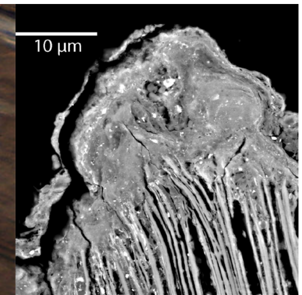
Case Hardening: Turning Weathering Rinds into Protective Shells



Backscatter electron image of Mn–Fe–Si case hardening biotite. Sample is from Tibet. Scale bar = 10 µm

Ronald I. Dorn[1], William C. Mahaney[2], and David H. Krinsley[3]

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Case hardening is the process by which the outer shell of an exposed rock surface hardens due to near-surface diagenesis. Rock coatings and weathering rinds are distinct phenomena: rock coatings accrete on surfaces; weathering rinds derive from mineral dissolution and mechanical fracturing of the outer millimeters of a rock to create porosity. Ongoing reaction with rain, dew, or melted snow results in the downward migration of rock-coating components into weathering-rind pores. Initially, pore infilling protects the outer surface of the rock from flaking. As case hardening progresses, however, ongoing mineral dissolution underneath the case-hardened zone eventually leads to detachment. This sudden loss can destroy rock art, the surfaces of stone monuments, and facing stones of buildings.

Keywords: rock coating, weathering rinds, case hardening, diagenesis

INTRODUCTION

Geochemical case hardening is the formation of a hard protective "shell" on the surfaces of rocks, and the process can dramatically change the appearance of Earth's landforms. The discontinuous spalling, or detachment, of these protective shells from the rock surface facilitates the formation of features such as limestone towers (Mitchell et al. 2003), pedestal rocks, tafoni (multiple small cave-like erosional features on rock surfaces) (Migon and Goudie 2003), and a variety of other erosional forms (Conca and Rossman 1982). Case hardening alters historic buildings, including the pyramids of Egypt (Emery 1960), as well as prehistoric rock art (Whitley 2001). Planetary geologists have invoked case hardening to explain differential rock decay observed on Mars (Thomas et al. 2005).

THE ROLE OF WEATHERING RINDS

Weathering[4] rinds (Oguchi 2013) are ubiquitous terrestrial features that contain potential archives of information about rates of mineral alteration (Brady et al. 1999) and paleoenvironments (Mahaney et al. 2012). Mineral alteration is an important part of rind development (Navarre-Sitchler et al. 2011; Oguchi 2013). Rinds are formed as rock minerals are dissolved or mechanically fractured and transported away from the rock surface, leaving behind a porous layer. Trapped moisture derived from rain, dew, or snow increases rind porosity through mineral dissolution, after which a threshold is reached and the rind detaches from the less-decayed rock.

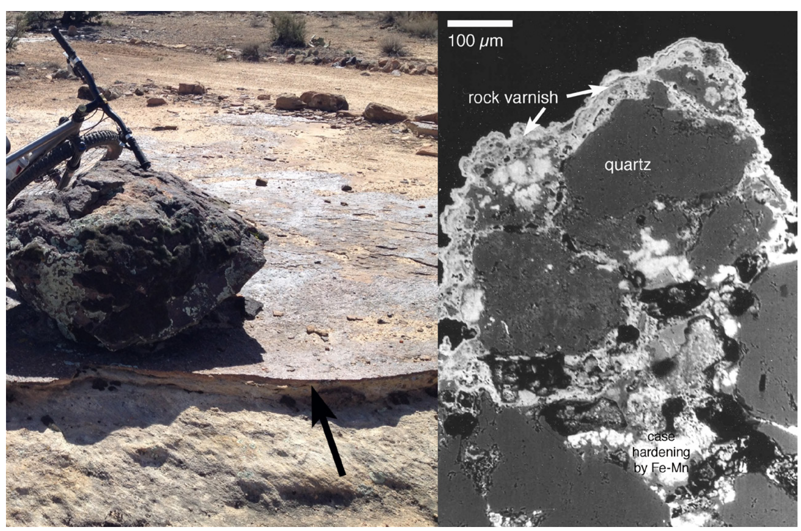

Figure 1 (**Left**) A case-hardened surface of sandstone (identified by the black arrow) at Gooseberry Mesa, Utah (USA). (**Right**) Back scattered electron image of two hardening agents that indurate the sandstone surface: (1) an outer coating of rock varnish; (2) Mn–Fe, mobilized from the varnish, has infilled former pores in the weathering rind and now forms the cement binding quartz grains together.

1 School of Geographical Sciences & Urban Planning
Arizona State University
Tempe AZ 85287-5302 USA
E-mail: ronald.dorn@asu.edu

2 Quaternary Surveys
26 Thornhill Ave.
Thornhill, Ontario, Canada, L4J 1J4
E-mail: arkose41@gmail.com

3 Department of Geological Sciences
University of Oregon
Eugene, OR, 97403 USA
E-mail: krinsley@uoregon.edu

4 The general term 'weathering' is best expunged from Earth science for reasons elaborated elsewhere (Hall et al. 2012). Thus, the term 'rock decay' is used as a synonym for 'weathering' in this paper. But we are forced to use the general term 'weathering rind' because there is no better alternative at present.

Porosity in the outer few millimeters of a rock surface is a precondition for spalling of rinds (Gordon and Dorn 2005) and rindlets (Behrens et al. 2015) and for the development of case hardening. Figure 1 exemplifies the dual importance of porosity: (1) pores generate a weakness that can lead to surface detachment; (2) pores provide spaces that can be infilled by secondary minerals (e.g. Fe or Mn oxides, clays, silica) that then act to strengthen and protect the outer surface of the rock.

CASE HARDENING OF ROCK SURFACES

The outer surfaces of rocks can be hardened by "indurating agents"—the Fe or Mn oxides, clays, and silica minerals mentioned above. Although some believe that the source of the indurating agents are elements leached from the underlying rock and subsequently reprecipitated, there is very little evidence that indurating agents have an internal origin. Rather, externally derived abiotic and biotic materials (e.g. accreted rock coatings) increase the resistance to detachment in the outer few millimeters of a rock surface (Dorn et al. 2012).

A rock coating alone can sometimes produce case hardening to strengthen the outer surface of a rock. This is particularly true for organisms that grow on rock surfaces—such as fungi (see Gadd 2017 this issue) and lichens (Mottershead and Lucas 2000)—that form what are known as lithobiont rock coatings (Viles and Goudie 2004). Inorganic rock coatings can also case-harden surfaces (Dorn 1998). However, the hardening effect of a rock coating alone is minimal compared to when the constituents of the rock coating migrate downward into the porous weathering rind.

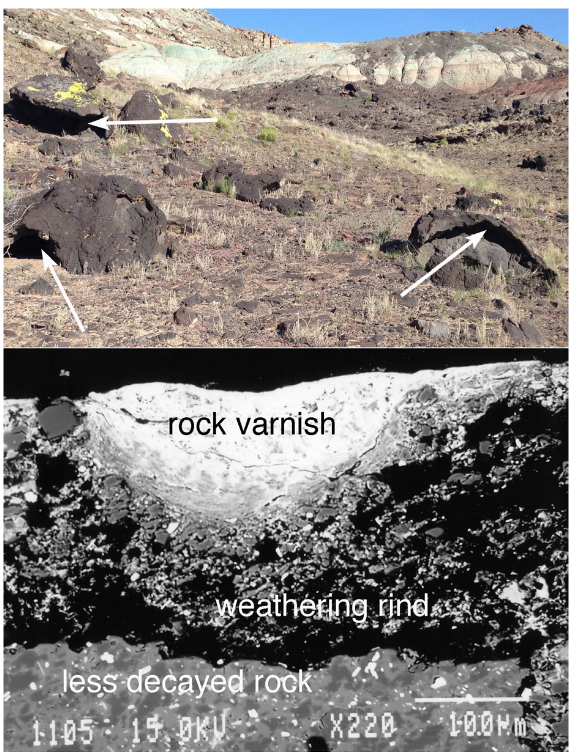

Figure 2 (**Upper**) Hollowed out sandstone blocks (1 m diameter) from the Cedar Mountain Formation, Moab, Utah (USA). These blocks experience both case hardening of the outer shell and core softening (white arrows) of the block interior. (**Lower**) Backscatter electron (BSE) image of the Mn–Fe-rich rock varnish that is responsible for case hardening the sandstone blocks. Spalling occurs along the base of the weathering rind where porosity (dark open spaces) is greatest.

Over time, rock coatings accrete on surfaces and, at the same time, mineral dissolution and mechanical fracturing of the outer millimeters of a rock creates porosity in the weathering rind. Ongoing precipitation of the coating results in the downward migration of rock-coating components into weathering-rind pores. At first, pore infilling protects the outer surface of the rock from flaking. As case hardening progresses, however, ongoing mineral dissolution underneath the case-hardened zone eventually leads to detachment (Fig. 2) and the sudden loss of features such as rock art, the surfaces of stone monuments, and the facing stones of buildings.

INFUSION OF WEATHERING-RIND PORES WITH THE PRODUCTS OF ROCK-COATING DIAGENESIS – EXAMPLES

Rock Varnish

Although rock coatings represent accretions that typically thicken over time, they also undergo diagenetic alteration. Rock varnish formation (a Mn-rich rock coating that forms in all environments) requires nanoscale diagenesis to mobilize Mn and Fe from bacterial casts into clay minerals (Dorn 1998; Krinsley et al. 2009). Some of the dissolution products of rock coatings mobilize downward and reprecipitate in weathering-rind pore spaces (Fig. 3).

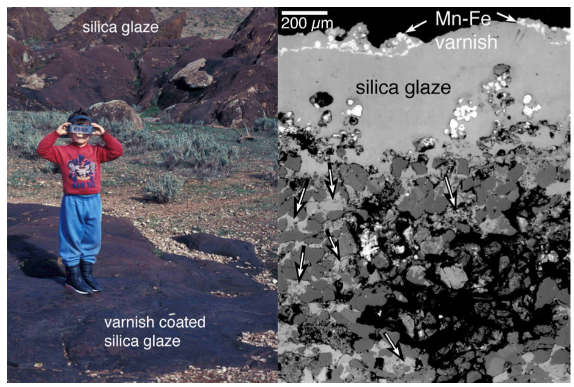

Figure 3 (**Left**) Silicified dolomite at Wharton Hills in South Australia covered by a 0.5 mm coating of dusky brown-colored silica glaze. The silica glaze itself is coated by a patchy Mn–Fe varnish that turns the rock surface black. (**Right**) Backscatter electron image of the Wharton Hills rock coatings shows that dissolution–reprecipitation processes have operated in the pore spaces of the weathering rinds (black arrows with thin white center).

Petroglyphs

Whoopup Canyon in western Wyoming (USA) illustrates case hardening via the infusion of rock-coating materials into the underlying weathering rind (Fig. 4). Whoopup Canyon hosts a world-class petroglyph site, where the rock art experiences ongoing flaking (Fig. 4A), after which weathering-rind porosity increased to the point when detachment took place (Fig. 4B). The prehistoric peoples of Wyoming were able to create the engravings because there was a mixture of rock-coating materials that had been remobilized into the underlying weathering rind to case harden its surface (Fig. 4B).

Silica Glaze

Perhaps the most common agent of case hardening is silica glaze. Soluble aluminum–silicon (Al–Si) complexes [$Al(OSi(OH)_3)^{2+}$] dissolve from the silica glaze and infiltrate down into pores in the weathering rind. The transition

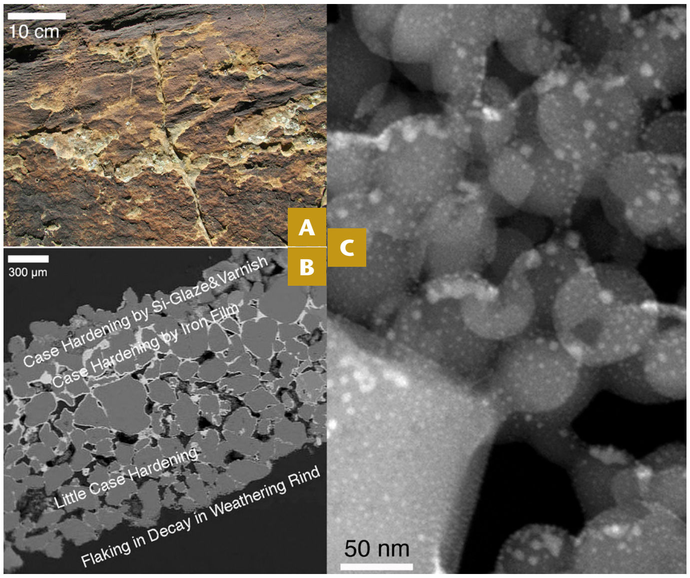

Figure 4 (**A**) Petroglyphs in Whoopup Canyon, Wyoming (USA) are case hardened by a mix of different materials that includes silica glaze, rock varnish, and iron films. Underneath this case-hardened surface, dissolution of the rind continues until the petroglyph experiences detachment. (**B**) Backscatter electron image of the case-hardened surface. This detachment surface derives from one of the flaked-off surfaces in 4A. (**C**) High-resolution transmission electron microscope image of silica glaze spherules deposited in a weathering-rind pore. Sample is from Tibet.

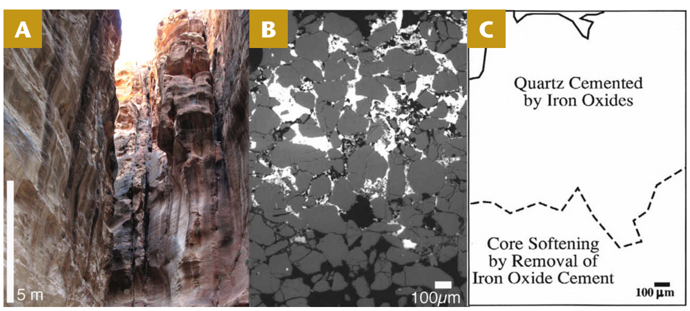

Figure 5 (**A**) Dark streaks on the sandstone at Petra (Jordan) formed, at least partially, of iron oxides. (**B**) A backscatter electron image shows that iron oxides (white) have been reprecipitated into the weathering rind, infilling pore spaces and indurating the rock face. (**C**) Map of the structural zones in the rind shown in 5B. Core softening of the weathering rind beneath the iron oxide cement is an important part of rock-face spalling.

between complete and partial wetting on silica surfaces occurs at about 20–70 nm for liquid droplets. Upon crossing this transition, a metastable wetting film is ruptured, initiating the formation of silica glaze through spheroid deposition (Dorn 1998). This explains the size of the silica spherules (Fig. 4C) being deposited in weathering rinds, as discovered through high resolution transmission electron microscopy analysis of a sample from the Ashikule Basin in Tibet (Langworthy et al. 2010).

Dark Streaks on Cliffs

Water streaks on cliff faces have to be one of the most photographed contexts involving case hardening. It is often difficult to discern the reason for these dark streaks in the field. Although these dark streaks are often attributed to rock varnish (sometimes termed "desert varnish"), fungi, lichens, oxalate, iron films, organics embedded in silica

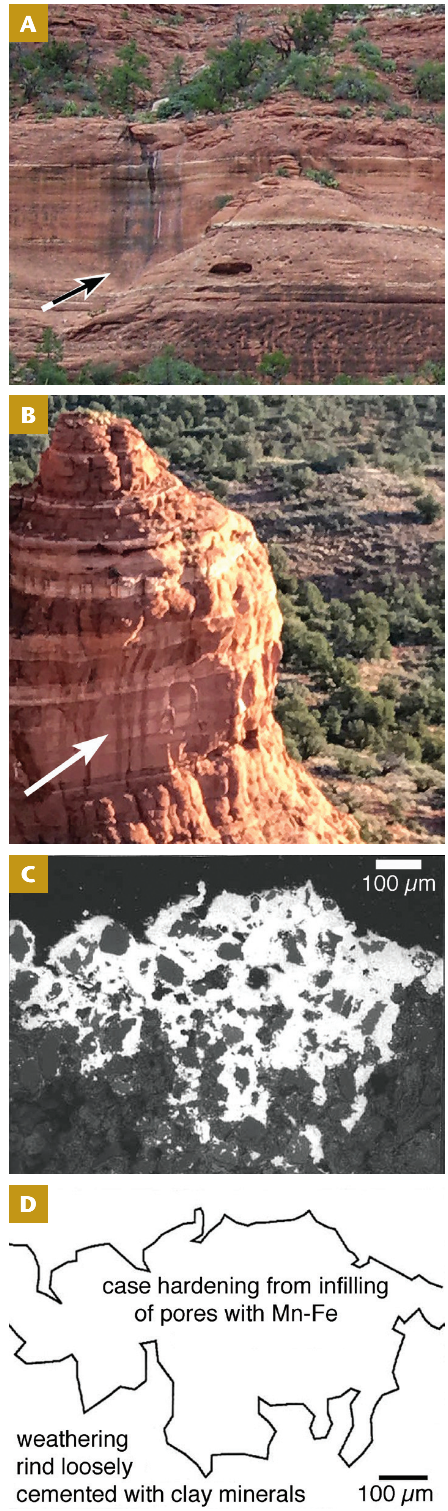

Figure 6 (**A**) Surficial dark streaks (indicated by arrow) that impregnate the sandstone of Sedona, Arizona (USA) consist of heavy metals (mostly Fe and Mn) that have been mobilized from rock varnish. (**B**) A second outcrop of sandstone from Sedona, Arizona (USA), showing similar dark streaks to 6A. (**C**) Backscatter electron (BSE) image of a sample collected from the arrowed location in 6A. (**D**) Map explaining the structural and compositional features of the BSE image shown in 6C. The Mn and Fe have replaced the former silica cement of the sandstone and, thus, case hardening the outer surface of the cliff.

glaze also produce streaks of similar dark appearance. Case hardening as a result for iron oxide development can also be a cause of streaks (Fig. 5), or streaks can result from a mixture of manganese and iron oxides (Fig. 6).

Pedestal Rocks

As exemplified in Figures 1–6, case hardening displays a considerable range in thickness, from tens to hundreds of micrometers. However, case hardening does not have to be particularly thick to indurate a rock surface, as illustrated by the granite rocks of the MacDowell Mountains of Arizona (USA) (Fig. 7). The cap of the pedestal rock is coated with a < 10 µm layer of rock varnish (Fig. 7B), but it is not the varnish that creates the cap. The top of this pedestal has been indurated where biotite splitting has been slowed. Biotite hydration and oxidation is a common cause of the grussification of this granite, as illustrated by the splitting seen in Figure 7B. However, the top surface has partially stabilized where the remobilized constituents of the varnish (Fig. 7B) reprecipitated within the splitting biotite (arrow in Fig. 7B). This case hardening is not continuous, nor is it thick; however, the effect produces the observed cap to this "mushroom rock".

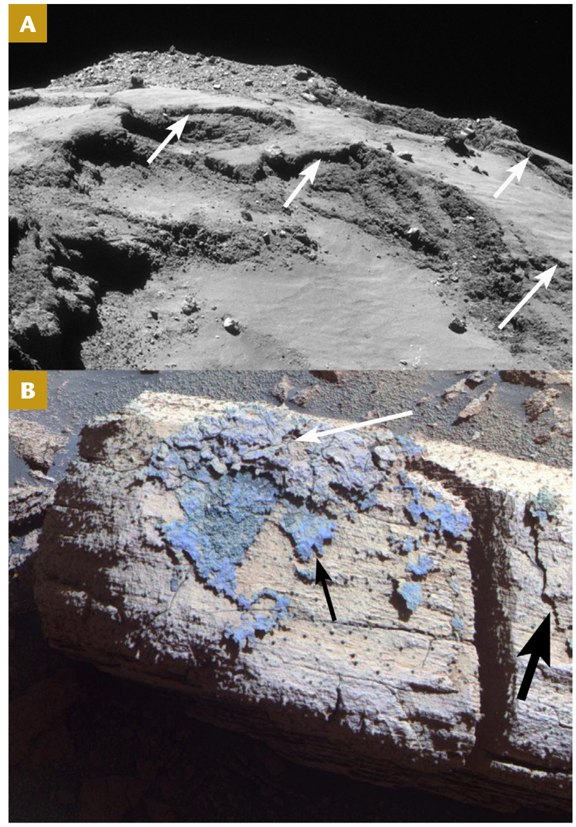

Figure 8 Examples of extraterrestrial case hardening. (**A**) Image of the surface of comet 67P/Churyumov–Gerasimenko (view is ~900 m across). While dust appears to generate smooth surfaces, unknown agents have created induration features, as evidenced by eroded edges of the crust (arrowed). Image from NASA's *Rosetta* spacecraft. (**B**) False color image of a boulder about 25 cm wide, nicknamed Chocolate Hills, on the edge of Concepción Crater on Mars. The thin black arrow identifies a section of case hardening where the coating could be related to impact melt. In addition, two other types of surfaces also display case hardening (white arrow and thick black arrow) with the cause(s) of the indurations unknown. Image by NASA's *Opportunity* rover.

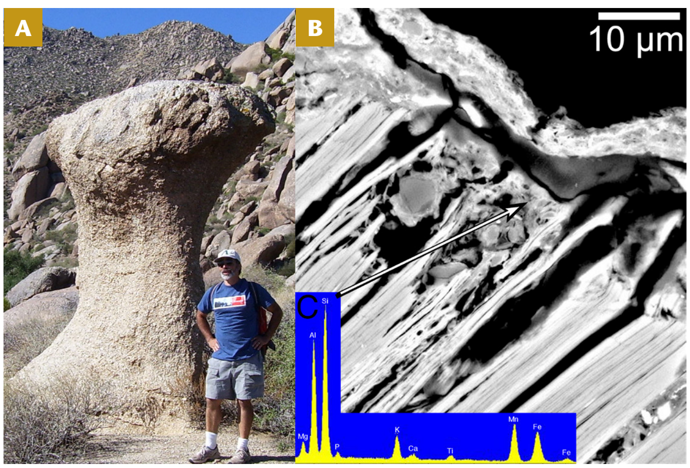

Figure 7 (**A**) Pedestal rocks commonly occur in granitic rock types. Example here is from the McDowell Mountains of Arizona (USA). The rough sides of this pedestal display a texture typical of grussification, here caused by the splitting of biotite minerals due to hydration and iron oxidation (**B**) Backscatter electron image of biotite splitting from the granite shown in 7A. Rock varnish forms on the surface of the pedestal and is then remobilized and precipitated into the biotite fractures (arrow in B). (**C**) Energy dispersive spot analysis reveals the composition of this material in the biotite fractures shown in 7B is similar to the overlying varnish: a mixture of Al and Si from clay minerals and Mn–Fe oxides.

CONCLUSION AND THE IMPORTANCE OF SCALE

Case hardening on Earth requires that two different types of processes operate in tandem: decay of the outer rim of the host rock, which opens up pore spaces, and the remobilization of rock-coating constituents that then infills these pores. Though the processes generating extraterrestrial forms are not known at the present time, case hardening forms certainly appear to exist on Mars and other non-terrestrial planetary bodies (Fig. 8).

The literature on case hardening (Table 1) ascribes induration to a wide variety of agents that operate on different rock types in vastly different environmental settings. Because of this, case hardening is sometimes offered as support for the notion of *equifinality*—that the same end state can be reached by many potential processes in an open system (Phillips 1997; Turkington and Paradise 2005). Consider, for example, the coated and case-hardened rock surfaces in Figures 2 and 3 that are visually similar in the field, but yet very different processes led to the accumulation of silica (Fig. 3) and rock varnish (Fig. 2) at the different sites. While dark streaks on the sandstone of Sedona (Arizona) and Petra (Jordan) (Figs. 5 and 6) appear similar in the field, case-hardening processes led to the accumulation of both manganese and iron at Sedona, but just iron at Petra. While case hardening and rock coating processes occur at nanometer and micrometer scales on Earth, they produce a broadly similar range of surface features that suggest a convergence of similar surface forms seen at the scale of meters on a rock face.

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Table 1 CASE-HARDENING STUDIES CONSISTENT WITH EQUIFINALITY

Rock Type	Location	Case-Hardening Agents	Reference
Andesite	Yalour Islands, Antarctica	calcium phosphate	Arocena and Hall (2003)
Basalt	Hawai'i, USA	silica glaze	Gordon and Dorn (2005)
Dolerite	Antarctica	iron, silica	Conca and Astor (1987)
Granite	Alaska, USA	calcite	Yoshikawa et al. (2006)
Gypsum	Spain	lichen	Mottershead and Lucas (2000)
Lahar	California, USA	hydrous silica, ankerite	Arnold (1962)
Sandstone	Antarctica	silica glaze	Weed and Norton (1991)
Sandstone	Arizona, USA	heavy metal skins	Dorn (1995)
Sandstone buildings	United Kingdom	iron	McAlister et al. (2003)
Sandstone	Italy	iron oxide, calcite, quartz	McBride and Picard (2004)
Sandstone	Nevada, USA	kaolinite, calcite	Conca and Rossman (1982)
Trachyandesite	Tibet	silica glaze, rock varnish	Krinsley et al. (2009)

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