



## The influence of mineral detritus on rock varnish formation

Ronald I. Dorn <sup>a,\*</sup>, David H. Krinsley <sup>b</sup>, Kurt A. Langworthy <sup>c</sup>, Jeffrey Ditto <sup>c</sup>, Tyler J. Thompson <sup>a</sup>

<sup>a</sup> School of Geographical Sciences and Urban Planning, Arizona State University, Tempe, AZ 85287-5302, USA

<sup>b</sup> Department of Geological Sciences, University of Oregon, Eugene, OR 97403-12723, USA

<sup>c</sup> CAMCOR, Department of Chemistry, University of Oregon, Eugene, OR 97403-1241, USA

### ARTICLE INFO

#### Article history:

Received 2 March 2013

Revised 25 April 2013

Accepted 25 April 2013

Available online 21 May 2013

#### Keywords:

Dust

Diagenesis

Manganese

Rock coating

Weathering

### ABSTRACT

A mix of high resolution electron microscope methods imaged the textures and chemistry of rock varnish samples from 19 field sites on five continents. The vast majority of aeolian mineral is not incorporated into manganese-rich rock varnish. Of those dust particles that are enveloped, submicron sized oval-shaped quartz minerals are the most common type of detritus seen, as they rest conformably between laminated layers. The dominance of quartz as the most common detrital mineral, combined with the relative rarity of feldspars – is consistent with the hypothesis that feldspars experience *in situ* decay into clay minerals. After the detritus is buried in varnish, mineral boundaries often develop enhanced porosity. Some porous zones around dust particles develop submicron skins of redeposited Mn–Fe. In other cases, the porous zones aid in the transport of capillary water that mobilizes and redeposits Mn–Fe as stringers in fissures. Larger dust particles ~10 μm in diameter are deposited in microtopographic depressions, such as tubes created by acid-producing lithobionts. Varnishes growing in particularly dusty regions form alternating dust-rich and varnish-rich layers that potentially correlate to alternating dusty and less dusty periods. The very foundation of varnish, the underlying rock, is often less stable in the surficial environment than varnish – leading to enhanced porosity and mineral decay in the substrate. Sometimes, physical collapse of varnish into the underlying void space mixes varnish and rock; more commonly, however, remobilization of varnish constituents into these pore spaces creates case hardening of the weathering rind in the underlying rock.

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### 1. Introduction

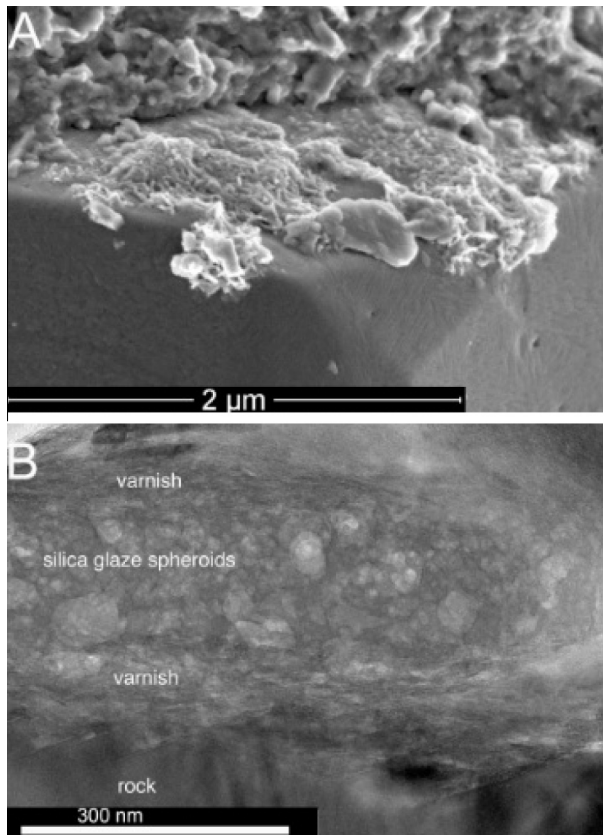
The influence of the underlying rock on the formation of rock (or desert) varnish has been a controversial topic. von Humboldt (1812) postulated that submillimeter manganese-rich coatings formed as a deposit on top of the rock (Dorn et al., 2012c; von Humboldt, 1812). Researchers advocating von Humboldt's accretionary hypothesis, however, were rare (Basedow, 1914; Francis, 1921; Klute and Krasser, 1940; Krumbein, 1969) prior to the use of electron microscopy. There existed a clear consensus throughout much of the late 19th and 20th centuries that the constituents of "desert varnish" – as most called it – derived from solutes mobilized from decayed mineral matter in the underlying rock (Bard et al., 1978; Birot, 1969; Blake, 1905; Engel and Sharp, 1958; Glennie, 1970; Holmes, 1965; Hume, 1925; Hunt, 1954; Linck, 1901, 1928; Longwell et al., 1950; Lucas, 1905; Marshall, 1962; Merrill, 1898; Peel, 1960; Walther, 1891; Wilhelmy, 1964; Woolnough, 1930).

As can be the case in science, the clear consensus turned out to be wrong, but it required a new technique to change perspective. Just as the use of satellite imagery played a role in recognizing the role of catastrophic flooding (Bretz, 1923) on the channeled scablands (Baker and Bunker, 1985), the use of different electron microscope techniques supported von Humboldt's accretionary hypothesis (e.g. Fig. 1) through the visualization of very clear contacts between the depositing varnish and underlying minerals (Potter and Rossman, 1977). Continued research using light (Liu and Broecker, 2000, 2008a; Perry and Adams, 1978), secondary (Dorn, 1986; Dorn and Oberlander, 1982), back-scattered (BSE) (Dorn, 2009a; Krinsley et al., 1990), and high resolution transmission electron microscopy (HRTEM) (Krinsley, 1998; Krinsley et al., 1995, 2009) led to a new consensus that manganese-rich subaerial rock varnish is an aeolian deposit.

Since this latest shift in consensus back to von Humboldt's (1812) accretionary hypothesis, relatively little concern has been paid to the role of rock material – whether the underlying rock or aeolian mineral particles – on varnish formation. Research on the influence of the rock has been limited to rock-spalling events that also remove rock coatings (Etienne, 2002; Gordon and Dorn, 2005; Tratebas et al., 2004; Turkington and Paradise, 2005) and case hardening (Conca, 1982; Conca and Rossman, 1982; Dorn

\* Corresponding author.

E-mail addresses: [ronald.dorn@asu.edu](mailto:ronald.dorn@asu.edu) (R.I. Dorn), [krinsley@uoregon.edu](mailto:krinsley@uoregon.edu) (D.H. Krinsley), [klangwor@uoregon.edu](mailto:klangwor@uoregon.edu) (K.A. Langworthy), [ditto@uoregon.edu](mailto:ditto@uoregon.edu) (J. Ditto), [tjthomp9@asu.edu](mailto:tjthomp9@asu.edu) (T.J. Thompson).



**Fig. 1.** Clear contact between varnish deposited on relatively fresh minerals of the underlying rock. (A) Secondary electron image of manganese-rich rock varnish formed on quartz collected from von Humboldt's research site along the cataracts of the Orinoco River between the missions of Carichana and Santa Barbara (von Humboldt, 1812, pp. 242–246); source: Dorn et al. (2012c). (B) HRTEM image of varnish deposited on the underlying rock (darker material at the bottom of the image). Layered rock varnish forms a 50 nm thick deposit, followed by accretion of silica glaze spheroids, and then a return to layered rock varnish; source: Langworthy et al. (2010).

et al., 2012a; Washburn, 1969). In this paper, however, we postulate that aeolian detrital minerals deposited on rock surfaces are subsequently enveloped, altering varnish formation and its diagenesis. In evaluating this hypothesis, we use samples from different environmental settings and we employ a variety of electron microscope techniques.

The next section of this article provides a background of current thinking on rock (or desert) varnish formation. The methods section describes sampling sites, sample preparation methods, and the different electron microscopic techniques employed. An integrated results and discussion section presents imagery in microstratigraphic order from the top (youngest) to the bottom (oldest) of varnish, analyzing interactions between aeolian mineral detritus from the 'dust cycle' (Shao et al., 2011) with rock varnish processes.

## 2. Overview of rock varnish formation

The literature on rock (or desert) varnish formation contains four general types of conceptual models graphically portrayed in Fig. 2. One model (Fig. 2A) involves abiotic enhancement of manganese relative to iron, explaining the Mn:Fe ratio in varnish that is 60 times greater than that found in the underlying rock or dust, which results from cycles of acid solutions separating Mn (II) followed by oxidizing conditions concentrating Mn in varnish (Engel and Sharp, 1958; Hooke et al., 1969; Smith and Whalley, 1988).

Another set of hypotheses purport that lithobionts or their organic remains (e.g. spores, polysaccharides, oxides, humic substances) play a role in binding varnish and concentrating manganese and iron (e.g. Fig. 2B) (Allen et al., 2004; Gorbushina, 2003; Krumbein, 1969; Kuhlman et al., 2006; Parchert et al., 2012; Perry et al., 2003; Scheffer et al., 1963; Staley et al., 1983; White, 1924). A third hypothesis argues that silica binding of detrital grains, organics, and aerosols (Dorn, 2007a; Perry and Kolb, 2003; Perry et al., 2006; Perry and Sephton, 2007) results in varnish formation (Fig. 2C).

We favor a polygenetic model (Fig. 2D) focusing on clay–bacteria–interactions (Dorn, 1998; Dorn and Krinsley, 2011; Dorn et al., 1992; Krinsley, 1998); varnish formation starts with the oxidation and concentration of Mn (and Fe) by bacteria. Wetting events dissolve nanometer-scale fragments of Mn. Ubiquitous desert dust supplies interstratified clay minerals. The Mn–bacterial fragments fit into the weathered edges of clays, playing a role much like mortar cementing a brick wall. All four mechanisms are reviewed and compared in detail elsewhere (Dorn, 2007b, 2009a).

The polygenetic model (Fig. 2D) starts with physical attachment of dust particles held onto rock surfaces (Bishop et al., 2002; Ganor et al., 2009; Jordan, 1954). Then, bacteria concentrate manganese and iron (Dorn, 2007b; Dorn and Oberlander, 1981; Grote and Krumbein, 1992; Hungate et al., 1987; Krinsley et al., 2012; Northup et al., 2010; Palmer et al., 1985; Wang et al., 2011). While some bacterial sheaths survive as in tact microfossils (Dorn, 1998; Dorn and Meek, 1995; Krinsley, 1998), most break down into fragments that then dissolve (Krinsley, 1998). This ongoing diagenesis of Mn–Fe casts release nanometer-scale fragments seen in HRTEM as having a granular texture. Fixation of the Mn occurs only a few nanometers away as hydroxides are mobilized into mixed-layered clays (Potter, 1979).

The rate of varnish formation can vary tremendously, depending on the macroenvironment and microenvironment of sampling. For the types of locations best suited for analyzing microlaminations, rates of formation are typically microns per millennia (Dorn, 1998; Liu and Broecker, 2000). However, more mesic locales can produce rates of formation on the order of microns per century (Dorn et al., 2012b; Krinsley et al., 2012; Spilde et al., 2013) – high enough to preserve Mn-enhancing bacteria microfossils (Dorn and Meek, 1995). Because the vast majority of varnish takes millennia to accrete microns, Mn-enhancement must be extraordinarily rare, contributing a few cell-wall crusts of manganese per millennia (Dorn and Krinsley, 2011). Even the higher rates of formation would preclude a role for the vast majority of organisms found in association with varnish (Allen et al., 2004; Krumbein, 1969; Kuhlman et al., 2006; Parchert et al., 2012; Perry et al., 2003; Scheffer et al., 1963; Staley et al., 1983; White, 1924), because typical formation rates would be microns per year if all of this organic activity truly played a role in varnishing (Dorn and Krinsley, 2011).

The importance of ongoing diagenesis, after the initial aggradation of clays and bacteria, has been recognized as a key process, well after the initial redistributing Mn from bacterial sheaths to clay minerals. Many electron microscopy-viewed textures are produced by ongoing dissolution and reprecipitation of oxides. Organic acids (Dragovich, 1987, 1993) dissolves oxides and leach cations from pockets with porous textures (Dorn and Krinsley, 1991; Krinsley et al., 1990), where the dissolved Mn and Fe precipitates along the rims these pores (Garvie et al., 2008; Krinsley et al., 1990). The redistribution of Mn and Fe in capillary channels forms crosscutting submicron Mn stringers and wider cracks filled with oxides (Garvie et al., 2008; Krinsley et al., 1990).

Despite considerable prior work on varnish formation and its subsequent diagenesis, this article's focus turns towards a topic not explored previously in the varnish literature: the influence of mineral dust on varnish formation and subsequent diagenesis. Cer-

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