Mars is untenable until abiotic origins are falsified for Martian conditions, a clever strategy to falsify (or confirm) abiotic origins on Earth would similarly aid terrestrial research.

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