Case Hardening Vignettes from the Western USA: Convergence of Form as a Result of Divergent Hardening Processes

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ABSTRACT

The rock weathering literature contains the hypothesis that case hardening exemplifies equifinality, where the same end state can be reached by many potential processes in an open system. We present analytical data from six different sites in the western USA to assess the hypothesis of equifinality. Case hardening can be produced on: (1) sandstone in Petrified Forest National Park, Arizona, from the addition of silica glaze, rock varnish and heavy-metal skins; (2) sandstone in Whoopup Canyon, Wyoming, from silica glaze that formed originally inside subsurface joints combined with externally applied iron film, silica glaze, and rock varnish; (3) welded tuff in Death Valley, California, from the accumulation of rock varnish and heavy metal skins of Mn and Fe; (4) sandstone in Sedona, Arizona, from the protective effects of rock varnish accretion and heavy metal skins of Mn and Fe; (5) basalt on the Big Island, Hawai'i, from the accumulation of silica glaze inside vesicles; and (6) sandstone at Point Reyes, California, from a lithobiont mat of fungi and lichen. Each developed the general form of a case-hardened shell, protecting the surface from erosion. In accordance with the hypothesis of equifinality, the processes that led to similar appearance differ.

Introduction

Differential weathering of rocks leads to varying degrees of resistivity of different rock types to erosion. Such differences in weathering provide a fundamental control on Earth's topography (Ollier 1984, Pain and Ollier 1995), as exemplified by different classic landforms settings. For example, differential weathering has led to differences in erosion of the sedimentary layers of the Colorado Plateau, resulting in certain resistant sedimentary layers serving as caprocks in a staircase topography (Dutton 1882). The talus flatirons that occur in front of such cuestas develop because the talus rock falls from the caprocks, in turn protecting the weaker rock beneath (Gerson 1982). Of particular importance is the concept of topographic inversion, where the most erosion-resistant materials become topographically prominent features within the landscape, despite a depositional origin within a topographic low (Pain and Ollier, 1995). Examples include basalt flows where lava flowed down valleys, eventually becoming the high point on the landscape(Ollier 1967); raised channels in Oman, where former stream-channel deposits are now preserved as relatively high topography (Maizels 1990); and even duricrusts like calcrete (Reeves 1993) and silcrete (Summerfield 1983), at a much larger scale.

We examine the role of differential weathering on the scale of individual boulders or rock outcrops. Case hardening exemplifies the importance of differential weathering influencing the differential erosion of rock surfaces—in our study, at the scale of meters to millimeters. Often darkened by coatings such as rock varnish, case hardening creates a differential resistance to detachment where indurated surfaces erode more slowly than unprotected rock. Hardening the outer shell of a rock surface can also promote the formation of visually interesting forms such as honeycombed weathering features and rock shelters used by prehistoric people.

Although there exists a long-held belief that weathered solutions rise up from the inside of the rock to reprecipitate on the surface (Loew 1876, Walther 1891, Peel 1960, Longwell et al. 1950, Holmes 1965), very little evidence exists for an internal origin of indurating agents. Instead, available evidence indicates that case hardening occurs when abiotic or biotic materials, applied externally, increase the resistance to detachment in the outer few millimeters of a rock surface (Dorn 2004, 1998).

Case hardening is important in physical geography and stone conservation. Geomorphologists connect case hardening to such issues as tafoni formation (Mellor et al. 1997), cliff retreat (Emery and Foster 1956), and

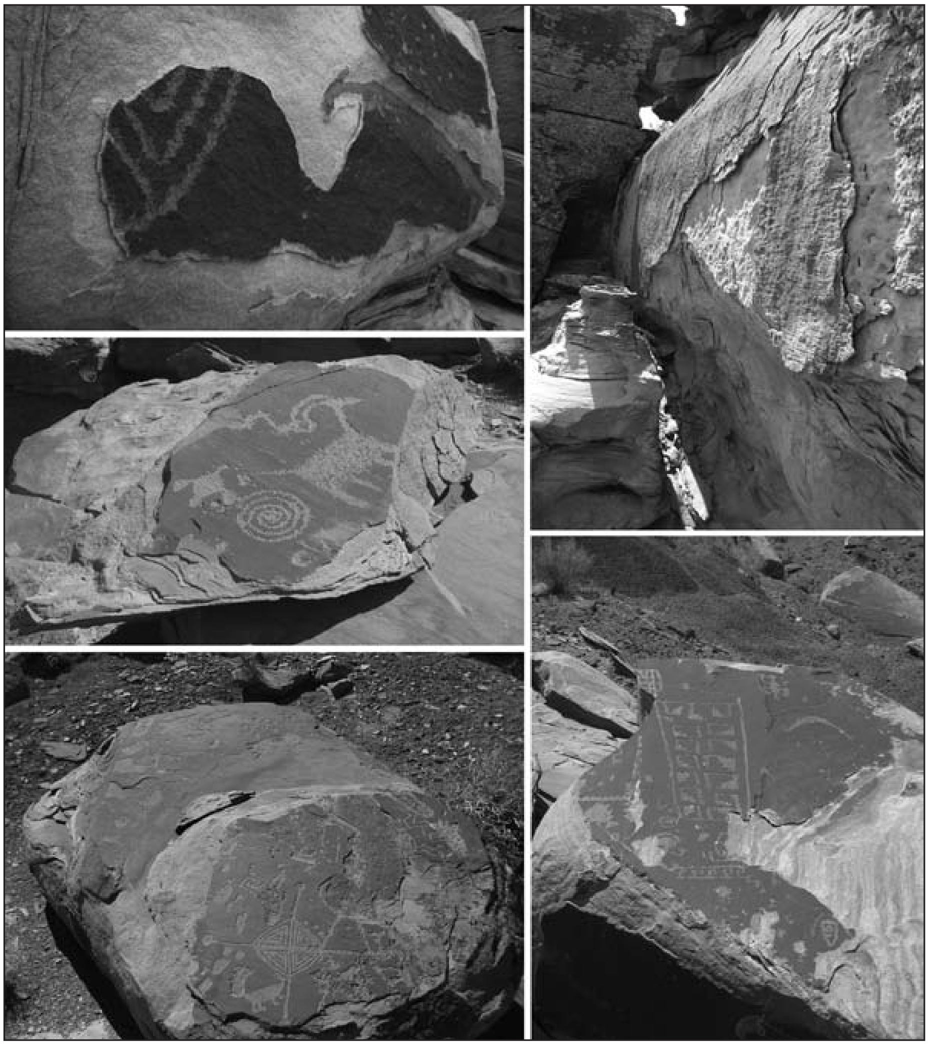

Figure 1.—Newspaper Rock member sandstone within Petrified Forest National Park hosts many examples of case-hardened sandstone surfaces. Each image in this figure displays petroglyphs originally engraved into the case hardening on a planar joint surface darkened by rock varnish. Many of the engravings in the park range from 600 to 1100 calendar years BP (Dorn 2006). Decayed engraved surfaces are progressively undermined by erosion of the underlying rock. With the assumption that the engravings were manufactured when the case hardened surface was fully intact, the rate of erosion of many panel faces can be roughly estimated as five to ten percent of a panel surface per century.

pedestal rocks (Crickmay 1935). Case hardening processes may play a role in the preservation and decay of historic buildings (Fitzner et al. 1997), contemporary buildings (McAlister et al. 2003), and rock art (Tratebas et al. 2004, Cerveny et al. 2006, Cerveny 2005).

Weathering forms such as case hardening support the geomorphic concept of equifinality (Goudie and Viles 1999, Turkington and Paradise 2005, Ollier 1978). In equifinality the same end state can be reached by many potential means in an open system. We present analytical data from different sites in the western United States to assess the hypothesis of equifinality for case-hardened surfaces.

Field Sites

Sampling sites analyzed for this study were not selected randomly. We compiled analyses collected for other projects that have been repurposed to understand case hardening in selected western United States sites. For example, the granodiorite of South Mountain, Arizona, was sampled to explore the effect of paintball on stone surfaces. Welded tuff in Death Valley was collected to understand rock varnish processes, and the basalt on the Big Island of Hawai‘i was collected as part of a petroglyph dating project. Thus, the electron-microscope imagery gathered in previous studies can be used in our attempt to assess equifinality of case-hardened surfaces.

Four sampled sites in three very different environments involve sandstone. Samples from the high desert of Petrified Forest National Park (PEFO) on the Colorado Plateau were collected to understand rock art chronology (Dorn 2006). The pine forests of the Black Hills provide the environmental backdrop for samples collected to understand how fire impacts rock art panels (Tratebas, Cerveny, and Dorn 2004). Marine terrace-derived sandstone from Point Reyes was sampled to understand the nature of rock coatings in this maritime climatological setting, as were Sedona's semi-arid cliff faces. In addition to samples collected for electron microscopy, Petrified Forest National Park provided the setting for a systematic study of petroglyph panel stability. Students from multiple institutions collected data on over 2,500 panels distributed across the park.

Methods

Different microscopic techniques generated imagery and chemistry to understand the nature of case hardening at different sites. Light microscopy provides information on the scale of microns to millimeters. Scanning electron microscopy (SEM) generates a topographic perspective using secondary electrons (SE). SEM with a back-scattered electron detector (BSE) generates an image of average atomic number (Z) of a flat surface that, here, is typically a cross-section from the surface of a sample down into the rock.

Energy dispersive X-ray (EDS) and wavelength dispersive (WDS) analyses measures the elemental composition of specific areas—typically micron-sized spot sizes.

In addition to electron microscopic techniques, case hardening was studied in the context of a rock art project carried out at PEFO. The Rock Art Stability Index (RASI) is a triage technique for condition assessment of rocks containing Native American rock art (Dorn et al. 2008, Cerveny 2005). RASI is used extensively throughout PEFO, and in this study college students and K–12 teachers gathered data relating case-hardening with adjacent flaking and scaling erosion. The methodology requires field researchers, typically docents or introductory science students in college, to utilize basic training to gather observation field-data for approximately three dozen weathering characteristics. Scores are compiled in the laboratory and a value of stability assigned on a panel-by-panel basis. Generalizations or regional causation for specific weathering patterns can then be analyzed and communicated, giving sound data for site managers to make informed conservation and preservation decisions. In the PEFO research, over 2,500 panels were measured using RASI, resulting in data being gathered on case hardening for an unprecedented number of sites.

Results

Petrified Forest National Park

Case hardening at Petrified Forest National Park (Figure 2A) results from a mixture of different added constituents. The process starts when silica glaze is added to the walls of buried joint faces. Water moving through joints carried dissolved silica that reprecipitated in pores (Figure 2C). Then, upon exposure of a joint at the surface, rock varnish formed. Although portions of varnish are geochemically stable, much of the varnish can dissolve. Remobilized iron and manganese has then moved into the pores in the sandstone and added to the case hardening (Figure 2B).

Reports were collected on the weathering condition of over 2,500 rock art panels in Petrified Forest National Park. The RASI scoring system is an index amounting to a score of 0 if there is no weathering and over 60 if the panel is falling apart from rock decay. Because case hardening provides a stabilizing influence, researchers scored case hardening with negative numbers in an ordinal scale of not present (0), present (-1), obvious (-2), or dominant (-3). The overall pattern (Figure 3) reveals that case harden-

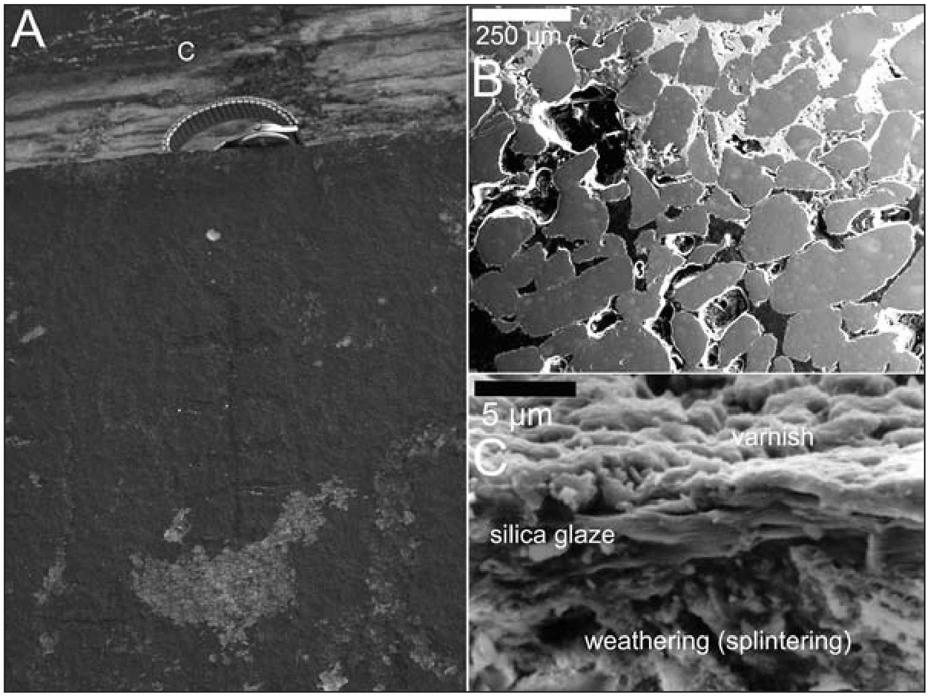

Figure 2.—Case hardening of sandstone at Petrified Forest National Park. (A) A case-hardened joint face forms a stable surface used for carving of a bird motif and an earlier anthropomorphic image. Note, however, that the case hardening has been breached—with wristwatch for scale. (B) Back-scattered electron-microscope image of a cross-section collected at location "c" in image A. The bright material between the grains is a heavy metal skin of iron and manganese constituents, likely dissolved from rock varnish and mobilized into the sandstone to stabilize the upper millimeter of a surface. Note also the abundant porosity underneath the case hardened heavy metal skin. Once the case hardening is breached, this porosity makes erosion rapid. (C) Another type of case hardening exists at the very surface of this panel. A mixture of silica glaze and rock varnish can offer additional stability in the upper few microns, where this secondary electron image was from a sample also collected from the letter C above the watch in image A.

ing is present in about forty-two percent of the scored panels, and that case hardening dominates only five percent of the rock art panels.

The spatial distribution reflects the presence of the Newspaper Rock member sandstone, the locations of petroglyph manufacturing, as well as a clustering of dominant case hardening whose cause has not yet been determined.

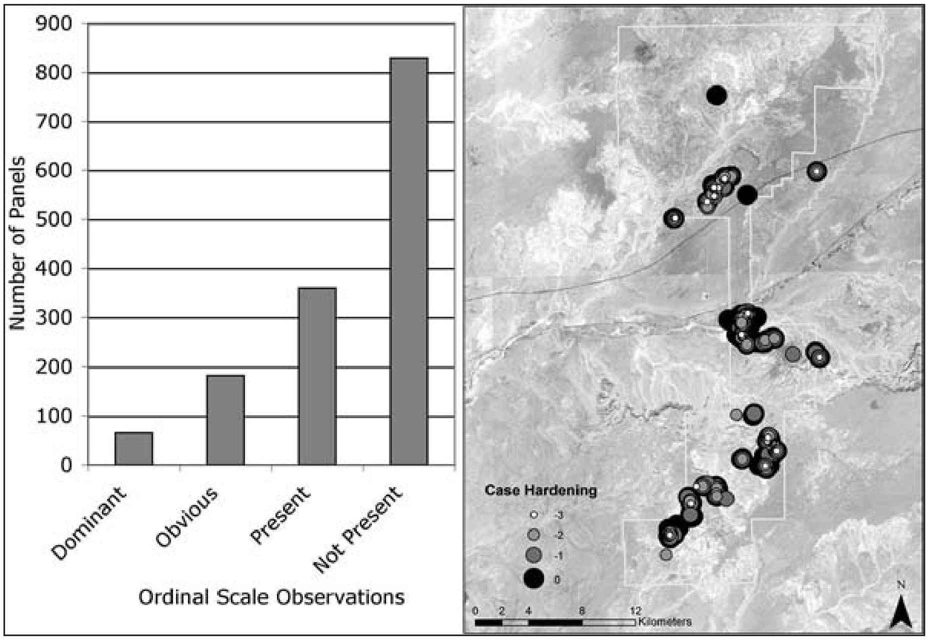

Figure 3. —Histogram and mapping of observations of case hardening at rock art panels in Petrified Forest National Park. "Dominant" observations of case hardening are the smallest symbol on the map; they represent the smallest number of observations and hence are visible because they are portrayed on top.

Whoopup Canyon, Black Hills, Wyoming

Whoopup Canyon in the Black Hills, Wyoming, exhibits sandstone joint faces that were originally case hardened by silica glaze before the joints became exposed. Iron film then remobilized under acidic conditions and further impregnated the sandstone. Later rock varnish formation led to remobilization of the varnish constituents that also moved downward into the rock to mix with silica glaze. Thus, the case hardening is a complex mixture of different materials. The porosity from enhanced weathering in the underlying sandstone allows detachment of rock fragments as rock flaking.

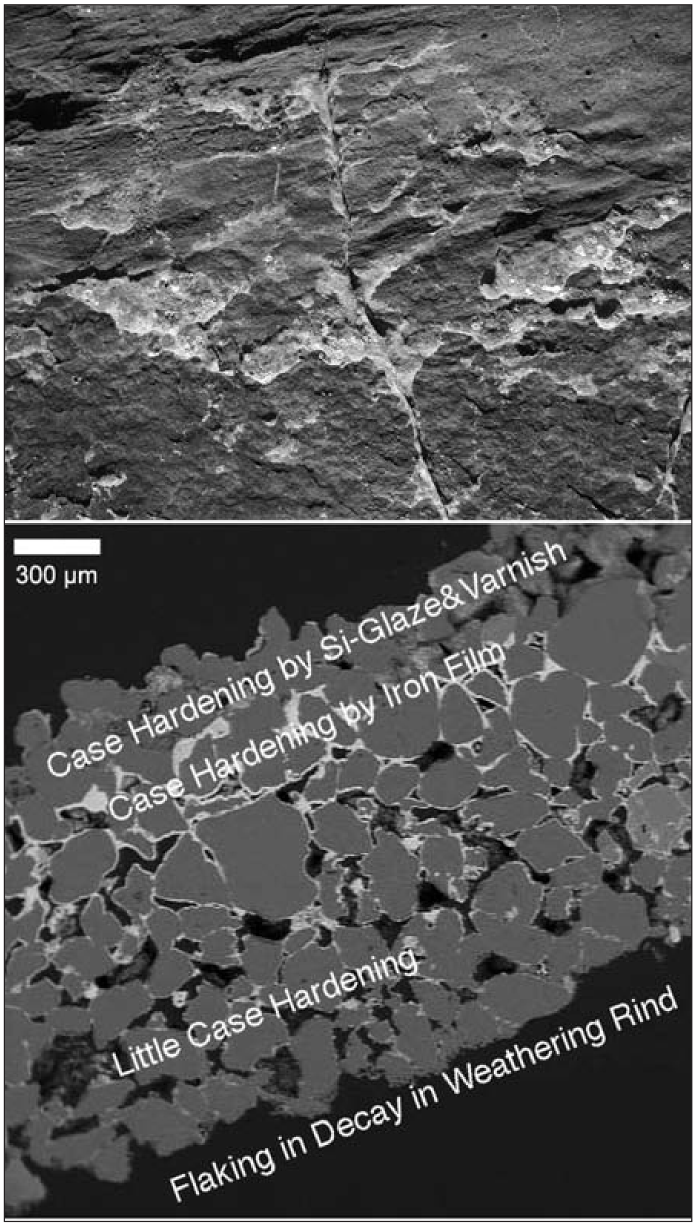

Figure 4.—Sandstone surface at Whoopup Canyon, Black Hills, Wyoming (width of upper image about 30 cm) has case hardened due to the accumulation of three types of materials as revealed in the lower back-scattered electron-microscope image. First, silica glaze impregnated a joint surface, while it was still unexposed in the subsurface. Second, iron seeped into the sandstone and filled in pore spaces to cement sand grains together. Third, rock varnish formed on the surface and also remobilized to mix with silica glaze. Enhanced dissolution of quartz underneath the case hardening led to detachment of the millimeter-scale flake.

Death Valley, California

Studies of rock varnish in Death Valley have yielded insight into the importance of lichens, even in hyperarid settings. Lichens colonizing the surfaces of rock varnish secrete acids.

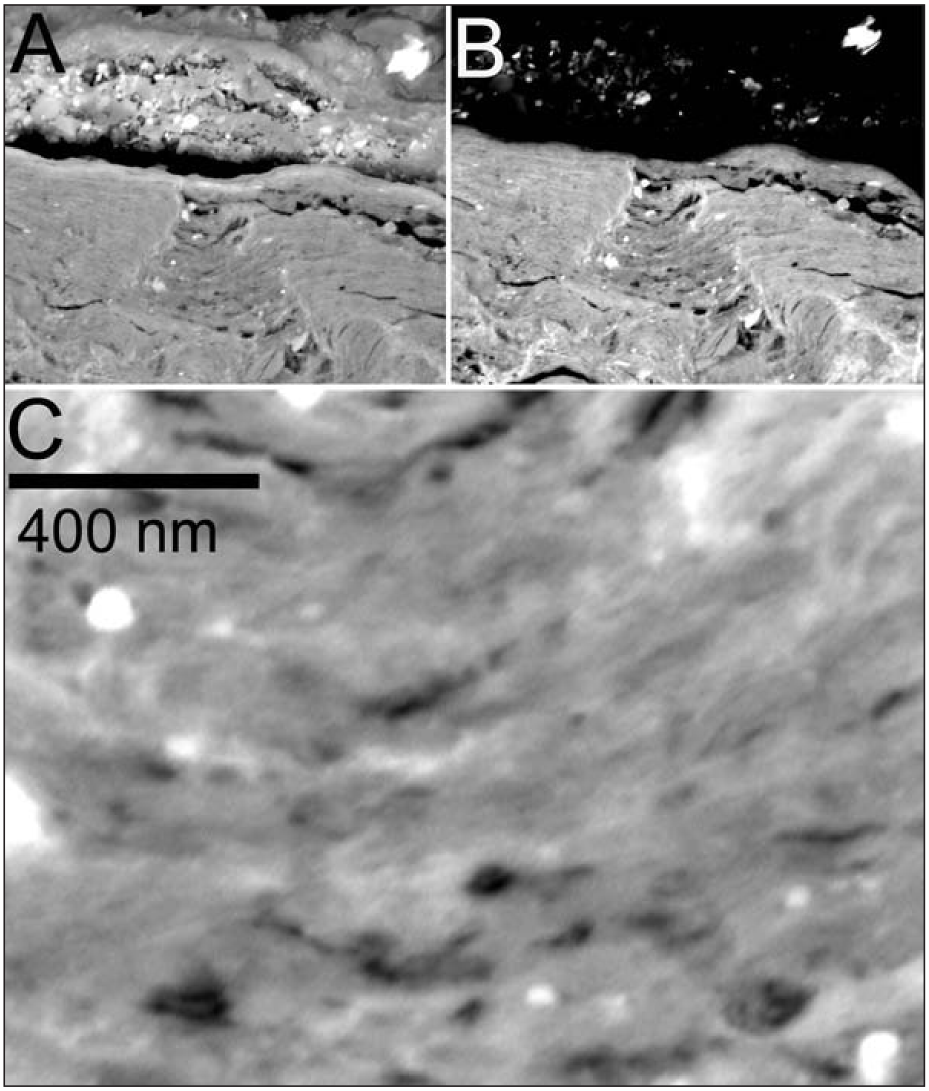

Figure 5.—Death Valley rock varnish undergoing dissolution from the acid-producing activity of lichens. (A) Secondary electron (SE) image that shows the topography of a cross-section. (B) Back-scattered electron (BSE) image that shows the atomic number (Z) of the material in this cross-section. Notice that most of the lichen turns black in the BSE image, because of its lower atomic number. The bright specks in the lichen are oxalate minerals that often precipitate inside lichens. (C) Close-up BSE image of the pocket of porous material underneath the lichens.

The acidity reduces Mn (IV) and Fe (III), which causes the varnish to develop nanoscale pore spaces (**Figure 5C**) as the Mn (II) and Fe (II) migrate into the underlying rock.

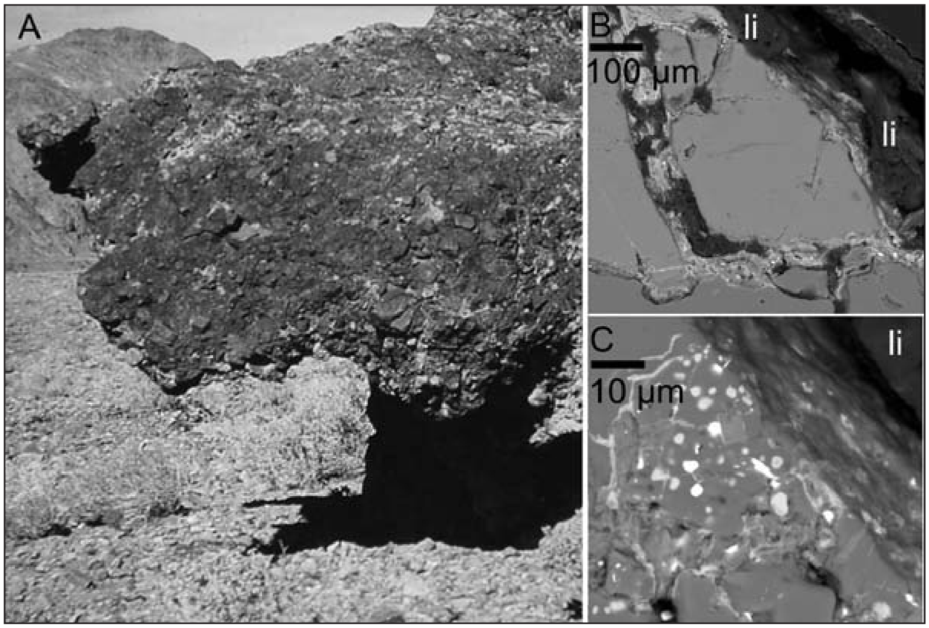

Figure 6.—(A) Welded tuff, Death Valley, forms a rock shelter, because of a case-hardened outer shell. Image A is 2 meters wide. (B) In this back-scattered electron image, the brighter material accumulating in the fractures is manganese (Mn)-Iron (Fe)-clay rock varnish. C) In addition, some of the Mn and Fe have reprecipitated in micron-sized pore spaces. The lichens (li) appear in images A and B because of its lower atomic number.

The process of varnish remobilization was studied at the nanoscale level through energy-dispersive X-ray analyses. Prior electron-microscope elemental data on rock varnish chemistry generated only data from micrometer-scale spot analyses that are typically two microns in diameter. Through the use of higher-resolution electron microscopy and higher energy levels, spot sizes were reduced to about 1.3 nanometers. The descriptive statistics of these data reveal tremendous variability that could be from the ongoing dissolution of the varnish. Whereas larger spot sizes would "average" these tiny pores, the tremendous nanoscale chemical variability suggests that varnish undergoes uneven dissolution on a submicron scale.

Table 1. Descriptive statistics of 128 nanoscale measurements of rock varnish undergoing remobilization from lichens.

Element	Average	Median	Standard Deviation	Minimum Value	Maximum Value	Range
C	0.14	0.00	1.20	0.00	11.21	11.21
F	3.32	1.45	3.71	0.00	13.18	13.18
Mg	1.46	1.31	1.42	0.00	18.34	18.34
Al	17.89	18.11	1.24	10.72	19.90	9.18
Si	11.43	10.96	2.78	1.58	21.56	19.98
P	1.17	1.22	0.24	0.37	1.69	1.32
Cl	0.00	0.00	0.03	0.00	0.20	0.20
K	0.48	0.44	0.21	0.23	1.56	1.33
Ca	0.69	0.58	1.41	0.26	17.78	17.52
Ti	0.73	0.00	2.86	0.00	15.50	15.50
Mn	14.90	15.48	4.08	3.96	24.21	20.25
Fe	6.57	6.85	2.02	0.77	12.04	11.27
Cu	0.95	0.92	0.18	0.50	1.76	1.26
Zn	0.00	0.00	0.06	0.00	0.68	0.68
Ba	0.94	1.24	0.84	0.00	2.97	2.97
Ce	0.28	0.00	0.38	0.00	1.32	1.32
Re	0.01	0.00	0.09	0.00	0.80	0.80
O	39.06	39.06	2.96	33.10	55.23	22.13

The instability of varnish very much relates to case hardening. The indurated rock has formed a rock shelter where rock varnish and heavy metals have been dissolved by lichens. After uneven dissolution of nanoscale pockets, some of the varnish moves into fractures in the rock and reprecipitates. Occasionally, just the iron and manganese fill in pore spaces as heavy metals without the clays. Thus, even in a hyperarid environment, the acidity produced by lithobionts can be important in freeing up case-hardening agents to penetrate into the rock.

Sedona, Arizona

The case hardening of sandstone by the accumulation of manganese in the pore spaces does not necessarily have to do with the dissolution of varnish constituents, as exemplified in the previous results sections. The dark streaks at Sedona sometimes result from the precipitation of manganese (Figure 7).

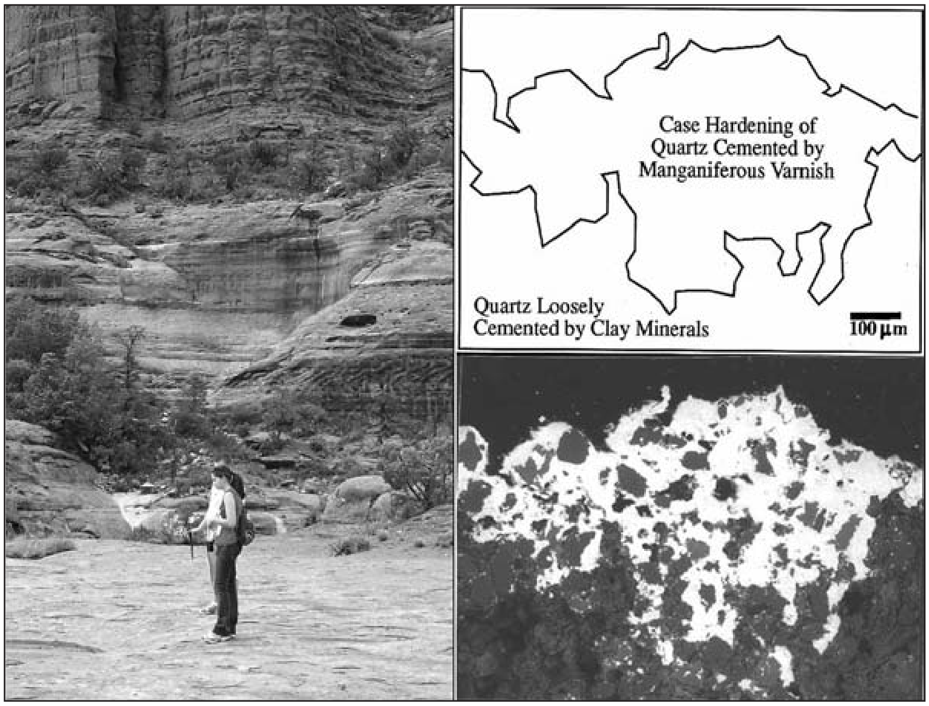

Figure 7.—Waterflow streaks at Sedona can form through the accumulation of fungi, lichens, heavy metal skins, and rock varnish. In this case, the sampled streak is a mixture of rock varnish (at the surface) and heavy metal skins (remobilized magniferous varnish) that move downward through pore spaces to impregnate the sandstone of Sedona, at Schnebly Hill Road, Arizona.

The manganese moves into the pore spaces between the sand grains and sometimes pushes the grains apart. The material composing these dark streaks is often a mix of true clay-Mn-Fe rock varnish and heavy metal skin dominated by manganese. The case hardening can extend into the rock up to a millimeter.

Hawai'i

Basalt surfaces on the rainshadow portions of the island of Hawai'i often accumulate silica glaze. The silica glaze that coats flow surfaces dissolves and reprecipitates in vesicles inside the basalt. One result is a color change from the dark black of a basalt flow to the light brown of a silica-glaze coated surface. A second result is the case hardening of the basalt surface.

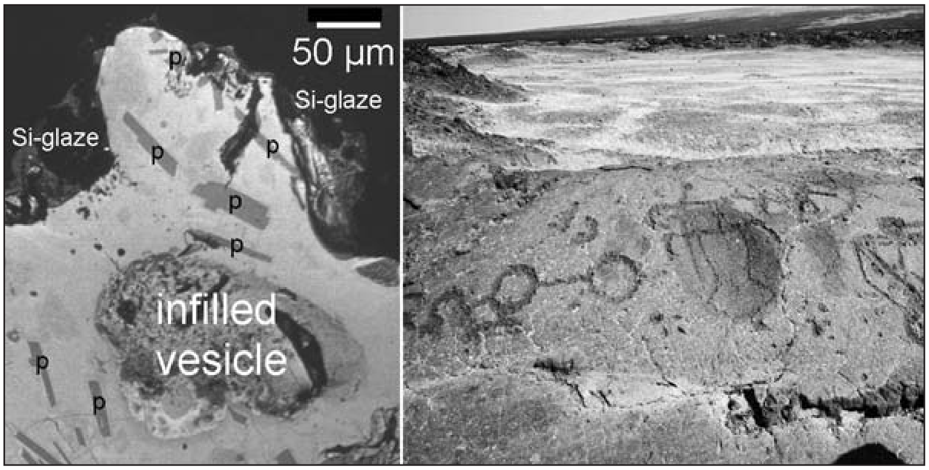

Figure 8.—Hawai'ian petroglyph panels and petroglyphs are often case hardened by silica glaze that originally accretes on surfaces, and then remobilizes into the rock and infills vesicles. The back-scattered electron-microscope image on the left shows dark-colored silica glaze, where about 30% of a vesicle has been filled by silica glaze. In addition to silica glaze, other precipitates (e.g. iron skins, rock varnish, carbonate) formed inside the vesicle. The image on the right from the Ki'I site on the Big island of Hawai'i shows a panel composed of basalt, but the lighter color of the engraved surface in the foreground derives from silica glaze.

Point Reyes, California

Sandstone weathering at Point Reyes includes a variety of forms, such as tafoni, alveoli, gnamma pits, and case hardening. A sample of case-hardened sandstone reveals the presence of a lithobiontic crust composed of lichen mixed with fungi. The biofilm also contains calcium oxalate minerals, perhaps secreted by the lichens. The biofilm was typically less than 0.1 mm thick. However, the filaments are clearly able to bind the underlying sandstone in a way that indurates the surface.

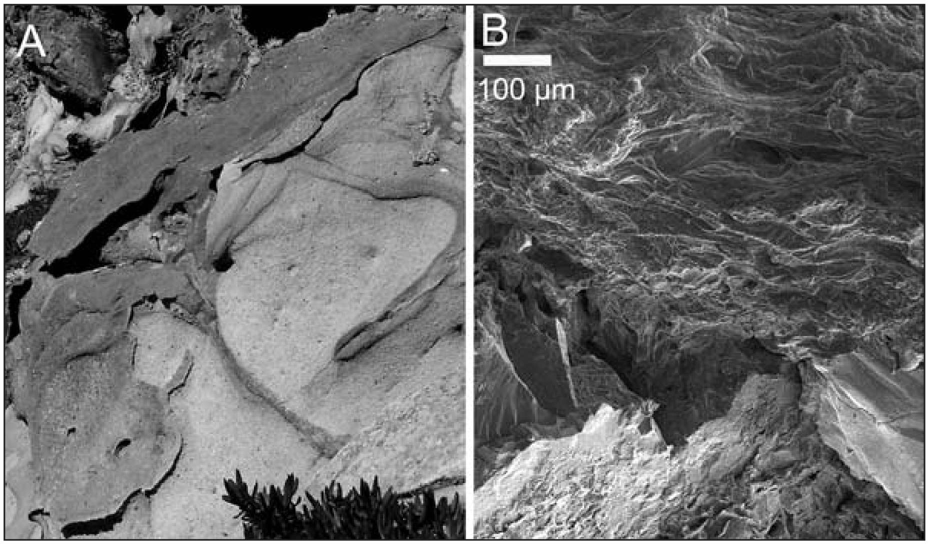

Figure 9.—Point Reyes case hardening in Image A, where the ice plant in the lower right provides scale. The indurated sandstone erodes because of undermining as the unhardened sandstone detaches. A secondary electron image of the case hardened shell reveals that it is composed of a ~40 µm thick layer of a mat of lichen mixed with fungi. The angular materials underneath the filamentous mat are minerals in the underlying sandstone.

South Mountain, Arizona

We think it is important to mention anthropogenic agents in this discussion of case hardening, since humans continue to influence natural surfaces. One way that natural rock surfaces are impacted rests in graffiti and activities like paintball gaming. The study of modern paints on rock surfaces has heretofore been limited to conservation efforts designed to remove or hide these scars.

In a pilot study to examine the influence of paintballs, we examined samples of natural rock surfaces hit by this recreational activity using back-scattered electron microscopy. Preliminary results indicate that the paint has begun the process of physically separating from the underlying rock coating. There are still abundant attachment points. However, in the unknown amount of time between the paintball attachment and sampling, substantial physical separation has occurred. Thus, paintballing may not become a case-hardening agent and will eventually detach itself from rock surfaces, eliminating paintballs as agents of rock case hardening.

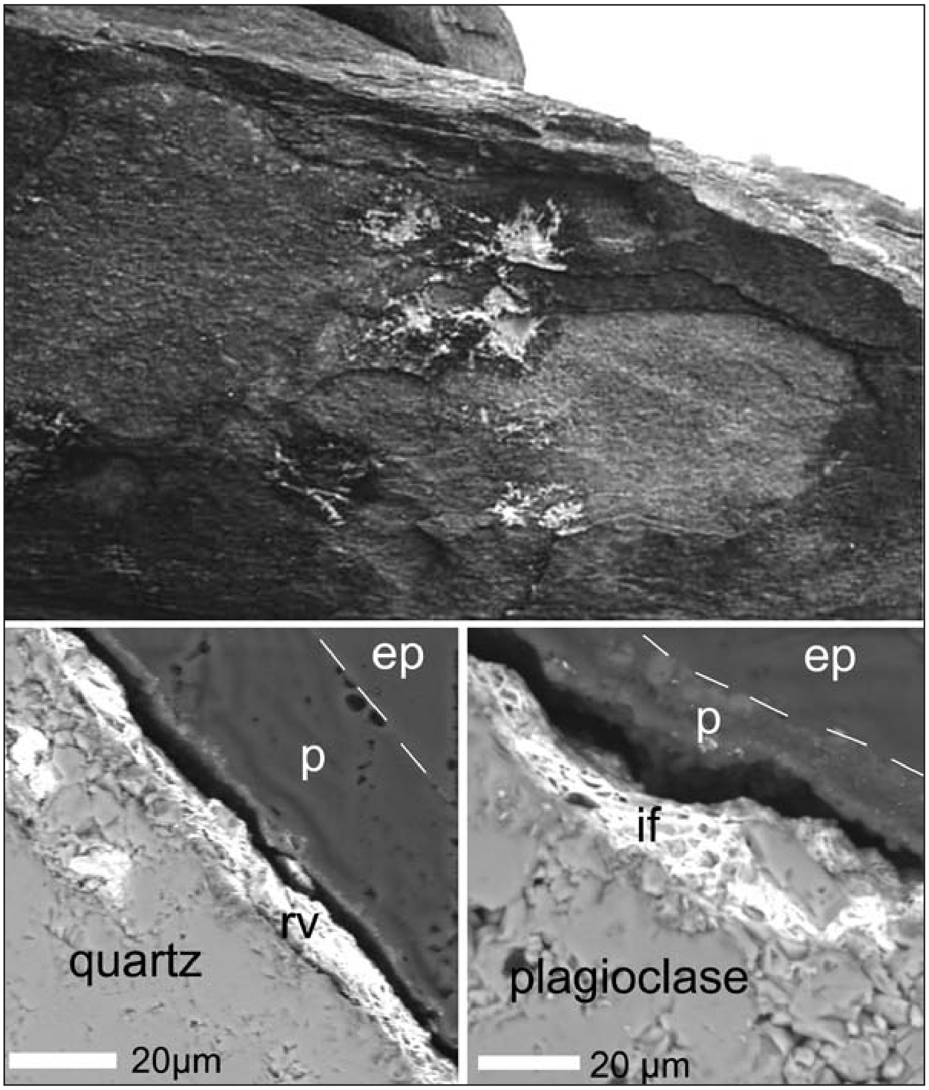

Figure 10.—Anthropogenic paint balls applied to granodiorite rock surfaces at South Mountain Park, Arizona. BSE imagery reveals that the anthropogenic paint (p) separates from the underlying rock surface after application of epoxy (ep) application of the vacuum used to carbon coat the samples. The BSE imagery and EDS analyses also reveals two case-hardening agents are present on the rock surface: rock varnish (rv) and iron films (if). The iron films tend to incorporate silt-sized fragments as preprecipitating containing iron envelope dust particles that are ubiquitous on rock surfaces. Note: normally, BSE imagery shows epoxy as black. However, the contrast and brightness were adjusted in a way to minimize contrast and reveal the epoxy and the paint.

Discussion

Our findings indicate that equifinality does appear to be valid for the wide variety of study sites and environments in the western United States that were studied using electron microscopy. Case hardening can occur through lithobiontic crusts composed of fungi and lichen, by lichens dissolving heavy metals that are then reprecipitated in the outer shell of a rock, by silica glaze infusing into vesicles in basalt flows, and by mixtures of silica glaze, rock varnish, and heavy metals that hold sandstone grains together.

The persistence of equifinality can be understood further by examining environmental change over time for the studied sandstone surfaces of Petrified Forest National Park and Whoopup Canyon.

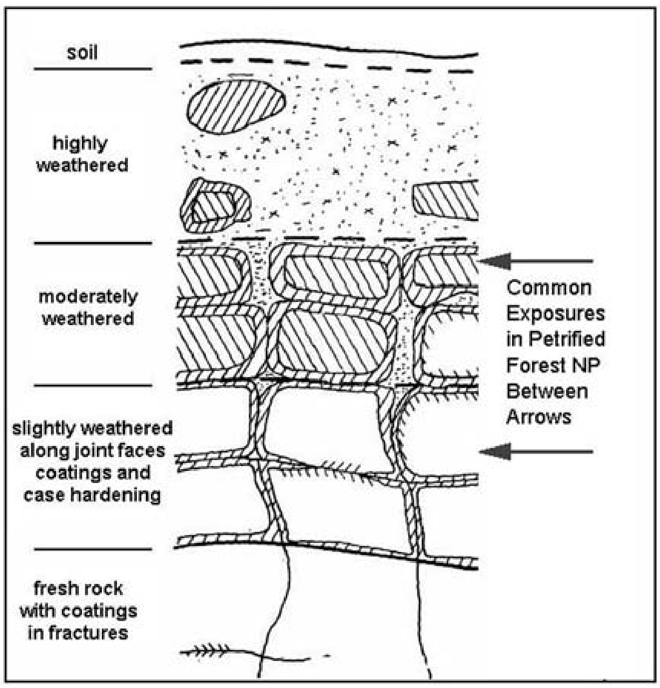

Figure 11.—Weathering profiles in many different rock types develop in a fashion generalized in this diagram. Then, enhanced erosion can strip the overlying weathering zone. At Petrified Forest National Park, for example, the soil and highly weathered rock materials that may have been present during the late Pleistocene have eroded away. Moderately weathered and slightly weathered rocks are now exposed at the surface. The silica glaze that formed inside joint faces represents the first step in case hardening. This diagram is modified from (Ehlen 2005).

The first step involved the formation of silica glaze inside unopened joint faces that started the process of case hardening. Second, erosion of soil and more weathered rock exposed silica-glaze impregnated joint faces to the subaerial environment. Third, subaerial rock varnish formed on the surface. Fourth, leaching of the iron and manganese out of the rock coating and into the underlying rock added to the initial case hardening started by the silica glaze. Thus, the equifinality of case hardening forms that started with silica glaze inside a subsurface joint was enhanced by completely different processes operating in a surficial environment.

Another perspective on equifinality can be understood by examining a time sequence of case hardening on a single rock face (Turkington and Paradise 2005), where case hardening stabilizes a surface for a time as the underlying rock continues to weather. When the hardened surface is breached, this leads to rapid erosion of the underlying heavily decayed weathering rind. After the weathered material erodes away, the surface can restabilize and begin to case harden.

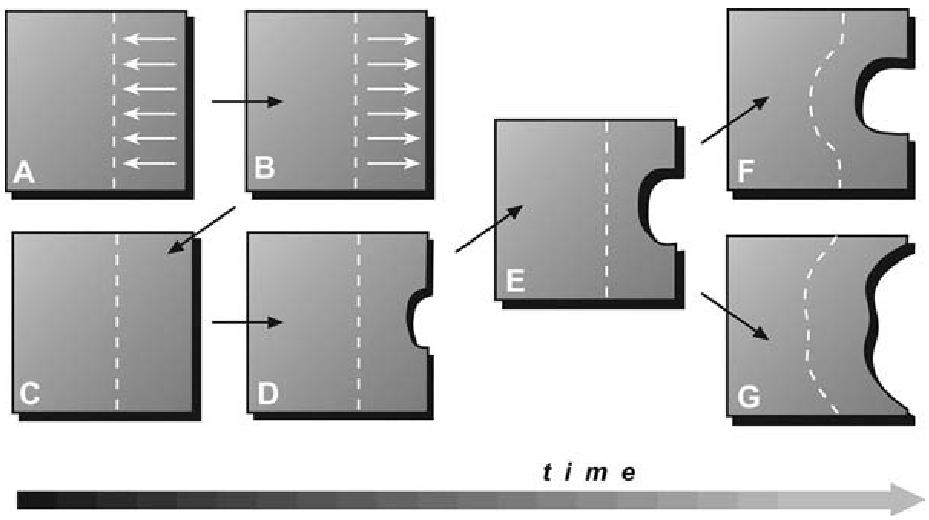

Figure 12.—From Turkington and Paradise (2005), a sandstone surface can undergo a series of changes. In this idealized diagram, subsurface dissolution leads to the creation of a weathering rind (A), followed by the surficial accumulation of minerals and lithobions (B) to case harden surfaces (C). Then, the case-hardened surface is breached (D), leading to rapid erosion of the decayed weathering rind underneath (E and F). Eventually, the new surface stabilizes (G).

This generalized sequence can be seen in operation at the Petrified Forest site. Case hardening has stabilized the surface, but the back-scattered electron-microscope image reveals that weathering has continued underneath as indicated by the abundant porosity in this weathered rind. The breach keeps growing until the weathered rind is eroded down to fresher rock, at which time a new round of case hardening takes place. The cycle continues when this new case hardening is breached. With forty-two percent of panels hosting case hardening, and a process that reforms induration after

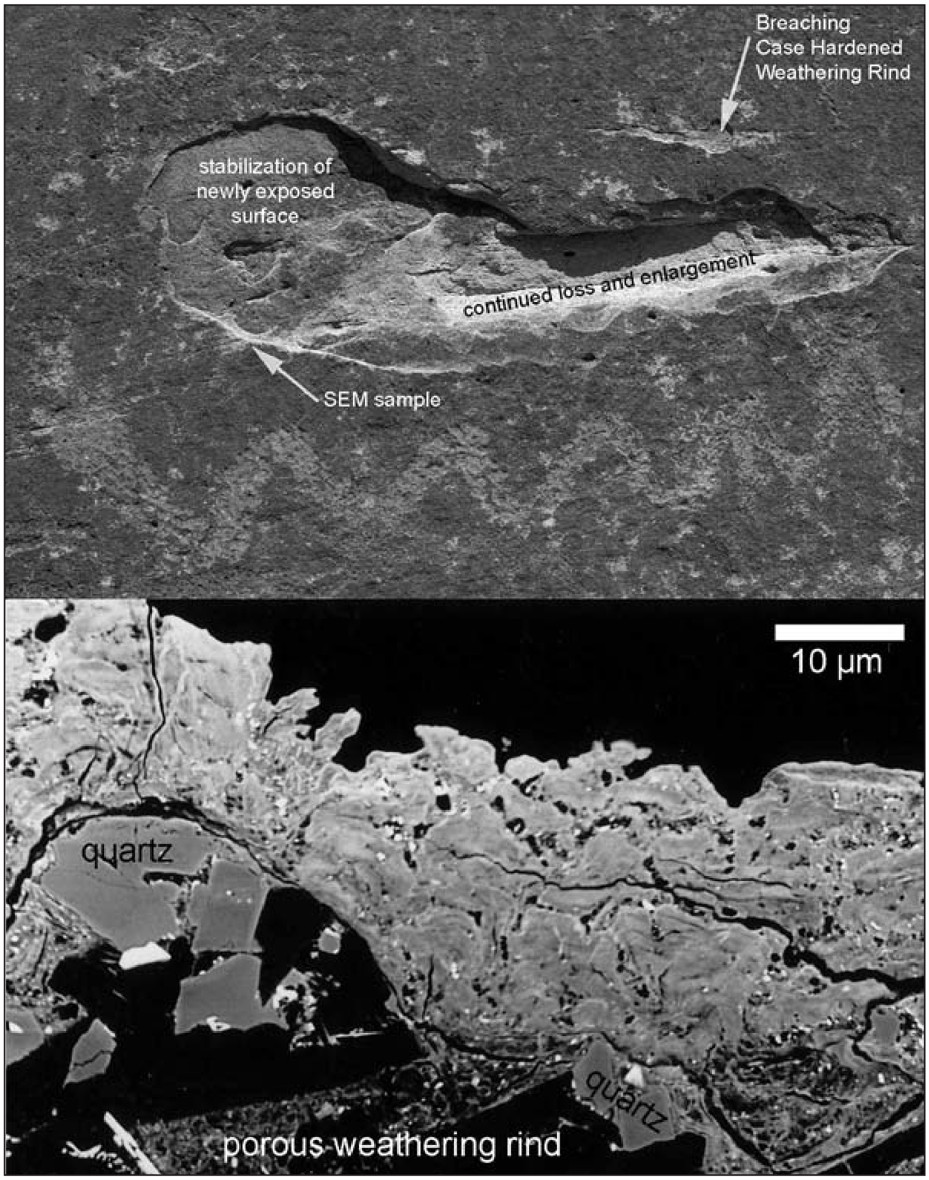

Figure 13.—A petroglyph panel of sandstone at Petrified Forest National Park supports the general model of sandstone face erosion (Turkington and Paradise 2005), where the outermost case-hardened panel was breached, leading to the enlargement of the cavity. Then, after the weathered rind eroded away, the surface restabilized with the formation of rock varnish and some case hardening. Then this restabilized surface was breached in turn. The lower, back-scattered electron-microscope image (collected from SEM sample arrow) shows how the rock underneath the varnish-stabilized surface continues to decay. Much of the quartz has dissolved, and the porosity of the weathering rind has increased over time.

breaching of the initial surface, case hardening appears to be a persistently developing land surface within the Park.

Conclusion

The general field of rock decay concerns itself with processes and forms produced by biogeochemical and biophysical mechanisms. The end result of rock decay is typically thought of as unidirectional, where processes of rock decay promote further rock decay. The "output" of decay is typically thought of as products transported by erosional processes, where sufficient particle-size dimunition eventually generates transportable material.

Through investigation of rock data from six different sites around the western United States, we explored whether the concept of equifinality applies to case hardening. In each of the sites from which data were collected, case hardening had occurred in a way that was both unique and consistent with the environment that housed the rock. Stone surfaces collected from all locales demonstrate evidence of case hardening due to a variety of external factors. Although silica glaze is present in half the sites we considered, the conditions under which that glaze formed were different at each location. Furthermore, case hardening caused by rock varnish and heavy metal skins of Mn and Fe was observed at two sites in Arizona, and we determined that case hardening was caused by an accumulation of fungi and lichen in California. Thus, we concluded that despite different processes coming into effect at each of the sites, a protective covering or shell that performs the same ultimate function—case hardening—is present in all cases. These findings support our hypothesis of equifinality.

Case hardening stands as a testament to the existence of negative feedbacks in this progression of rock decay, where the products of rock decay act to inhibit erosion. In doing so, case-hardened rock surfaces stand out as similar forms in a host of different rock types and different environmental settings. There is an outer shell, typically only millimeters thick, that stands out in relief through the more rapid erosion of unprotected rock.

Negative feedbacks, where the products of rock decay promote surface stability, appear to be a universal phenomenon where many different types of processes can produce the form of case-hardened surfaces (Turkington and Paradise 2005, Phillips 1997, Grab et al. 2011). The research presented here is consistent with and fully supportive of the hypothesis of equifinality. In different open systems involving the decay and reprecipitation of rock materials, many different processes have produced case hardening.

Our conclusion is that with equifinality being such a persistent negative feedback to surface denudation in a host of different contemporary bare-rock geomorphic settings, case hardening may have been a very important process in Earth's early history. Prior to the advent of land plants 700 million years ago and land fungi 1.3 billion years ago (Heckman et al. 2001), Earth's surface could have been protected from erosion by the action of case hardening. To the best of our knowledge, the possible role of case hardening in protecting the early Earth is a hypothesis that has not yet been considered in the scholarly literature.

Acknowledgments

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