

RAPID FORMATION OF ROCK VARNISH AND OTHER ROCK COATINGS ON SLAG DEPOSITS NEAR FONTANA, CALIFORNIA

RONALD I. DORN

Department of Geography, Arizona State University, Tempe, AZ 85287, U.S.A.

NORMAN MEEK

Department of Geography, California State University, San Bernardino, CA 92407, U.S.A.

*Received 10 January 1994
Accepted 19 December 1994*

ABSTRACT

Manganiferous rock varnish, silica glaze and iron skins have formed on 20- to 40-year-old slag piles near Fontana, southern California. Rapid rock-varnish formation is associated with an unidentified cocci bacterium that grows rapidly in culturing experiments, combined with the likelihood that Mn-rich solutions flow over slag surfaces. A new model is proposed for the formation of silica glaze, involving soluble Al–Si complexes and the nature of wetting films. Iron skins occur where runoff is concentrated, and where iron bacteria grow.

Observations indicate: (i) substrate can be important in supplying Mn, as well as maintaining a stable surface and channelling runoff to microspots where varnish grows; (ii) ignorance of boundary layer pH/Eh conditions makes chemical–physical models of varnish formation speculative; (iii) the balance between cementation of recently nucleated varnishes and erosional shear stresses is poorly understood, but is probably an important limiting factor on varnish growth rates; and (iv) there must be at least two steps in biotic varnishing—accretion of Mn–Fe in casts, followed by cementation of clays by either *in situ* cast residue or Mn–Fe remobilized from casts. Varnish accretion may be limited by the rate at which both steps occur. Rapid development of readily distinguishable manganiferous rock varnishes at this post-1952 site highlights the danger of speculation on the ages of landforms based solely on the appearance of rock-varnish coatings.

KEY WORDS rock varnish; silica glaze; iron skins; rate of formation; genesis; weathering; geomorphology

INTRODUCTION

Rock varnish is a dark coating that forms on natural and artificial surfaces. Typically, clay minerals comprise half to two-thirds of varnish by weight, with manganese and iron making up another third (Potter and Rossman, 1977). The black and orange colours are caused by the manganese and iron oxides, which cement the clays together and also to the rock. Although rock varnish is best known in deserts, it is also found in numerous terrestrial weathering environments, including Antarctica (Dorn *et al.*, 1992c), Norway (Whalley *et al.*, 1990) and Hawaii (Dorn *et al.*, 1992b).

Most observers believe that the rate of rock-varnish accretion in deserts is so slow that it takes tens of thousands of years to completely coat rocks (Dorn and Oberlander, 1982; Whalley, 1983). For example, rock surfaces on the *c.* 14 000-year-old (^{14}C dated) shoreline of Searles Lake in eastern California have not been completely coated with varnish, and the \sim 2000-year-old Nazca geoglyphs in Peru (Dorn *et al.*, 1992a) have developed only millimetre to centimetre sized spots of varnish. Some claim, however, that there are circumstances in which rock varnish can form rapidly (Engel and Sharp, 1958). Controversy has surrounded this issue (Elvidge, 1982; Dorn and Oberlander, 1982) because scientists have used the slow growth of varnish over rock surfaces as a means of estimating ages for ancient landforms, petroglyphs and artifacts (Carter, 1980; Shlemon, 1978).

The abundant evidence of slow-growing varnish does not, however, contradict the hypothesis that varnishes *can* grow at much faster rates. Throughout the Colorado Plateau, U.S.A., varnish forms more rapidly in places where water flows over sandstone scarps (Hunt, 1974). Moreover, the percentage of varnish cover within portions of a single desert petroglyph can vary by over 300 per cent. Mn-Fe skins can form on river cobbles in less than a year (Cerling and Turner, 1982; Brick *et al.*, 1993). Manganiferous rock varnish formation can develop in a few decades on moraines (Höllerman, 1963; Dorn and Oberlander, 1982) or in a subglacial position of an active glacier (Whalley *et al.*, 1990).

We have found a site in San Bernardino County, near Fontana, California, where visually obvious rock-varnish coatings have developed within three decades. Differential degrees of varnish formation can be seen on 20-year-old slag piles of the former Kaiser Steel Plant (Figure 1). In addition, there are three other types of surficial alteration: weathering rinds have developed, silica glaze has coated exposed slag, and iron skins have covered surfaces and penetrated into slag fractures.

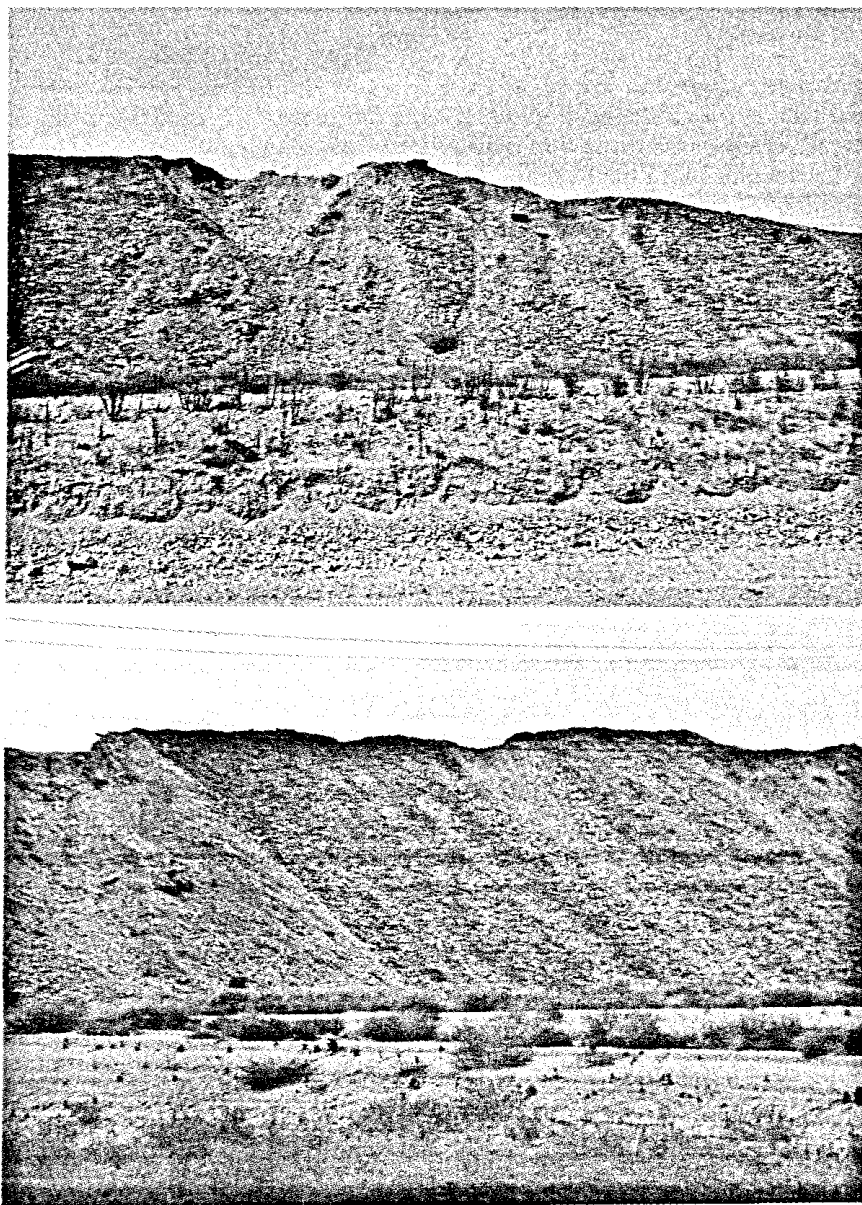


Figure 1. Ground view of differential development of rock coatings on the west slag pile

A basic problem in the rock-coating literature is a lack of understanding of why certain coatings grow so rapidly at a few sites and more slowly elsewhere. The importance of this study rests in gathering information of use in the development of a general theory of geographical variations in rock-coating development. In addition, it is risky to use visual appearance as a tool to estimate age (Shlemon, 1978; McFadden *et al.*, 1989) until the circumstances in which rock varnishes and other rock coatings form unusually fast are understood. Thus, the objective of this paper is to document the nature of these rock coatings at a site where they have grown very rapidly, and to use this knowledge to constrain future models of rapid formation of rock varnish, silica glaze and iron skins.

THE STUDY SITE

The old Kaiser Steel Plant is located near Fontana, in San Bernardino County, California (Figure 2). The plant began operating in December 1942, primarily to supply wartime steel plating for the H. J. Kaiser ship-building operations in Richmond, California, and Portland, Oregon. In the late 1970s, this plant was the largest steel mill west of the Mississippi River, producing more than 3 million tons of finished steel each year. Although all operations at the plant had ceased by December 1983, renewed, limited operations by California Steel Industries, Inc. began in 1984 and are continuing at some facilities on the site.

The original Kaiser operation first converted iron ore to pig iron in a blast furnace. Nearly all of the iron ore came from the Eagle Mountain mine in Riverside County, with limestone from mines in Lucerne Valley. The by-product of this process was a comparatively light-weight, vesicular, blast-furnace slag. Subsequently, pig iron was converted to steel in an open hearth, again using limestone in the process. The by-product of this process was a more dense open-hearth slag (Table I).

The two large slag piles are visible from the Interstate 10 freeway, just east of its interchange with the Interstate 15 freeway (Figure 2). The slag piles lie between Calabash and Etiwanda Streets, and San Bernardino Avenue and Valley Boulevard. The east and west slag piles are divided by a north-south flood-control channel. The east slag pile (UTM: 45300 mE, 377010 mN, zone 11) consists of blast-furnace (iron) slag and various materials mingled in a landfill area. It was constructed between the late 1940s and about 1952.



Figure 2. Aerial photograph and map overlay of east and west slag piles. BF = blast furnace slag, CS = comingled blast furnace, open hearth, basic oxygen-furnace and soaking pit debris, L = landfill area, M = mining area

Table I. Average composition of iron and steel slag, and attached dust (weight per cent)

Oxide	Sampled slag*	Sampled dust*
CaO	34.02 ± 3.17	28.46 ± 4.11
SiO ₂	31.04 ± 2.55	30.03 ± 5.34
Al ₂ O ₃	14.13 ± 3.48	16.40 ± 2.46
SO ₃	0.74 ± 0.33	3.14 ± 0.77
MgO	6.20 ± 4.20	4.18 ± 0.98
FeO	5.02 ± 2.03	5.28 ± 0.59
MnO	2.89 ± 1.40	3.03 ± 0.24

* Data from wavelength dispersive electron microprobe measurements of fused beads of slag samples ($n = 9$) and dust samples ($n = 5$). Samples were homogenized in a flux of lithium metaborate before measurement with a 30 μm beam width (see Dorn *et al.*, 1990)

We collected samples from the west slag pile (Figures 1, 2), which consists of blast-furnace slag along with open-hearth (steel), basic oxygen-furnace (steel) and soaking-pit debris (steel). The west pile (UTM: 452200 mE, 3770100 mN, zone 11) was constructed between 1952 and 1972. Since the early 1980s, the centre of the western pile has been mined by the Heckett Corporation. So that the area can be redeveloped, the entire plant is presently being demolished and the slag piles removed.

Unlike most rock types, manganese and iron are in abundance, with similar proportions in the slag we collected (Table I). Silt-sized dust particles in contact with five pieces of slag were also collected and chemically analysed (Table I). This silt could only have been deposited as dust, since the collected slag fragments were not in a position to receive runoff from upslope surfaces. The chemistry of the dust is within the same range as the slag; hence it is reasonable that the dust fallout is, in part, derived from the local slag piles.

The pH of precipitation, collected at the nearby El Monte wet-acid deposition station, has been 4.74 ± 0.43 from August 1984 through to June 1987 (California Air Resources Board, 1988). This is low enough to reduce and mobilize both iron and manganese (Brookins, 1988) from slag weathering rinds and dust. Also, chemical reactions in fog/dew and rain can contain dissolved Fe(II), which increases in concentration with lower pH and exposure to light (Behra and Sigg, 1990). The solutions that are in contact with the rocks, therefore, could have substantial quantities of Mn(II) and Fe(II).

CAUSE OF THE COLOUR CHANGE

The colour change of different landslide scars, clearly visual to the eye (Figure 1) and reminiscent of differential development of rock coatings on desert alluvial fans (White, 1990), is a product of several different types of rock-surface alterations acting in combination.

Weathering rinds

The slag develops a weathering rind through the loss of mass around the outer rim of the slag clasts. The lightest coloured landslide we sampled had virtually no rind development. Backscattered electron microscopy of the darkest slag revealed rind thicknesses from 0 to 1.5 mm.

Iron skins

Iron skins are found where water concentrates and flows over the slag. Iron oxides comprise over three-quarters of the iron skins (Table II). The remaining ions could be adsorbed to iron hydroxides (cf. Sverjensky, 1993). The backscattered electron (BSE) micrograph in Figure 3A, and other scanning electron microscopy (SEM) work, reveals clear contacts between the iron skins and slag. This morphological evidence indicates that 'leaching' from the rock immediately underneath the skin is not important. The precipitation

Table II. Chemistry of different rock coatings observed on the west slag pile, Kaiser steel plant, as measured by wavelength dispersive electron microprobe with a 10 μm spot size. Each probe measurement reflects a position along a transect that is located in the specified figure. Low oxide (weight per cent) totals are from porosity, water and organic matter

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	BaO	Total
Iron skin (transect in Figure 3A)	BLD	BLD	4.08	1.08	1.44	0.11	BLD	0.77	0.15	0.74	81.00	BLD	89.37
	BLD	BLD	5.15	2.19	1.50	0.17	BLD	0.84	0.23	0.99	80.14	BLD	91.21
	BLD	BLD	2.99	1.44	1.05	0.23	BLD	0.85	0.33	0.74	79.05	BLD	86.68
	BLD	BLD	3.15	1.05	1.49	0.28	BLD	0.70	0.42	0.80	76.88	BLD	84.77
	BLD	BLD	3.81	1.06	1.61	0.22	BLD	0.74	0.17	1.03	79.57	BLD	88.21
Silica glaze (transect in Figure 4)	0.98	1.23	21.15	43.40	0.23	2.05	BLD	1.01	BLD	2.57	4.34	BLD	76.96
	1.01	1.05	22.18	41.07	0.30	3.23	BLD	1.23	BLD	2.63	4.60	BLD	77.30
	0.74	2.05	23.51	47.24	0.39	1.97	BLD	1.44	BLD	2.74	4.67	BLD	84.75
	0.37	1.75	26.30	41.87	0.44	2.44	BLD	1.74	BLD	2.60	4.80	BLD	82.31
	0.14	1.11	25.22	42.17	0.35	3.00	BLD	1.40	BLD	2.64	5.71	BLD	81.74
Rock varnish (transect in Figure 5B)	0.80	5.19	14.25	30.04	0.17	0.59	0.18	25.17	0.72	3.90	4.07	BLD	85.08
	2.64	1.66	6.41	17.71	0.25	0.87	0.29	3.46	0.59	28.32	2.07	BLD	64.27
	1.00	1.74	11.04	14.36	0.54	0.95	0.23	2.93	1.05	23.87	9.08	BLD	65.79
	1.51	1.31	14.30	19.85	0.55	1.15	0.47	3.46	1.47	18.92	7.73	BLD	69.21
	0.94	1.49	14.46	19.74	0.47	1.20	0.69	4.69	1.45	11.03	9.24	BLD	64.46
	1.56	1.91	11.63	18.17	0.65	0.82	0.63	5.95	0.90	15.78	9.92	BLD	66.36
	0.78	0.95	15.94	22.28	0.14	0.90	0.43	4.84	1.28	14.70	6.64	BLD	68.10
	0.74	0.77	15.41	19.10	0.84	0.95	0.41	5.46	1.27	14.43	6.57	BLD	65.21
	0.65	1.29	12.85	19.76	0.52	1.03	0.46	4.34	1.47	15.73	9.98	BLD	67.43
	0.28	1.48	15.60	20.24	0.75	0.91	0.65	6.78	1.58	8.92	9.59	BLD	66.50
Underlying slag	1.06	1.67	16.07	22.81	0.24	1.18	0.27	5.40	0.98	11.08	6.39	BLD	67.15
	0.43	11.14	16.25	32.44	0.07	0.19	0.24	29.30	1.20	3.40	5.04	BLD	99.70
	0.74	1.19	14.46	19.89	0.53	0.80	0.44	2.67	0.98	13.67	13.94	0.14	68.71
	0.54	1.23	14.55	17.00	0.72	0.80	0.57	3.68	1.04	12.23	5.16	0.16	57.14
	BLD	BLD	2.09	8.50	1.57	0.21	0.18	0.48	0.22	28.70	5.00	BLD	46.95
Rock varnish (transect in Figure 5C)*	BLD	BLD	2.47	6.77	1.85	0.27	0.24	0.17	0.20	30.11	3.17	BLD	45.25
	BLD	BLD	1.14	7.04	2.04	BLD	0.20	0.58	0.18	22.18	5.10	BLD	38.46
	0.34	BLD	3.51	8.04	1.84	BLD	0.16	0.40	0.25	18.46	6.03	BLD	39.03
	0.19	BLD	4.07	10.11	1.50	BLD	0.16	0.51	0.19	10.15	4.14	BLD	31.02

BLD, below limit of detection

* Spot size reduced to 2 μm , owing to small size of bacteria

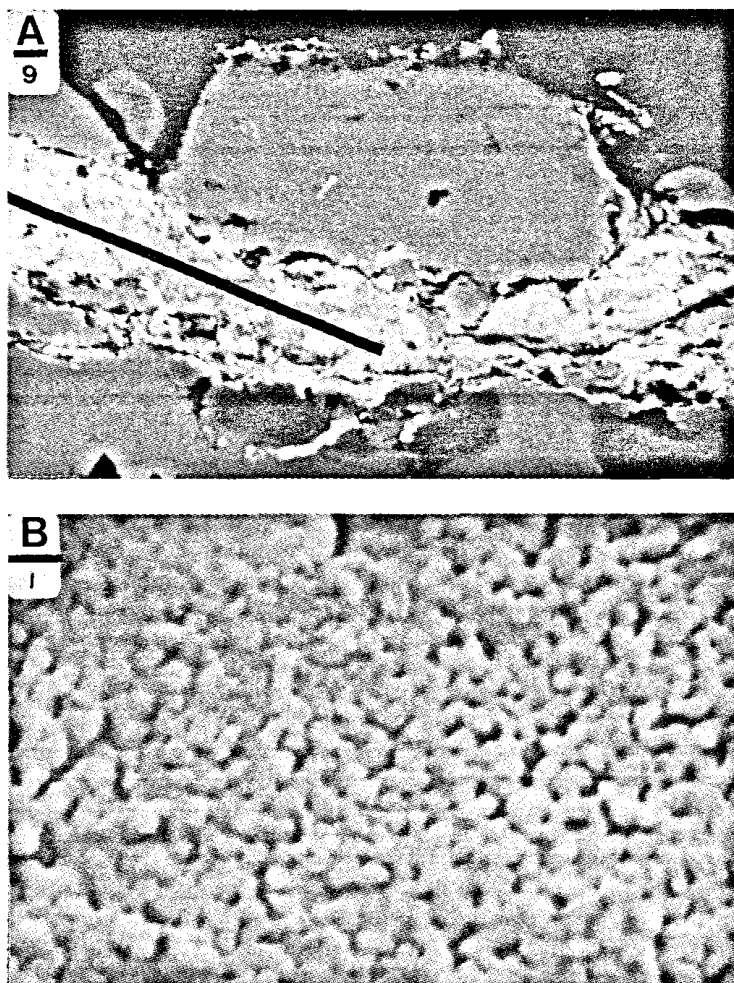


Figure 3. Electron micrographs of iron skins. Scale bar in micrometres. (A) Backscatter electron (BSE) micrograph of an iron coating which has penetrated a slag clast from the surface along a fracture. The surface of the clast is at the top of the micrograph. Line identifies electron microscope transect in Table II. This weathering produces silt-sized pieces of slag, and exemplifies the artificial nature of the separation between physical and chemical weathering. (B) Secondary electron image showing what are probably iron bacteria growing on the surface

of iron is not limited to the surface; it occurs in fractures within the slag. Intra-slag iron precipitation leads to a type of weathering known as 'iron fracturing', where silt-sized fragments are detached from cobbles (Figure 3A).

Iron-skin constituents could be derived from airborne fallout, fog, rain, dissolved constituents of weathering rinds in water flow over slag surfaces, or all of the above. Table II reveals that whatever mechanism is precipitating iron is not precipitating manganese in the iron skins; the concentration of Mn in the iron skins is less than in the underlying rock or dust.

Three mechanisms could deposit iron in the skins. Of these, however, only bacterial activity could fractionate Fe from Mn. (a) A pH increase could cause iron oxidation (Brookins, 1988), but if a pH change occurred Mn(II) would be oxidized and deposited before Fe(II). (b) Evaporation of water could deposit iron but Mn would also be deposited (Brettschneider, 1981). (c) Precipitation of iron can occur rapidly by bacterial activity where acid water flows (Nealson, 1983). Although chemoautotrophic bacteria were not cultured, what could be cocci iron bacteria were observed on the surface of the iron skins (Figure 3B). Bacterial precipitation of iron from acid water flows would deposit iron and leave manganese in solution.

Silica glaze

Coatings of amorphous silica have formed on the slag in micropositions where water does not collect or flow (Figure 4; Table II). Silica glaze occurs in a wide variety of environments, including warm drylands

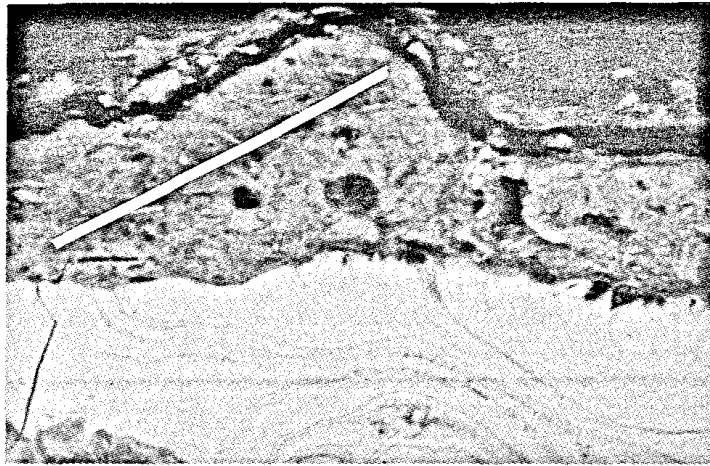


Figure 4. BSE micrograph of silica glaze, which coats the west slag pile. In this case, the silica glaze has accreted on top of material that is greatly enriched in Fe and Mn (energy dispersive analysis reveals Mn: Fe ratio of ~1:3, with minor amounts of Si and Al). The line identifies the 80 μm -long electron microprobe transect in Table II

(Hobbs, 1917; Fisk, 1971; Smith and Whalley, 1988), Antarctica (Weed and Norton, 1991), tropical areas (Alexander and Lequarre, 1978; Curtiss *et al.*, 1985), and various archaeological settings (Hamilton, 1984; Nobbs and Dorn, 1993). In different environments, however, different elements can occur in substantial quantities; for example, Al_2O_3 can reach >50 per cent in some glazes from Hawaii, or Fe_2O_3 can reach >10 per cent in some glazes on desert pavement cobbles from Peru and the southwestern United States. In this case, iron comprises about 5 per cent of the coating (Table II) and gives it a light orange colour.

Current models of silica glaze genesis involve precipitation of silica from solution (Fisk, 1971; Curtiss *et al.*, 1985; Weed and Norton, 1991; Robinson and Williams, 1992). Alternative mechanisms involve precipitation from a 'gel' (Krauskopf, 1956), perhaps involving organic acids (Krauskopf, 1979), microbial activity (Ferris *et al.*, 1986), freezing (Wada and Nagasato, 1983), or some combination of agents. Silica can be put into solution in a number of ways (Krauskopf, 1956), for example, by either very acid or very alkaline solutions (Brookins, 1988). Both pH extremes are possible at this site. The pH of 15 samples of dust were measured in a 1:1 paste; pH values ranged from 2.4 to 13.2 with no clear mode.

The formation of silica glaze on slag can be constrained by chemistry and texture. Three types of evidence suggest that at least some constituents were not deposited from solution, but as pieces of detritus, as in Hawaiian silica glazes (cf. Curtiss *et al.*, 1985). (1) BSE imagery reveals a detrital texture, where casts are either submicrometre in size, or orientated subparallel to the surface (Figure 4). (2) Iron and manganese are present in the silica glaze and dust in similar quantities (Table II), which would be consistent with deposition of dust as detritus, rather than precipitation by bacteria that might fractionate Mn from Fe. (3) Sulphur is greatly enriched in the silica glaze compared to the underlying slag. However, similar concentrations are found in the dust, some of which could derive from sulphur-rich slag in a different part of the pile, or air pollution sources in the region. Sulphur dioxide is a large component of smog, which dominates the Fontana area.

The model of silica glaze formation proposed here involves soluble aluminium silicate complexes and the nature of wetting fronts. Soluble Al-Si complexes $[\text{Al}(\text{OSi}(\text{OH})_3)_2]^{2+}$ are ubiquitous and are critical in the formation of new metastable minerals at the water-rock interface (Lou and Huang, 1988; Browne and Driscoll, 1992). These may be released first from the weathering of phyllosilicate minerals (Robert and Tessier, 1992, pp. 86, 78). Soluble Al-Si should occur under the geochemical conditions at this slag pile, as well as in more 'natural' settings.

A key in the stabilization of soluble Al-Si complexes might be very gentle wetting (e.g. dew deposition), when the silica glaze starts to form. Curtiss *et al.* (1985) observed that silica glazes in Hawaii could be

disturbed by violent wetting events (e.g. heavy precipitation or runoff). Similarly, the microposition of the silica glazes on slag is on centimetre-scale topographic highs, where water does not collect or flow. This suggests that wetting occurs only with dew and light rainfall, not where water collects in millimetre-scale depressions or where runoff occurs. We note that the slag pile is extremely porous and permeable.

Rupturing of metastable films on silica surfaces could disturb an incipient glaze. The transition between complete and partial wetting on silica surfaces rests at about 50–70 nm (Zorin *et al.*, 1992). When this transition is crossed, the metastable wetting film on the silica surface is ruptured (Zorin *et al.*, 1992). Violent wetting (intense rain, runoff) on silica surfaces would cross this wetting threshold and disturb an incipient bond between glaze and rock. In contrast, if the wetting is 'gentle' (e.g. dew, or short duration, low intensity rain), a bond between the rock and soluble Al–Si could occur, which initiates glaze formation.

Once the coating is well established, silicic acid and soluble Al–Si complexes could more readily bond to the silica glaze than the rock. Casey *et al.* (1993, p. 255) found that 'silicon need have no residence time in solution as silicic acid before it is incorporated into a solid reaction product at the surface of a mineral'. This undoubtedly plays a role in the rapid formation of silica glazes on historic basalt flows in Hawaii (Curtiss *et al.*, 1985) and could do so at this site. There is no method available to measure the pH or Eh of these wetting fronts, but it is likely that redox changes are important in the accretion of silica glazes.

Rock varnish

Rock varnish occurs in microdepressions where water collects rather than areas where surface flows are concentrated (iron skins). It is uncommon on protuberances, which are sites of silica-glaze formation.

ROCK VARNISH CHARACTERISTICS

Manganiferous varnish on slag is chemically similar to varnishes found elsewhere, in that it is dominated by silicon, aluminium, manganese and iron (Table II). The other measured cations are all within ranges of natural varnishes. Similarly high sodium values have been observed in coastal varnishes of southern Peru and in varnishes near the margin of the Death Valley playa (Dorn *et al.*, 1990). High calcium values can be found in varnishes forming adjacent to exposed calcrete (Dorn, 1989). Although titanium values are two to three times greater than typical varnishes (Dorn *et al.*, 1990), similar levels have been measured in varnishes rich in titanomagnetites and where titanium domes have developed *in situ* (Dorn, 1989). Low barium levels (<0.2 per cent) are often found where the varnish has formed in a subaerial position (Dorn, 1994); in contrast, crack varnishes typically have significantly higher barium levels (Carlos *et al.*, 1993; Dorn, 1994).

This rock varnish is texturally quite different from varnishes found elsewhere (see Dorn and Oberlander, 1982; Whalley, 1983; Dragovich, 1988; Krinsley *et al.*, 1990; Dorn *et al.*, 1992b). Almost all varnishes observed have a granular texture, rather than a layered appearance, when viewed in BSE images (Figure 5A,B). Some granularity may derive from casts of bacteria (Figure 5C). We did note, in one sample where manganiferous varnish interdigitated with silica glaze, a layered botryoidal structure (Figure 5D) similar to 'stromatolitic' features observed in other rock varnishes (Krinsley *et al.*, 1990).

If any locality were susceptible to varnish formation by 'leaching' and 'reprecipitation' of constituents dissolved from the underlying rock (cf. Loew, 1876; Walther, 1891; Shlemon, 1978), it should be this site: manganese and iron are abundant in the underlying slag (Table I), there is acidic precipitation, and a weathering rind has developed from the mobilization of cations in the underlying rock. Yet, there is a clear boundary between underlying rock and varnish (Figure 5A,B), similar to that in other rock varnishes (Potter and Rossman, 1977; Dorn and Oberlander, 1982). There is even a clean boundary between Fe–Mn-rich slag material and silica glaze (Figure 4).

Two types of data that were gathered from slag varnish are consistent with a bacterial origin for manganiferous rock varnishes (e.g. Dorn and Oberlander, 1981; Krumbein and Jens, 1981; Jones, 1991; Staley *et al.*, 1991; Drake *et al.*, 1993). The following discussion focuses first on the casts of cocci bacteria that were observed, and second, on varnishes grown from test-tube cultures of the bacteria.

Casts of cocci bacteria were commonly observed in the upper portions of slag varnishes. Figure 5C shows

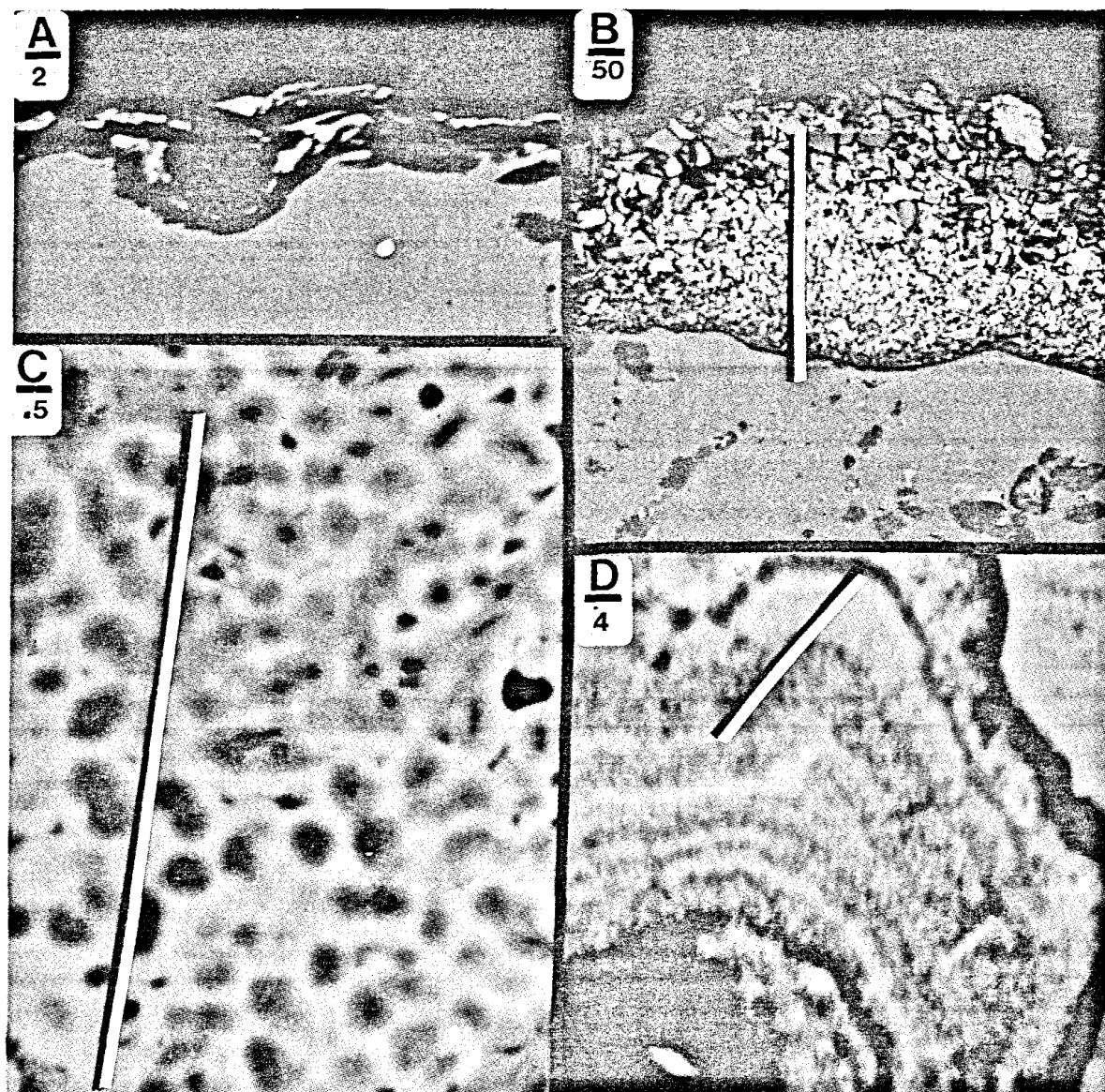


Figure 5. BSE image of rock varnish formed on the west slag pile, as viewed in a polished section. Lines represent transects that correspond to the analyses in Table II. Scale bars in micrometres. (A) Incipient rock varnish on lightest coloured slag. (B) Thickest rock varnish observed in darkest slag. (C) Bacterial casts found near the surface of the rock varnish. (D) Interdigitation of 'stromatolitic' varnish and silica glaze

a BSE image of the upper $8\ \mu\text{m}$ of slag varnish, revealing cocci-shaped pseudomorphs. A secondary electron image shows no bacteria in the darker void space. These casts are visible only in the upper few micrometres of the varnish, and only with gentle hydrofluoric acid etching of the cross-section. A focused microprobe transect in Figure 5C reveals that casts closer to the subaerial surface are enriched in manganese compared to those deeper in the varnish (Table II); this is consistent with the more defocused microprobe data from Figure 5A (Table II). We speculate that the manganese is remobilized from the bacterial casts after their initial formation, which collapses the structure of the bacterial casts and explains why they are not found lower in the section. In addition, the recent age of this site documents that the growth and collapse of bacterial casts can take place quite rapidly.

Bacterial casts have been found in other natural varnishes. Sometimes they are visible owing to cation leaching which weakens the varnish matrix (Dorn and Krinsley, 1992). Elsewhere, etching with HF is required to make casts visible (Figure 6A), but in other circumstances they can be seen naturally (Figure 6B). However, Smith and Whalley (1988), Jones (1991), Staley *et al.* (1991) and Drake *et al.* (1993) correctly

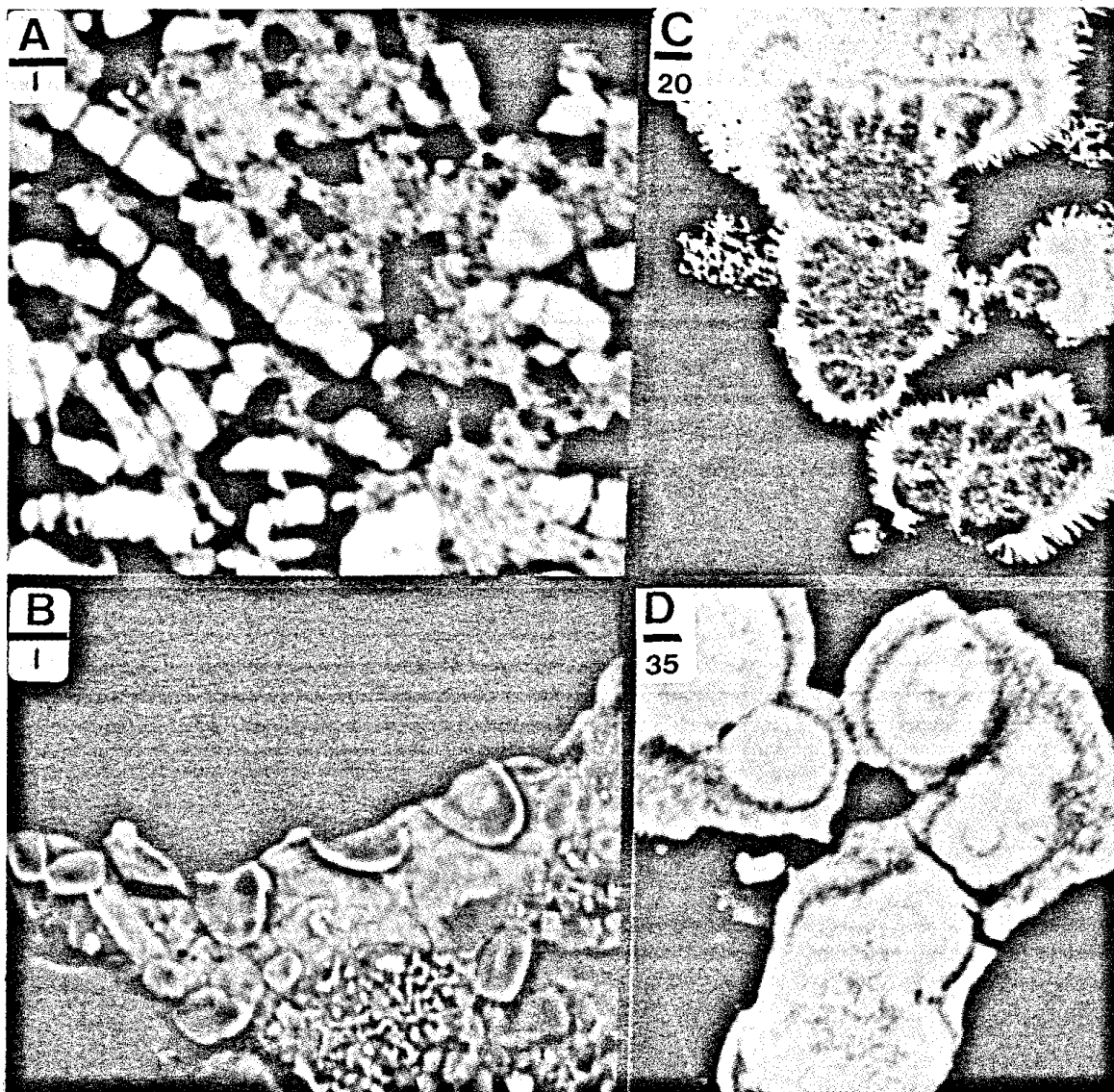


Figure 6. Evidence of direct bacterial concentration of manganese and iron, provided by BSE micrographs. (A) Cast of bacteria in rock varnish from Death Valley, where the polished cross-section was etched with HF. This etching process removed the clay matrix, thus revealing the Mn-Fe bacterial cast that was not apparent before HF treatment. (B) Natural cast of bacteria in rock varnish, collected by Tanzhuo Liu, from the Kunlun Mountains of Tibet. (C) Nodule of Mn-Fe bentonite clay, made in 3 weeks by unidentified cocci bacteria cultured from the Fontana slag pile (see discussion in text). (D) Nodule of Mn-Fe bentonite clay, made in 6-12 months by unidentified cocci bacteria cultured from botryoidal varnish near the top of Kitt Peak, Arizona (see discussion in text)

note that surficial and intra-varnish bacterial remains are not commonly seen on or in Mn-rich varnishes. The reason may be the low resistance of bacterial cast structures to Mn remobilization and their subsequent rapid structural collapse.

The uncommon presence of bacterial casts has a previously unexplored implication for the genesis of manganiferous rock varnishes: biotic varnish formation may be a two-stage process. Bacterial (or fungal, or algal) enhancement of Mn would result in casts, as seen here. Their gradual breakdown, as inferred here, may be due to remobilization of Mn and Fe. Krinsley *et al.* (1990) have documented fracture zones where some of this Mn and Fe is subsequently reprecipitated. Yet, these obvious reprecipitation features can only account for a small fraction of the Mn-Fe in rock varnish. The bulk is locked up in the clay-oxide

matrix (Potter and Rossman, 1977). If Mn (and Fe) is concentrated by micro-organisms, but Mn-Fe casts are uncommon, then Mn-Fe must either cement the clays *in situ* after the cast structure collapses, or be remobilized and reprecipitated to cement clays together and to the rock, or both. Regardless of whether Mn enhancement in varnish occurs biotically or abiotically, the true key to the genesis of rock varnish rests at the nanometre scale of how clays and Mn-Fe oxides interact.

Gram-negative cocci bacteria were cultured from the slag varnish on an autoclaved medium of 0.005 per cent sodium acetate, 0.05 per cent $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 0.05 per cent $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, c. 2 per cent natural dust (including organic and inorganic components), and 0.0001 per cent cupric citrate, zinc carbonate hydroxide monohydrate, vanadium oxide on silica gel, lead carbonate and chromium sulphate hydrate. The isolates were placed in test tubes with this media adjusted to pH 7, along with c. 5 per cent autoclaved natural dust and sand collected from rock surfaces in the Sonoran Desert.

The other types of Mn-oxidizing bacteria cultured from the site (two unidentified rods, one *Bacillus*) did not form nodules or artificial varnishes on sand-grain surfaces. Controls, consisting of the same medium (pH 7) but lacking bacteria, and the medium inoculated with bacteria but at pH 8, also failed to produce nodules or test-tube grain coatings. By 'failing to produce' nodules or grain coatings, we do not mean there was an absence of deposits. There were mottled orange and brown stains, easily wiped off with a glove, as in the experiments of Dorn and Oberlander (1982). Yet, these spots did not show SEM textures or chemical similarities to natural varnish.

The gram-negative cocci bacteria, in contrast to previous experiments, grew relatively quickly and demonstrated oxidation of manganese within 3 days. In previous culturing experiments, bacteria took weeks to months to develop such an ability. The cocci produced nodules with a tendency towards botryoidal or stromatolitic growth forms within 3 weeks (Figure 6C). This growth form is similar to other nodules, which, given the same experimental conditions, formed after 6 months from the growth of gram-negative cocci bacteria cultured from Kitt Peak, Arizona (Figure 6D).

We are cautious about over-interpreting this laboratory study in biomineralization. As noted in Krumbein and Jens (1981) and Dorn and Oberlander (1982), this type of experiment cannot possibly replicate real rock varnish. Time-scales are over a thousand times too short. Hardnesses are very different. Real-world varnishes that occur in deserts form at rates of $< 1-20 \mu\text{m/ka}$, completely non-analogous to laboratory nodules and coatings. Real varnishes are subject to wetting and drying and ultraviolet radiation not found in test-tube cultures. Furthermore, the nutrients available and used by micro-organisms on rock surfaces are not known. Still, there has been considerable speculation over the role of different types of bacteria on the development of different varnish structures. This study provides the first direct evidence that botryoidal (stromatolitic) growth forms may be from a particular type of bacterium (or bacteria).

SPECULATIONS ON RAPID GROWTH RATES OF ROCK VARNISH

There is nothing to indicate that the growth of silica glazes or iron skins over a few decades is anomalous. In Hawaii, for example, silica glazes are known to develop on historic basalt surfaces (Curtiss *et al.*, 1985, p. 50). Similarly, iron skins have developed where there is acid drainage on 20th century mine tailings in Arizona, Nevada, and Wyoming (R. I. Dorn, unpublished observations). There are very few documented cases where silica glazes or iron skins have been studied at sites with a known age of surface exposure. However, subaerial sites with historic manganese rock-varnish formation are comparatively rare. The focus of this discussion must turn, therefore, on why manganese rock varnish has formed so quickly at this site.

One possible reason for its rapid formation may be the type of bacteria growing on the Fontana slag. Dorn and Oberlander (1982) stressed that the ability to culture Mn-oxidizing bacteria or to grow test-tube varnish does not *prove* a bacterial origin; still, it can be suggestive. The cocci bacteria cultured from the slag varnish demonstrate oxidation of Mn(II) five to ten times more quickly than bacteria cultured from arid varnishes. Furthermore, pseudo-varnish nodules developed amazingly rapidly, within 3 weeks, or eight times faster than in previous experiments.

An additional factor could be the abundance of manganese in the environment. The weathering rind indicates that the Mn-rich slag is being mobilized chemically, which would be consistent with the acidic

pH of the precipitation. Further fractionation of Mn could occur when iron skins are precipitated without manganese. The solutions that periodically occupy the millimetre-scale depressions are even more enriched in manganese. The abundance of manganese in solutions could certainly speed varnish accretion.

IMPLICATIONS

Three types of rock coating have formed on blast furnace slag in Fontana, southern California, within 20–40 years. Iron skins may form by the precipitation of iron by bacteria. Silica glazes may form where soluble Al–Si complexes are precipitated by gentle wetting films. Manganiferous rock varnish appears to be precipitated by cocci bacteria from solutions that are probably greatly enriched in manganese. Rapid formation of silica glaze and iron skins does not appear to be anomalous, but the rapid development of rock varnish is unusual.

Different types of rock coating exist in different microenvironments. Iron skins form where acid runoff occurs. Silica glazes occur where the least wetting occurs, primarily on the high points of the slag clasts. Rock varnishes form in the intermediate position—where water collects in small depressions. Interdigitation of rock varnish and silica glaze also occurs (Figure 5D), much like that observed in natural settings (Nobbs and Dorn, 1993).

One could argue that these results are a product of an unusual field situation, and that implications for 'natural' environments could be limited. However, the processes by which these coatings developed can place constraints on a general model of rock-varnish development.

(1) *Substrate is important.* Substrate stability has been recognized as important in determining whether or not a rock varnish has time to develop (Dorn and Oberlander, 1982; Drake *et al.*, 1993). Substrate type can also affect how varnish growth occurs (Dorn *et al.*, 1992a). This study adds another factor—the abundance of manganese in solutions flowing over rocks—as a way in which substrate can potentially influence varnish.

(2) *Boundary layer pH/Eh is a critical unknown.* An alternative to biotic enhancement of manganese, not yet discussed, is physical–chemical fractionation (Smith and Whalley, 1988). This model cannot be examined because it is not now possible to measure the pH or Eh of the capillary water interacting with the rock coatings. Discussion of a physical–chemical model of Mn enrichment is, therefore, speculative until a technological breakthrough occurs that allows *in situ* measurements of capillary water redox chemistry, or laboratory experiments succeed in replicating abiotic varnishes.

(3) *The transition between recently nucleated varnishes and older varnishes is poorly understood.* SEM observations of varnish surfaces formed on historic surfaces in more arid regions (Dorn, 1989) indicate that they have a laminar appearance, similar to older varnish surfaces (Dorn, 1986). SEM observations of varnishes formed in more humid regions often have botryoidal morphologies (Dorn, 1986, p. 564), but the botryoidal surfaces are layered, not granular. In contrast, the rapidly forming varnish on Fontana slag has a granular texture (Figure 5A), except where varnish interdigitates with silica glaze (Figure 5D). This granular varnish is grossly similar to the granular, poorly organized surficial varnish observed by Krinsley and Dorn (1991, pp. 112–113) in the Marble Mountains of the Mojave Desert.

A limitation on the rate of varnish accretion may be the initial cementation of this poorly organized layer. Well cemented layers can survive disturbances from wetting transitions (cf. Zorin *et al.*, 1992) associated with violent wetting or aeolian shear stresses, whereas weakly cemented material may not. The ubiquitous smooth lamellate or smooth botryoidal surfaces may simply result from the erosion of poorly cemented detritus, before it can be firmly cemented to varnish. If so, the poorly organized Fontana varnish may have survived owing to the abundance of manganese being precipitated.

(4) *The biotic model of rock-varnish formation requires at least two steps.* The first stage is precipitation of Mn–Fe from solution by bacteria or other organisms. Different types of bacteria may oxidize manganese and iron at different rates. The Fontana slag varnish has a transition from Mn-rich casts of cocci bacteria near the surface, to bacterial casts less enriched in Mn just underneath, to no casts below the upper few micrometres. This suggests a collapse of the cast structure. The second stage, therefore, is the cementation of the other varnish constituents (clays) by either chemical remnants of the casts or Mn–Fe remobilized from the clasts. The gradual reduction in Mn concentration from the top (younger?) bacterial casts to the lower

(older?) casts suggests that remobilization occurs at the Fontana slag site. Remobilization also occurs in other varnishes (Krinsley *et al.*, 1990; Dorn and Krinsley, 1991). The rate of varnish accretion, therefore, would also be limited by the rate at which both steps occurred.

In summary, evidence from the Fontana slag site indicates that rapid rock-varnish formation can occur in circumstances that can potentially be found in a natural setting. This undermines efforts to generalize time information from superficial observations about the general development of rock varnish at a site. This case study clearly illustrates that there are site-specific factors that control rates of varnish formation. We hope that data and observations from the Fontana slag site will be useful in developing an accurate quantitative model of the formation of rock varnish and related rock coatings.

ACKNOWLEDGEMENTS

The authors thank anonymous reviewers for excellent suggestions, Mr Rob J. Hartman, Director of Environmental Projects at Kaiser Resources Inc., for assistance in researching the plant history, and Mr Robert Maxwell, State of California Air Resources Board, for assistance in researching acid deposition in the Fontana area. This project was supported, in part, by NSF PYI award to R. I. Dorn.

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