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Manganese-rich rock varnish does occur in Antarctica

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ABSTRACT

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Despite accounts to the contrary, we have found that Mn-rich rock varnish is present in Antarctica, as others have before. It is chemically and texturally similar to many varnishes found in lower latitudes. Antarctic varnishes show considerable potential as a dating and paleoenvironmental research tool.

1. Introduction

Rock varnish is a coating of manganese and iron oxides, clay minerals and trace elements (Potter and Rossman, 1977, 1979a, b). A partial list of environments where rock varnish has been studied includes hot deserts (White, 1990), coastal deserts (Jones, 1991), arctic (Whalley et al., 1990), cool–humid (Douglas, 1987), cave (Peck, 1986), spring (Mustoe, 1981), subsurface rock fractures (Weaver, 1978) and alpine (Glazovskiy, 1985) terrestrial weathering environments. Since Mn-rich rock varnish was first characterized in deserts and since it is ubiquitous and noticeable in deserts, a common name (although a misnomer) is "desert varnish".

Mn-rich rock varnish has a dark reddish-brown to black color that reflects high concentrations of Mn- and Fe-oxides, typically > 20% by weight. Varnish is also universally characterized as an accretion on rocks (e.g., Potter and Rossman, 1977; Allen, 1978; Dorn and Oberlander, 1982; Jones, 1991), although minor amounts of rock debris are trapped as the coating grows (Krinsley et al., 1990). Both abiotic (Smith and Whalley, 1988) and biotic (Dorn and Oberlander, 1981; Krumbein and Jens, 1981; Jones, 1991) hypotheses have been proposed to explain the great enrichment in Mn, typically ~50–100-fold over its abundance in the surrounding rocks, soils, eolian dust and plant material.

Initial investigations of rock weathering in Antarctica mention "desert varnish" in passing (Kelly and Zumberge, 1961; Claridge, 1965; Selby, 1971, 1977) or place siliceous crusts within a general framework of accre-

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TABLE 1

Electron microprobe (JEOL® superprobe), particle-induced X-ray emission (PIXE, Cahill et al., 1984; Cahill, 1986), and previously published analyses of Antarctic and selected lower-latitude rock varnishes

Oxide (wt%)	Beacon Valley*[1], Ross Desert, Antartica	Clark Mountains*[2], Antartica	Lathrop Wells*[3], Cinder Cone, southern Nevada, U.S.A.	Arena Valley*[4], Ross Desert, Antartica	Previously*[5] published Antarctic data
Na_2O	–	0.16	0.41	–	
	–	–	–	–	
MgO	1.19	1.42	1.97	–	0.03
	2.14±0.7	1.86±0.66	1.72±0.88	0.75±0.28	0.23
Al_2O_3	14.0	18.41	15.86	–	1.58
	16.35±3.72	16.36±3.71	18.71±2.85	13.02±1.83	2.15
SiO_2	35.22	30.11	26.56	–	
	26.41±13.24	21.98±7.04	22.79±5.38	37.34±5.51	
P_2O_5	0.91	1.81	–	–	
	1.99±0.61	2.5±0.9	3.03±1.19	0.63±0.12	
SO_3	–	–	–	–	
	0.18±0.22	0.24±0.31	0.13±0.31	–	
K_2O	3.05	1.3	0.91	–	
	1.28±0.52	1.16±0.38	0.80±0.54	2.75±0.41	
CaO	1.62	2.82	1.45	–	0.10
	1.77±0.64	1.92±1.14	1.48±0.47	0.53±0.30	1.13
TiO_2	0.47	0.66	0.70	–	
	0.55±0.19	0.61±0.26*[6]	0.63±0.21*[7]	1.04±0.37	
MnO	18.04	15.69	12.55	–	6.43
	16.38±7.38	20.15±11.58	10.86±6.15	9.83±2.76	4.18
FeO	21.07	18.73	15.94	–	18.14
	10.97±3.75	11.05±3.45	17.18±4.67	15.70±2.57	18.70
NiO	0.14	0.36	0.12	–	
	–	–	–	–	
CuO	0.21	0.09	0.14	–	
	0.11±0.12	0.04±0.06	0.06±0.06	0.10±0.06	
ZnO	0.24	0.30	0.25	–	
	0.06±0.06	0.08±0.07	0.05±0.05	–	
Rb_2O	–	0.32	0.18	–	
	–	–	–	–	
ZrO_2	–	0.10	0.36	–	
	–	–	–	–	
SrO	–	0.20	0.18	–	
	–	–	–	–	
BaO	1.30	2.48	0.99	–	
	1.48±0.78	1.90±1.15	0.72±0.66	0.11±0.08	
PbO	–	0.64	0.45	–	
	–	–	–	–	

TABLE 1 (*continued*)

For each value presented there are two measurements listed. The first measurement listed is by PIXE, providing a measurement of 20 mg of varnish material removed from a few cm^2 of the rock surface (cf. Dorn, 1989). The second measurement listed presents the average (and 1σ error) of spot analyses of varnish in a single thin section with wavelength dispersive electron microprobe. PIXE is a bulk measurement, whereas probe points measure μm-scale chemical variability. Results are not reported (–) when the oxide was not tested by the microprobe and when it was not reported or below the limit of detection for PIXE. Mn concentrations in the rock directly underlying the varnish in samples *1–4* are < 0.20% in every microprobe analysis.

*[1]Sample of varnish on sandstone from older moraine of Beacon Valley, Ross Desert, Antarctica, collected by Mort Turner. Microprobe results based on 50 points with 2-μm spot size.

*[2]Sample from Texas Tech University collection of varnish on granite, Mt. Van Valkenberg, Clark Mountains, in Marie Byrd Land. Microprobe results based on 49 points with 2-μm spot size.

*[3]Sample of varnish from the rim of the Lathrop Wells cinder cone, just north of the town of Lathrop Wells, southern Nevada. Microprobe results based on 69 points with 2-μm spot size.

*[4]Sample of varnish from Taylor II Moraine, Arena Valley (cf. Denton et al., 1989), collected by E. Brook and M. Kurz from sample KBA*89-102*. The underlying rock is sandstone. Microprobe results based on 45 points with 10-μm spot size.

*[5]Two measurements from Markov et al. (1970, p.273) are presented for each oxide. They are analyses of "crusts" formed on rocks in Antarctica. The upper measurement is from "Bunger Oasis [on] granite rocks. Bluish black varnish crusts on top of rock surfaces." The lower measurement is on "Larsemann Hills. Granite rock. Brown varnish crust on top of surfaces of rocks." The analyses are "extract with 20% HCl". The method of analysis was not provided. Only 5 oxides were reported, with iron reported as Fe_2O_3.

*[6]If two measurements of 20.7% and 3.68% are included, the average and standard error (S.E.) changes to 1.09 ± 2.94.

*[7]If measurements of 1.66%, 2.15% and 6.15% are included, the average and S.E. changes to 0.75 ± 0.72.

tions that include rock varnish (Weed and Ackert, 1986). Recent claims have been made in this journal and other publications that there are no Mn-rich varnishes in Antarctica (Glasby et al., 1981; Johnston and Cardile, 1984; Johnston et al., 1984; Hayashi and Miura, 1989); these assertions have been incorporated into the general Antarctic weathering literature (Campbell and Claridge, 1987). What is being called "desert varnish" by these researchers has been characterized as a complex phenomenon that involves rock weathering, sometimes mixed with external materials. While we find this work of high quality, we disagree with their conclusion that Mn-rich rock varnish is not present in Antarctica. The purpose of this paper is to point out that Mn-rich rock varnish does exist in Antarctica, and that this varnish shows potential as a paleoenvironmental indicator and dating tool.

2. Mn-rich rock varnish is present in Antarctica

Dark, Mn-rich rock varnishes have been observed in the Bunger Oasis of Antarctica (Markov, 1960; Glazovskaya, 1968, 1971; Markov et al., 1970). Antarctic rock varnish has been described as a crust that is "brown or reddish brown" and in places "bluish black" (Glazoskaya, 1968). Published chemical analyses report MnO concentrations of up to 6.43 wt%, although the method of analysis was not presented (Markov et al., 1970, p.273). Mn-rich dark coatings have also been reported in Victoria Land (Weed, 1985, p.113; Bockheim et al., 1989).

We have obtained samples of black coatings on rocks from Antarctica, collected by a number of scientists. The bulk and μm-scale chemistries of Antarctic rock varnishes analyzed in this study are quite similar to temperate rock varnishes (Tables 1–3), in that Mn is a dominant component, being enhanced ~50–100× above concentrations measured in the underlying rock. An example of in situ analysis of varnish is found in Table 2 that correponds to the line in Fig. 2 (p. 295). Concentrations of Al and Si are consistent with an important clay mineralogy component (cf. Potter and Rossman, 1977, 1979a, b). Stromatolitic, layered and abraded textures in Antarctic varnishes are

TABLE 2

Electron microprobe (wavelength dispersive) transect from the surface to the base of the varnish in Fig. 2

Depth (μm)	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO	CuO	BaO	Total
0	0.90	12.36	35.96	0.76	2.76	0.56	0.75	10.61	16.12	0.00	0.17	80.95
5	0.60	10.54	38.29	0.66	2.72	0.53	0.58	10.64	13.59	0.16	0.12	78.43
10	0.56	11.24	38.38	0.55	2.47	0.34	0.67	10.60	13.29	0.15	0.17	78.42
15	0.70	12.28	34.38	0.65	2.57	0.32	0.65	12.36	13.62	0.00	0.08	77.61
20	0.80	11.77	37.55	0.64	2.76	0.41	0.67	12.33	13.07	0.00	0.09	80.09
25	1.72	12.40	36.63	0.46	2.95	1.55	0.85	11.13	13.21	0.00	0.09	80.99
30	1.49	12.58	37.67	0.56	2.54	1.72	1.05	8.56	16.18	0.00	0.00	82.35
35	0.98	14.15	37.50	0.56	3.45	0.53	1.10	6.07	19.22	0.1O	0.25	83.91
40	1.31	13.51	39.30	0.66	3.75	0.55	1.17	6.97	17.66	0.00	0.13	85.01
45	0.86	13.19	37.70	0.72	2.85	0.64	0.90	8.72	18.22	0.16	0.20	84.16
50	0.56	13.81	39.66	0.67	3.14	0.48	0.88	8.35	16.76	0.13	0.20	84.64
55	0.58	12.98	39.30	0.74	3.45	0.48	0.88	8.78	15.17	0.00	0.16	82.52
60	1.46	7.78	60.50	0.34	2.96	0.69	0.77	3.72	9.22	0.00	0.00	87.44
65	2.15	13.77	70.51	0.90	0.95	0.63	0.25	0.15	2.74	0.00	0.10	92.14
70	1.64	15.12	59.79	1.00	0.93	1.01	1.36	0.25	3.63	0.00	0.00	84.74
75	1.78	17.33	66.45	1.46	0.86	0.61	1.32	0.14	2.21	0.00	0.00	92.16
80	1.44	10.91	69.35	1.09	0.43	0.29	0.14	0.26	0.83	0.00	0.00	84.73
85	1.11	28.43	62.40	1.75	0.33	0.54	0.59	0.32	4.46	0.00	0.00	99.93
90	1.70	18.78	73.99	1.46	0.49	1.21	0.11	0.13	1.97	0.00	0.13	99.97
95	1.73	12.60	61.42	0.62	0.39	1.67	0.28	0.16	2.10	0.00	0.00	80.97
100	2.33	10.77	70.61	0.59	0.99	0.46	0.82	0.14	5.44	0.00	0.00	92.15
105	1.45	9.50	78.61	0.49	0.58	0.67	0.65	0.10	2.43	0.00	0.00	94.46
110	2.10	17.55	65.03	1.11	1.92	1.18	0.28	0.38	1.65	0.00	0.00	91.20
115	1.72	12.98	80.18	0.96	0.45	0.36	0.09	0.31	1.01	0.00	0.15	98.21
120	1.66	15.06	77.07	1.33	0.58	0.39	0.06	0.10	0.96	0.00	0.12	97.32
125	1.50	13.56	71.69	1.18	0.50	1.07	0.09	0.05	0.97	0.00	0.00	90.62

The sample was collected by E. Brook and M. Kurz from the Arena Valley on a Taylor II moraine (cf. Denton et al., 1989). The upper 60 μm is Mn-rich varnish. The lower 65 μm is silica skin. The substrate is sandstone. Spot size ~ 2 μm.

also similar to those found in varnishes from lower-latitude deserts (Fig. 1c–h). Lastly, varnish in Antarctica can be found interfingered with siliceous crusts (Fig. 2; Table 2), similar to those described by Weed and Ackert (1986) and Mittlefehldt and Lindstrom (1991, p.80). Interfingering of siliceous crusts and Mn-rich rock varnish also occurs in hot drylands (Dorn et al., 1992).

Field descriptions of Mn-rich Antarctic varnish in the aforementioned literature have noted that it is patchy in occurrence. All samples, except one from the Clark Mountains in Marie Byrd Land, had rock varnish present only in mm-scale patches. A patchy distribution may explain why claims of "no Mn-rich varnish in Antarctica" can persist, despite published chemical analyses and field observations to dispute this assertion.

3. Implications of Mn-rich rock varnish in Antarctica

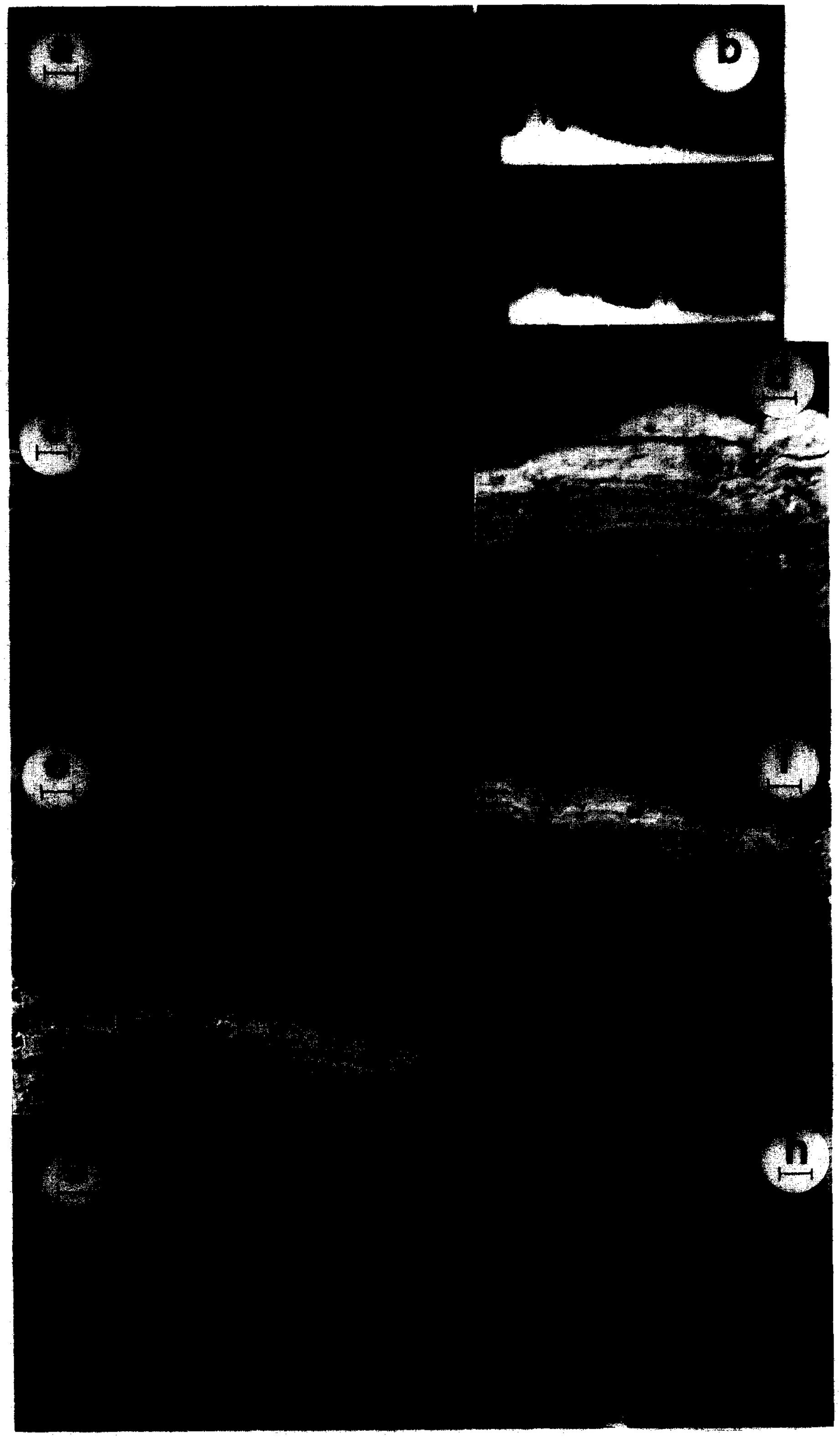
The chemical and textural similarity of Antarctic and temperate varnishes begs the question of a similar origin. While some argue for a physico-chemical mechanism of Mn concentration (Smith and Whalley, 1988; Whalley et al., 1990), the preponderance of research, however, suggests a key role for bacteria in Mn enhancement (e.g., Dorn and Oberlander, 1981, 1982; Krumbein and Jens, 1981; Mustoe, 1981; Palmer et al., 1985; Peck, 1986; Jones, 1991).

TABLE 3

Electron microprobe (wavelength dispersive) analyses of regions delineated in Fig. 1c (groups *1* and *2*) and Fig. 1h (groups *3* and *4*)

Description	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	BaO	Total	(K+Ca)/Ti
Fig. 1c,	1.23	17.74	26.23	0.99	0.87	0.72	14.48	9.94	0.39	72.59	3.35
group *1*	1.13	18.58	22.37	0.85	1.08	0.69	20.40	10.09	0.58	75.77	3.52
	1.09	18.86	19.96	0.84	1.20	0.69	21.73	9.70	0.61	74.68	3.76
Average ± S.D.	1.15 ± 0.07	18.40 ± 0.58	22.85 ± 3.16	0.89 ± 0.08	1.05 ± 0.17	0.70 ± 0.02	18.87 ± 3.86	9.91 ± 0.20	0.53 ± 0.12		3.54 ± 0.21
Fig. 1c,	1.18	21.20	31.09	1.06	0.61	0.82	10.21	11.53	0.25	77.95	2.69
group *2*	1.19	21.87	31.81	1.04	0.61	0.80	10.63	11.30	0.35	79.6	2.71
	1.17	20.92	29.35	1.00	0.68	0.79	12.48	11.54	0.42	78.35	2.79
Average ± S.D.	1.18 ± 0.01	21.33 ± 0.49	30.75 ± 1.26	1.03 ± 0.03	0.63 ± 0.04	0.80 ± 0.02	11.11 ± 1.21	11.45 ± 0.14	0.34 ± 0.09		2.73 ± 0.05
Fig. 1h,	1.59	17.71	29.52	1.58	1.34	0.60	9.32	10.06	5.56	77.28	6.31
group *3*	1.59	17.06	29.92	1.60	1.37	0.60	8.88	9.83	0.53	71.38	6.42
	1.63	16.58	31.79	1.58	1.34	0.59	8.21	9.61	0.55	71.88	6.31
	1.68	16.89	33.17	1.77	1.31	0.63	7.99	9.50	0.49	73.43	6.34
	1.8	17.25	32.97	1.83	1.36	0.70	8.85	9.25	0.60	74.61	5.93
Average ± S.D.	1.68 ± 0.09	17.10 ± 0.42	31.47 ± 1.69	1.67 ± 0.12	1.34 ± 0.02	0.62 ± 0.05	8.65 ± 0.54	9.65 ± 0.31	1.55 ± 2.24		6.26 ± 0.19
Fig. 1h,	0.34	7.86	75.90	0.54	0.26	0.32	1.94	4.20	0.12	91.48	3.37
group *4*	0.63	11.90	62.52	0.96	0.40	0.47	3.15	6.48	0.20	86.71	3.82
	0.94	15.25	53.06	1.27	0.49	0.57	4.13	8.28	0.19	84.18	4.15
	1.31	16.37	48.99	1.48	0.54	0.64	4.17	9.66	0.23	83.39	4.26
	1.67	17.45	44.70	1.77	0.61	0.68	4.67	10.87	0.25	82.67	4.66
Average ± S.D.	0.98 ± 0.53	13.77 ± 3.90	57.03 ± 12.4	1.20 ± 0.47	0.46 ± 0.14	0.54 ± 0.14	3.61 ± 1.08	7.90 ± 2.63	0.20 ± 0.05		4.05 ± 0.49

Analyses with 10-μm spot size. S.D. = standard deviation.


b
h

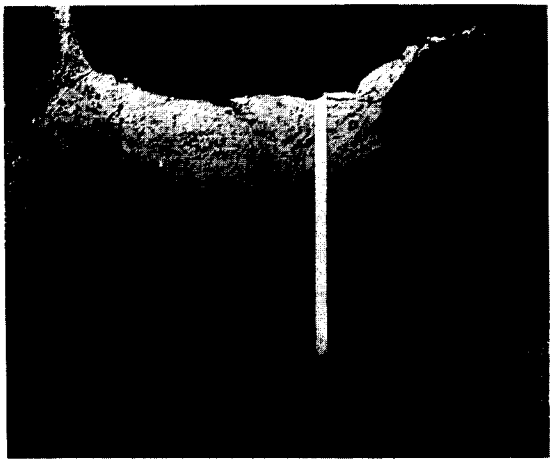


Fig. 2. Backscatter electron micrograph of Antarctic rock varnish on sandstone of a Taylor Valley II moraine in the Arena Valley, Ross Desert (cf. Denton et al., 1989). The ~ 125-μm-long line shows the location of the microprobe transect in Table 2. The brighter, upper half of the coating is Mn-rich rock varnish. The lower half is siliceous crust, similar to those described in Antarctica by Weed (1985) and Weed and Ackert (1986) for Ross Desert sandstones.

We have found budding bacteria actively concentrating Mn on the surface of Antarctic samples (Fig. 1a and b). Stromatolite-like botryoidal features associated with some biogenic lower-latitude rock varnishes (Krinsley

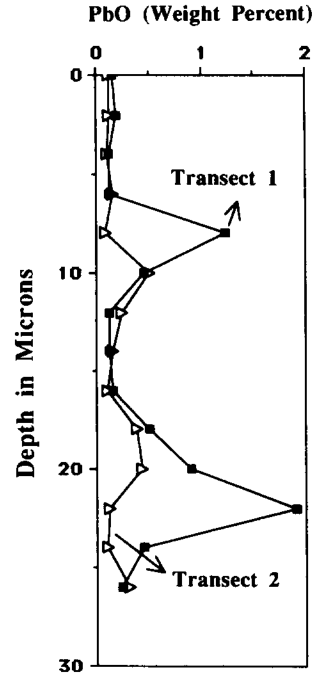


Fig. 3. Variations in PbO concentration with depth in rock varnish, on dolerate on an older moraine of upper Beacon Valley, Victoria Land, Antarctica (sample collected by Mort Turner). With a counting time of 200 s for Pb, the detection limit is ~0.08% for PbO. The two microprobe transects were from adjacent microdepressions.

Fig. 1. Secondary (a) and backscatter (c–h) electron micrographs, comparing Antarctic and temperate rock varnishes. *Scale bars* ~0.5 μm (a), ~15 μm (c), ~5 μm (d), ~10 μm (e), ~7 μm (f), ~15 μm (g) and ~15 μm (h). a. Unidentified budding bacteria on the surface of Beacon Sandstone, Dry Valleys, Ross Desert; sample collected by Ran Gerson. The filament just to the right of the *wavy white arrow* is typical of budding bacteria growing on temperate rock varnishes. b. Energy dispersive X-ray analysis is of a ~1–2-μm spot on the bacteria in (a) (lower analysis), compared to ~30-μm spot analysis of adjacent varnish material (upper analysis). This illustrates the relative enhancement of Mn (and some Fe) by the bacteria. c. Aeolian abrasion of the surface of Antarctic varnish, from Mt. Van Valkenberg, Clark Mountains, Marie Byrd Land. There is also some suggestion of an earlier episode of aeolian abrasion (just below *double black arrows*). Similar unconformities have been noted in temperate varnishes (Krinsley et al., 1990). *Arrow 1* (layered texture) and *arrow 2* (porous texture) indicate the areas where the electron microprobe measurements in Table 3 were made. d. A similar angular unconformity is found beneath the *wavy black arrows*; same site as (c). e. Stromatolite-like features (*arrows*) in the subsurface of varnish from the Bishop Tuff, eastern California, U.S.A. Similar features have also been noted in Arizona (U.S.A.) and Peru (Krinsley et al., 1990; Jones, 1991). f. Possible incipient stromatolite-like features (*arrow*) in the subsurface of varnish, from dolerite on an older moraine of upper Beacon Valley, Victoria Land, Antarctica. Sample collected by Mort Turner. g. Layered rock varnish texture, collected from a desert pavement on Pampa San Jose, near Nazca, Peru. *Double arrows* locate the presence of a mound at the top of a crack that penetrates through the varnish. A crack filled with redeposited Mn–Fe-oxides is just to the left of the *wavy black arrow*, similar to those in (c). h. Layered rock varnish texture [same site as (f)]. *Double arrows* locate the presence of a mound at the top of a crack, similar to the one found in (g). *Arrow 3* (layered texture) and *arrow 4* (porous texture) indicate the areas where the electron microprobe measurements in Table 3 were made.

et al., 1990; Jones, 1991; see Fig. 1c) may be in the incipient stage of development in Antarctic varnishes (Fig. 1f). An interesting point of speculation regards our culturing experiments of the budding bacterium *Metallogenium* (Dorn and Oberlander, 1981) (felt to be *Anthrobacter* by Palmer et al., 1985) by the approach described in Dorn and Oberlander (1981). The Mn-oxidizing bacterium was cultured from a varnish sample from the Upper Beacon Valley, Ross Desert, Antarctica, collected by Mort Turner. It is possible that bacteria colonized the surface of the varnish during transport or storage, so our experiment is not conclusive. Culturing studies of samples collected in Antarctica and placed immediately in sterilized containers will be required in future studies of the origin of Mn-rich varnish in Antarctica.

Textural and chemical data suggest that some of the constituents of Antarctic varnishes have been mobilized by water. The vertical lines in Fig. 1c are zones of Mn and Fe reprecipitation, similar to refilled wetting and drying cracks observed by Krinsley et al. (1990). Arrows in Fig. 1c and h juxtapose zones of layered and porous varnish. In both Fig. 1c and h, the porous varnish (*2* in Fig. 1c and *4* in Fig. 1h) has less Mn and lower ratios of $(K^+ + Ca^{2+})/Ti^{4+}$ than adjacent layered varnish (*1* in Fig. 1c and *3* in Fig. 1h). The chemical analyses in these zones are presented in Table 3. These observations are best explained by flow of capillary water mobilizing Mn, Ca and K, causing a porous texture from the breakdown of a layered texture.

Samples of Antarctic rock varnish that we have examined show considerable potential as a Quaternary dating and paleoenvironmental research tool. The Antarctic varnishes are nicely layered (Fig. 1c, d, f and h), similar to lower-latitude varnishes (Fig. 1g) that yield the best dating and paleoenvironmental results (Dorn et al., 1989; Dorn, 1990). For example, varnish dating may be important in deciphering whether the build-up of in situ cosmogenic isotopes (cf. Brown et al., 1989) on glacial moraine boulders is due to the prior exposure history of a glacial clast. Rock varnish also has possible uses in interpreting the eolian history of ice-free areas of Antarctica (Campbell and Claridge, 1988); backscatter imagery shows episodes of incomplete eolian abrasion in Antarctica (Fig. 1c and d). It is also possible to radiocarbon date varnish formed on fossilized ventifacts (Dorn et al., 1989). Lastly, we observed variations in PbO concentrations with depth in two electron microprobe transects (Fig. 3). A speculative interpretation, that will require more sampling to assess, is that these changes might correlate to PbO fluctuations in eolian fallout recorded in ice cores (cf. Boutron and Patterson, 1986).

4. Conclusions

Mn-rich rock varnish in Antarctica deserves further investigation. It may represent a completely different type of biogenic phenomena in Antarctica. Rock varnish is an accretion that is involved in local biogeochemical cycling of a wide variety of constituents, most notably Mn, Fe and clay minerals, and factors that control its distribution may yield clues to long-term biogeochemical patterns. It is also possible that organic matter present in rock varnish may be used as a tool to radiocarbon date exposure ages of such hard to date surfaces as ventifacts and till. Lastly, fluctuations in the geochemistry of varnish layers could record past variations in eolian fallout.

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