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SHORT COMMUNICATIONS

A COMMENT ON 'A NOTE ON THE CHARACTERISTICS AND POSSIBLE ORIGINS OF DESERT VARNISHES FROM SOUTHEAST MOROCCO' BY DRS. SMITH AND WHALLEY

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ABSTRACT

This note queries the discussion of the origins of 'desert varnishes' (Smith and Whalley, 1988), with particular reference to manganese-rich conditions. The case for a biotic model of varnish development is proposed and illustrated as opposed to the abiotic model put forward by Smith and Whalley.

KEY WORDS Desert varnish Manganese Biotic/abiotic models

Smith and Whalley (1988) make some detailed observations about 'desert varnish' on limestones with varying degrees of silicification in southeast Morocco. I have no objections with the high quality of the analytical data presented, nor with observations of the largely unappreciated interaction of varnish with 'silica glaze', nor with observations on the effect of lithologic stability on varnish. I do have objections to their discussion of the origin of 'desert varnish'.

Smith and Whalley claim 'we have seen no evidence in the optical or SEM observations to suggest that fungal hyphae or bacterial colonies are present on the varnish surfaces. . .' and 'the apparent absence of organic components to the varnishes would seem to argue against recent studies which have proposed the fixation of iron and manganese by organisms as a general model for varnish formation'. They argue, instead, for an inorganic explanation for the observed varnishes. I feel that their interpretations, based only on optical and SEM examination, should be examined carefully.

It is quite possible to sample varnishes for SEM analysis and not observe microorganisms in the sample, especially if it was collected long after a rain. I have collected samples without a clearly obvious and unequivocable presence of microbes. I wonder when the samples were collected; when was the last time it rained; whether any attempt at culturing microorganisms was made; whether any attempt was made to extract organic matter from the varnish? Whalley (1983), Dorn and Oberlander (1982), Mayer *et al.* (1984), and many others agree that varnishes in deserts grow very slowly. If microorganisms were present and active on every square millimetre of surface at all times, the rate of varnish growth would be much faster than observed. Varnish growth in deserts is slow, I believe, because the rate of varnish accretion is limited by the rate of manganese enhancement. If a physical–chemical mechanism of manganese-rich varnish formation truly exists, something that has not been demonstrated by field or laboratory evidence, it is unclear what reasonable theoretical reason would force such a slow rate of varnish growth.

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There has been a tremendous amount of very high quality research conducted on the biological origin of 'desert varnish' that was not cited by Smith and Whalley in their short note (Staley *et al.*, 1982; Staley *et al.*, 1983; Taylor-George *et al.*, 1983; Palmer *et al.*, 1985), nor was the ubiquitous literature on the biological genesis of related manganese-coatings (see list in Dorn and Oberlander, 1982, p. 319; also Emerson *et al.*, 1982; Ghiorse *et al.*, 1984; Chandramohay *et al.*, 1987; Ferris *et al.*, 1987). While not directly dealing with the observed varnishes in Morocco, these works argue for a closer inspection of a biological origin.

I have no objection to an inorganic explanation for manganese-depleted (iron-enriched) varnishes. Although microorganisms do appear to contribute to these varnishes (Krumbein and Jens, 1981; Dorn and Oberlander, 1982), a microbial component is not a requirement. Similarly, silica glaze (originally studied by Willet, 1901 and later by Fisk, 1971; Farr and Adams, 1984; Curtiss *et al.*, 1985) does interact and interlayer with true varnish (Butzer *et al.*, 1979; Oberlander, 1982); it could have a biological component (*cf.* Harder, 1965; Ferris *et al.*, 1986), but it is not required by physicochemical limitations. (I should note that I see *no* evidence that the iron and silica in true varnishes on silicified limestones in southwestern North America or Israel are derived from the underlying rock. Silica glaze may be different and should not be confused with varnish.) I agree that the minor and trace elements of aluminum, potassium, calcium, titanium, magnesium, copper, zinc, and others are derived from airborne material, probably brought in with the clays; some leaching may be imposed by biological activity.

The issue of manganese-rich varnishes, however, is quite different. This is the key to a general biotic model of varnish development. Smith and Whalley (1988) argue for a purely inorganic mechanism for the development of manganese-enriched coatings by as yet undocumented Eh–pH fluctuations (*cf.* Hooke *et al.*, 1969; Elvidge and Iverson, 1983). Reasons have been presented why manganese-enrichment in varnish does not occur by inorganic process. (1) The geographic distribution of varnish in deserts fits with a biological model. Varnish is best developed in extremely arid regions where water runs intermittently, supplying divalent manganese and a favourable microenvironment for microbial colonization. Varnish is best developed on porous surfaces that are low in organic material, thus favourable for mixotrophic bacteria. The patchy distribution of varnish on most rocks (not just on the silicified limestone of Morocco) is suggestive of a biological phenomenon; an inorganic system would be more likely to produce a more uniform coating. Varnishes are poorly developed on smooth substrates like quartz, where microbial colonization is slowed but physicochemical mechanisms of Eh–pH fluctuations would not be inhibited. Other arguments along these lines have been presented by Krumbein and Jens (1981) and Dorn and Oberlander (1981, 1982). (2) The pH conditions that have been observed on manganese-rich varnishes are near-neutral and not high enough to oxidize manganese by inorganic processes (e.g. Crerar *et al.*, 1980; Stumm and Morgan, 1981, pp. 448–468). (3) Rock surfaces adjacent to agencies, such as lichens, that can impose pH (and difficult to document Eh) changes often lack varnish altogether. (4) Purely physicochemical fixation of manganese by clay minerals is insufficient to produce the high concentrations of manganese observed in varnish (*cf.* El-Demerdashe *et al.*, 1982). (5) If pH–Eh fluctuations associated with a desert environment (and small microenvironments in a desert) are how manganese is enhanced, why are manganese-rich varnishes found in Iceland (*cf.* Douglas, 1987) and other acidic environments. (6) Organic material is common in varnishes, as many analyses of stable carbon isotope and radiocarbon measurements indicate (Dorn and DeNiro, 1985; Dorn *et al.*, 1986). It would be interesting to examine the character of the organic matter in the southeast Morocco varnishes. (7) Dorn and Oberlander (1982) argued that the frequency of manganese-rich varnishes decreases as one reaches more hyper-arid and hyper-alkaline regions; this is further supported by the recent work of Oberlander (1988) in the Atacama Desert who observed manganese-rich patches only in limited, more mesic microenvironments. Yet Mn-rich varnishes are largely lacking, we believe, because of the incompatibility between extreme alkalinity and manganese-oxidation (Mulder, 1972; Uren and Leeper, 1978; Schweisfurth *et al.*, 1980; Dorn and Oberlander, 1981). That is why manganese-rich varnishes are present in acidic, near-neutral and slightly alkaline environments, but not hyper-alkaline sites. It is just that the manganese in varnishes in the acidic environments are not particularly stable, as they can erode and form at the same time (*cf.* Douglas, 1987). (8) A biotic model explains contradictions in rates of varnish growth; varnishes develop rapidly in periglacial environments and riverine settings (*cf.* Dorn and Oberlander, 1982, p. 353; Glazovsky, 1985; Douglas, 1987) and slowly in deserts (cf. Dorn and Oberlander, 1982; Whalley, 1983; Mayer *et al.*, 1984). Periglacial, subsurface, and riverine environments are not noted for alkalinity or pH–Eh fluctuations of the sort to cross the manganese divalent–tetravalent boundary at about pH 9. Yet varnish grows rapidly. These conditions are favourable for the growth and development of manganese-enhancing microorganisms. Deserts are not. The abiotic model cannot explain this discrepancy.

A major difference in our views may derive from a different philosophy to the classification of manganese coatings. It is clear that Smith and Whalley (1988) wish to regard 'desert varnish' as a distinct manganese-rich coating. If 'desert varnish' is viewed as separate from other manganese-rich coatings (e.g. 'periglacial' varnishes), the above arguments comparing arid with non-arid varnishes might be considered irrelevant. If one takes a perspective that manganese-rich coatings in terrestrial weathering environments are related, insights can be gained by the geographical distribution of varnishes in different biogeochemical settings. At a bottom level, I accept the notion that pH–Eh fluctuations can theoretically mobilize and immobilize manganese. It may be that this process is indeed responsible for some manganese enhancement in desert varnishes. I have seen no field or laboratory evidence, however, that this process actually occurs on 'desert varnish' or that it concentrates the manganese in varnish in deserts or non-deserts. I challenge Smith and Whalley (1988) and other proponents of an abiotic hypothesis to support a precise physicochemical mechanism for manganese enhancement by laboratory and field measurements of pH and/or Eh, and by laboratory simulation experiments. I have tried to simulate varnish growth by Eh–pH fluctuations in the laboratory and failed. I feel that the biotic proponents have met this investigative burden at a first level, at least. Such measurements and experiments are desperately needed if the abiotic hypothesis is to get beyond the stage of deductive reasoning.

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