

Baking black opal in the desert sun: The importance of silica in desert varnish:

COMMENT AND REPLY

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Perry et al. (2006) contribute a fourth alternative, of silica binding, to three prior hypotheses of varnish formation: 1) abiotic Mn-Fe enhancement (e.g., Engel and Sharp, 1958); 2) biotic Mn-Fe enhancement (e.g., Dorn and Oberlander, 1982; Allen et al., 2004); and 3) a polygenetic clay-bacteria hypothesis (Dorn, 1998; Krinsley, 1998). Commentary by Berardelli (2006) also reveals that Perry et al. offer silica binding as a comprehensive model of how varnish forms.

A silica-binding model of varnish formation, however, is contradicted by prior literature in six independent ways. (1) A successful model of varnish formation must explain the tremendous enhancement of Mn in varnish (Engel and Sharp, 1958; Dorn and Oberlander, 1982; Potter and Rossman, 1979) but silica binding does not. Similarly, Mn-mineralogy of varnish (Potter, 1979; Potter and Rossman, 1979; McKeown and Post, 2001; Probst et al., 2002) is not explained by silica binding. (2) A successful model must explain the clear dominance of clay minerals in varnish (e.g., Potter and Rossman, 1977; Potter, 1979; Krinsley et al., 1995; Israel et al., 1997; Dorn, 1998 [Ch.10]; Krinsley, 1998; Probst et al., 2002; Allen et al., 2004) as opposed to the paucity of clay minerals in silica glaze (Curtiss et al., 1985; Dorn, 1998 [Ch. 13]), yet silica binding cannot. (3) A successful model must explain rock-coating geography. For example, one of Earth's best Mars analogs exists on the Tibetan Plateau, where a study of varnish from the Ashikule Basin of the West Kunlun Mountains finds varnish resting adjacent to silica glaze at scales of microns to meters (Dorn, 1998, [Ch.15]). Silica binding fails to explain this common geographical juxtaposition. (4) The "baking" requirement runs contrary to varnish in subsurface and cold-climate settings (Douglas, 1987; Whalley et al., 1990; Dorn et al., 1992; Douglas et al., 1994). (5) Varnish microlamination analyses of over 10,000 sedimentary microbasins (Liu and Broecker, 2000; Liu et al., 2000; Broecker and Liu, 2001; Liu, 2003; Liu, 2006; Liu and Broecker, 2006), a method subjected to blind testing (Marston, 2003), represents the single largest varnish data set (Dorn, 2006). Yet, silica binding does not explain systematic differential Mn-Fe patterns that dominate varnish. (6) A successful model must explain rates of accretion ~1–10 μm per millennia (Dorn, 1998; Liu and Broecker, 2000), confirmed by further studies (Liu, 2003; Liu, 2006; Liu and Broecker, 2006). Whatever process creates varnish must have the extreme rate-limiting step that silica binding lacks. Silica glaze, in contrast, accretes in microns per decade (Curtiss et al., 1985; Gordon and Dorn, 2005).

The conclusion held by Perry et al. (2006) that silica glazes and varnishes are genetically linked appears to be contradicted by six independent criteria used in prior literature. Thus, silica binding is not important in forming the vast majority of varnishes. However, it is possible that silica binding could play a role in the genesis of a very specific type of varnish: ground-line bands found in warm deserts (cf. Engel and Sharp, 1958; Dorn, 1998 [Ch. 10]). This is the type of varnish that appears to be featured in post-publication photographs and press releases (cf. Berardelli, 2006) about Perry et al. (2006).

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We welcome the opportunity to reply to Dorn (2007) who outlines the classical issues of desert varnish formation. We agree that most previous research has suggested a biological mechanism. Bacterial enhancement of manganese, in manganese-rich coatings is intriguing. However, as we have published (Perry et al., 2006), there is no evidence of a *direct* link with microbes and varnish formation. In our studies, we rarely see microbes in or on the surface, even after critically point-dried specimens are viewed. Similar observations have been made by others who also noted the lack of bacteria in desert varnish (Taylor-George et al., 1983).

In our recent research, we have also observed silica coatings that are enhanced in manganese in Antarctica. Few microbes are known to exist in these locations, which removes the possibility of biologically mediated processes. We note that manganese-rich varnishes from Antarctica have been investigated previously (Dorn et al., 1992) and it was suggested that budding bacteria might be the cause, but the authors could not rule out contamination added in transit or in the lab.

It has been established experimentally that microbes are not needed to enhance manganese (Krauskopf, 1957; Jones, 1991), and varnish-like coatings have been produced in the laboratory without microbial involvement (Kolb et al., 2004; Perry et al., 2005). However, microbes do co-exist with minerals on rock surfaces, and a microbial involvement in other locations should not be ruled out. Specifically, bacterial DNA has been extracted from varnishes (Perry et al., 2004; Kuhlman et al., 2005, 2006) and other biological compounds (Perry et al., 2003; Schelble et al., 2005) but a biological causal mechanism has not been established. As we suggest in *Geology*, biological materials are probably entombed within silica in rock coatings and hot-spring silica (Lynne et al., 2006; Perry et al., 2006).

Other authors have suggested that silica might be involved in desert varnish formation and have noted the existence of silica glazes inter-layered with manganese-enhanced silica-rich coatings (Farr, 1981; Smith and Whalley, 1988). Varnishes form by relatively slow accretion, and the source materials are dusts or dissolved constituents in the atmosphere introduced by direct deposition (Thiagarajan and Lee, 2004). It follows that varnish deposition will reflect components available in the environment. If the entities available vary, then silica glaze deficient in manganese, iron, or other trace metals might be deposited under one environmental condition and trace element enhanced deposits in another. Such a process causes a colorless glaze to be interlayered with desert varnish. The environmental control on coating formation is illustrated by the fact that desert varnish and glazes that are juxtaposed are not the same thickness, suggesting that different environmental controls, primarily related to moisture, might control differences in deposition rate.

Conventional interpretations also suggest that manganese and clays are the predominant mineral components in desert varnish. Our work, however, reveals that silicon is usually the predominant element in var-

nishes, and aluminum is sometimes the second most abundant. Aluminum quantities are highly variable and often not consistent with Al/Si ratios in clays. Clays are present in varnishes (Potter and Rossman, 1977), but we have only found minimal clay content in varnishes using particle size separations. The role of silica in desert varnish formation has been substantially neglected in previous research. We look forward to the contributions of others in furthering our understanding this enigmatic coating and elucidating its silica-based formation mechanism.

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