



Systematic Mn fluctuations in laminated rock varnish developed on coeval early Holocene flint artifacts along a climatic transect, Negev desert, Israel

Yonatan Goldsmith ^{a,b,*}, Yehouda Enzel ^a, Mordechai Stein ^{a,b}

^a The Fredy and Nadine Herrmann Institute of Earth Sciences, The Hebrew University of Jerusalem, Edmond J. Safra Campus, Givat Ram, Jerusalem 91904, Israel

^b Geological Survey of Israel, 30 Malkhei Israel St., Jerusalem 95501, Israel

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ABSTRACT

This study presents an assessment of the potential application of Mn content in rock varnish laminae as a paleoclimate indicator. To investigate the environmental controls on varnish formation, we determined Mn composition in rock varnish formed on flint artifacts produced during the earliest Holocene from eight coeval prehistoric sites in the Negev desert, Israel. These sites lie along a north–south annual rainfall transect ranging between 120 and 30 mm yr⁻¹. The varnish is ~100 times enriched in Mn relative to the content in the desert dust source material. Chemical profiles across the varnish display 4–6 distinct Mn peaks in all sampled sites, pointing to systematic fluctuations within the varnish along a wide range of environmental settings. The mean Mn contents in the various sites range between 10.7 and 15.6 at.%, yet within this range, the Mn content in the Negev varnish does not show a correlation with mean annual rainfall. As moisture is needed for Mn mobility, wetting cycles by dew or light rain, which are not adequately represented by the mean annual rainfall amounts but control the number of wetting–drying cycles may explain the variance within the results from the arid and hyperarid Negev varnish.

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Introduction

Rock (or desert) varnish comprises a thin (1–100s μm) coating formed primarily in micro-basins on exposed rock surfaces and is very common in arid and semi-arid regions (e.g. Liu and Dorn, 1996; Reneau et al., 1992). Former studies have shown that the varnish is composed of clay minerals and amorphous silica (70%) and Mn and Fe oxides (30%) (Dorn, 2007a; Garvie et al., 2008; Perry, 2004; Potter and Rossman, 1977, 1979). It typically displays a μm-scale alternating orange and black laminated structure which vary in Mn, Si, Al and Fe content. Mn is largely enriched to values of 10–30 wt% of oxides (Broecker and Liu, 2001; Garvie et al., 2008; Liu, 1994; Liu and Broecker, 2007, 2008a; Liu and Broecker, 2008b; Liu and Dorn, 1996; Perry and Adams, 1978; Reneau et al., 1992). At present, it is accepted that dust is the main source of varnish material (Bao et al., 2001; Fleisher et al., 1999; Garvie et al., 2008; Hodge et al., 2005; Potter and Rossman, 1977). The formation mechanism of rock varnish remains undetermined. Proposed mechanisms include abiotic chemical precipitation (Engel and Sharp, 1958; Hooke et al., 1969; Moore and Elvidge, 1982; Perry, 2004; Perry et al., 2005, 2006), biologically mediated precipitation (Dorn and

Oberlander, 1981; Dorn and Oberlander, 1982) or a combination of these two mechanisms (Dorn, 1998, 2007b, and see references there).

Varnish has been proposed as a paleoclimate archive, where its laminae record past millennial-scale climatic fluctuations (Broecker and Liu, 2001; Liu, 1994; Liu and Broecker, 2008a; Liu and Dorn, 1996; Liu et al., 2000). The most recent, surface lamina of the varnish is typically Mn-poor and yellow, attributed by the above researchers to formation during the recent drier stage of the Holocene in deserts. The dark, Mn-rich laminae were consequently associated with wetter climates (Liu, 1994; Liu and Dorn, 1996; Zerboni, 2008). In this way, Broecker and Liu (2001) hypothesized a general correlation between the Mn content and regional annual rainfall. In addition, compiled color layering sequences within the varnish were wiggle-matched to the sub-polar North Atlantic deep sea sediment record (Liu, 1994; Liu and Broecker, 2007).

The use of rock varnish as a paleoclimate indicator has been criticized based on uncertainties of the degree of variance in the varnish properties (Garvie et al., 2008; Reneau et al., 1992). In addition, no well-defined sampling method has been established and an investigation of the way modern analogs of varnish form across a large range of known modern climates under well-defined chronological contexts.

In this paper, we present a systematic field-based study of the characteristics of varnish formed on flint artifacts from eight coeval prehistoric sites located along a north–south climatic transect in the Negev desert, Israel. By using Holocene varnish formed under known climatic settings,

* Corresponding author at: The Fredy and Nadine Herrmann Institute of Earth Sciences, The Hebrew University of Jerusalem, Edmond J. Safra Campus, Givat Ram, Jerusalem 91904, Israel.

E-mail address: Yonatan.goldsmith@mail.huji.ac.il (Y. Goldsmith).

we try to determine whether Mn content in laminated rock varnish can serve as a climate recorder.

Method

General: Open issues in earlier research

The systematic sampling and analyses outlined below were constructed to address open or disputable issues in earlier research. In the past, rock varnish was sampled from various landforms: lava flows (Israel et al., 1997; Liu, 2003; Raymond et al., 1991; Reneau et al., 1992; Thiagarajan and Aeolus Lee, 2004), alluvial fans (Engel and Sharp, 1958; Krinsley et al., 1995; Liu and Broecker, 2007; Liu and Broecker, 2008a, 2008b; Liu and Dorn, 1996; Liu et al., 2000; Wayne et al., 2006), lake shorelines and wave-cut cliffs (Hodge et al., 2005; Liu and Broecker, 2007), desert pavements (Bao et al., 2001; Garvie et al., 2008), bedrock outcrops (Dietzel et al., 2008; Dragovich, 1988; Engel and Sharp, 1958; Hodge et al., 2005; Krumbain and Jens, 1981; Probst et al., 2002), rock engravings (Dragovich, 2000), prehistoric artifacts (Bierman and Gillespie, 1994; Liu and Dorn, 1996) and meteorites (Lee and Bland, 2003). Samples retrieved from unstable landforms (e.g. young alluvial fans or high stand shorelines) on one hand, or very long-lived stable features (e.g. ancient desert pavements or rock outcrops) on the other hand, pose a problem in determining a maximum age for the varnish formation. The problem is that inherited varnish might have remained on the rock from a previous deposition or erosion stage, which is virtually undistinguishable from newly formed varnish. During the production of prehistoric flint artifacts all previously formed varnish is removed from the surface, and therefore, all varnish formed on the fresh surface postdates the time of the archeological site. Thus, prehistoric artifacts insure that all varnish formed on the knapped surfaces of the artifacts are unequivocally later than the time of the archeological site, eliminating the problem of inherited varnish.

A second issue that affects varnish research is the lack of an accepted method to directly determine the age of the varnish (Beck et al., 1998; Bierman and Gillespie, 1991, 1994). The only way to determine the age of the varnish is through external independent chronology (Watchman, 2000). A shortage in independent ages of dated geomorphic features restricts progress of varnish research (Broecker and Liu, 2001). In this research, we used well-established independent ages (radiometric and high-resolution cultural-typological chronology) of human-made tools from prehistoric sites to overcome this limitation of previous research.

A third shortcoming in previous research is that the model correlating varnish formation with climate is based on a compiled stratigraphic scheme that is wiggle-matched to global paleoclimate data (Liu and Broecker, 2007). The problem with this form of correlation-based interpretation is that it interprets the past without a thorough understanding of the way present varnish develops throughout a range of climatic/environmental settings; i.e. the lack of systematic analogs. The focus in this paper is on varnish formed during the Holocene in the Negev, under the assumption that only minor climatic fluctuations occurred during the time interval since tool production, and that the overall climatic setting roughly resembles the current one (e.g. Amit et al., 2006; e.g. Enzel et al., 2008). This basic setting enables us to investigate the way relatively modern varnish formed throughout known diverse environmental conditions, and to assess, if not conclusively determine, if and which environmental factors affect the varnish variance.

Sampling sites

Rock varnish sampled in this study formed on surficial, sub-aerial flint artifacts from eight Pre-Pottery Neolithic B (PPNB) prehistoric sites (dated 10,500–8250 cal yr BP; Kuijt and Goring-Morris, 2002) distributed across a variety of climatic conditions in the Negev desert (Fig. 1, Table 1). Sites chosen for varnish research are only those situated on

flat stable surfaces that remained sub-aerial (i.e. not covered and/or deflated) from the time they were built to present. The PPNB period was chosen for the following reasons: (a) many sites are distributed across the entire Negev (e.g. Barzilai, 2009); (b) the techno-typological characteristics are unique and enable an exact attribution to a specific cultural entity without radiometric ages (e.g. Barzilai, 2009); (c) the duration of the PPNB period is relatively short (2 ka); (d) the PPNB is dated to the beginning of the Holocene, therefore the varnish was formed on the artifacts throughout a climatic period that apparently was not much different than today (e.g. Amit et al., 2006; e.g. Enzel et al., 2008). Site information is presented in Table 1 and Figure 1 (for detailed description of the sites see Goldsmith, 2011).

Field sampling

Sampling rock varnish in the field is not a trivial task and has been a topic of long debate (e.g. Liu, 1994; Liu and Dorn, 1996; Reneau, 1993; Reneau et al., 1992). The sampling procedure in this work is an adaptation of the procedure devised by Liu (1994) and is summarized as follows. An area suitable for sampling is situated on a stable elevated surface with respect to its surroundings, has a flat microtopography without local depressions (on the meter scale), is associated with a desert pavement, and is adjacent to in-situ man-made structures that do not show signs of weathering.

At the selected sites, hundreds of artifacts were examined in the field using a magnifying glass and portable binocular microscope. A chosen micro-basin on an artifact surface (e.g. Fig. 2B) is flat and elongated (depth/width $\approx 1/3$) (Fig. 2D), it is characterized by an upper surface with an appearance of a mud-crack pattern (Fig. 2B) and presents no signs of erosion on the upper surface of the varnish.

To ensure that the selected artifact has not been turned over, the bottom, ground-facing side is examined; selected artifacts have red patina stains (McFadden et al., 1989; Perry, 2004) (Fig. 2C) on the bottom but no varnish. The stains form on the lower parts of the sample embedded in the top soil, and varnish forms on the parts facing the sky (Perry, 2004). Selecting only artifacts with these characteristics ensures that they have been at their current position and orientation for a long time.

After examination under a binocular microscope, artifacts suitable for research were returned to their original position, photographed and the direction of the artifact was noted. The location of each artifact was marked by a GPS and plotted onto the schematic plan of the site. From each site 6–10 artifacts were sampled.

Laboratory procedure

We prepared 80 ultra-thin ($\sim 5 \mu\text{m}$) sections using a procedure developed by Liu (1994). The samples which showed the clearest and most organized laminated varnish were photographed using an Olympus E-330 camera mounted onto an Olympus B $\times 51$ light microscope (magnification lenses 100 \times , 50 \times , 20 \times) at the Center of Nanotechnology, The Hebrew University of Jerusalem.

The thin sections were visually analyzed; the samples with the longest continuous undisturbed laminations from each site were selected. The deepest and least disturbed area of each micro-basin was used for analysis. The samples were carbon coated, and a series of spot chemical analyses ($\sim 1 \mu\text{m}$ in size) along a transect perpendicular to the varnish surface was conducted at intervals of $\sim 1 \mu\text{m}$ using a Jeol JXA 8600 EPMA electron microprobe at the Institute of Earth Sciences at the Hebrew University of Jerusalem. Each chemical reading was analyzed for 60 s using a focused electron beam; acceleration voltage was 15 kV and the beam current was 10 nA. The X-rays were collected using a Pioneer-Norvar Energy Dispersive Spectrometer (EDS). The spectral data were reduced using the ZAF/PROZA processing procedure. The calibration was done using natural standards. The oxides composing the varnish are highly variable (Garvie et al., 2008). Therefore, the

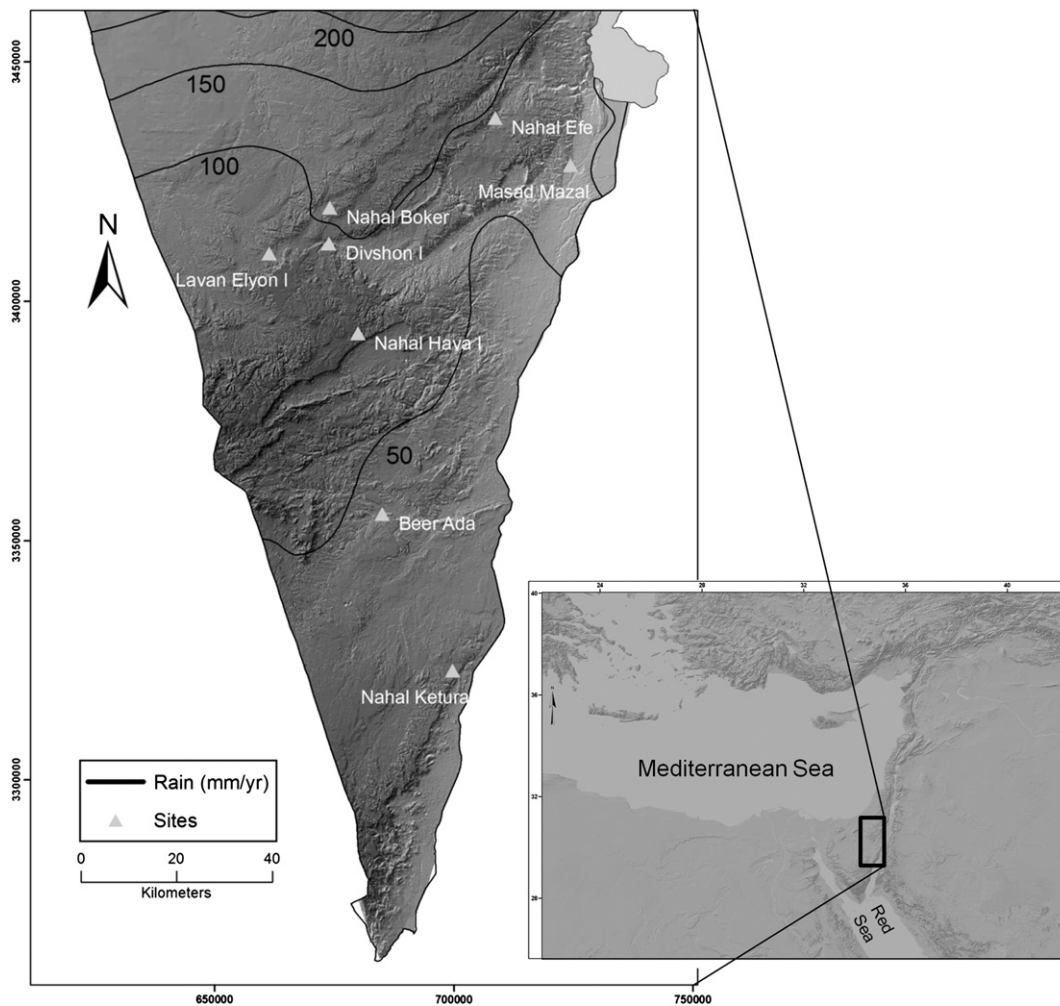


Figure 1. Sampled archeological sites and the mean annual rainfall across the Negev, southern Israel. The eight sites: Nahal Efe, Mazad Mazal, Nahal Boker, Lavan Elyon I, Divshon I, Nahal Hava I, Beer Ada and Nahal Ketura.

varnish chemistry was calculated in atomic percent using the “element” function in the electron microprobe (and not with the “oxide” function). In this way, the results are not calculated by adding oxygen; therefore, no prior assumptions regarding the nature of the oxides composing the varnish are needed. All results were calculated using the same ten elements, enabling a quantitative comparison among samples. In areas of spatially variable varnish colors (assumed by a color change in the composition mode of the microprobe) higher-resolution spot chemical analyses were conducted. To examine the variability within a single micro-basin, in four samples (NE9, NE11, NH6, and NH7) more than one profile was analyzed.

To assess the correlation between chemical composition and lamination color, the images from the light microscope were geo-referenced to the composition-mode images from the microprobe. Positions of the

spot chemical analysis were transferred onto the light microscope images using ArcMap 9.3 program.

Dust/soil sampling

Settling dust has been proposed as the source material of rock varnish (e.g. Bao et al., 2001; Fleisher et al., 1999; Hodge et al., 2005). Therefore, the element content in the varnish might be governed by differences in the dust chemistry. At each site, we sampled the vesicular A horizon with a silt/clay-silt texture into which the tools in the prehistoric sites are embedded. The fine grain (<20 μm) fraction of the vesicular A horizon should provide an approximation of the average chemical composition of the settling dust (e.g. Amit et al., 2011), at least since the sites were abandoned, which is also the duration of varnish accumulation

Table 1
Sampling site locations and description.

Site name	Location	Topography	Reference
Nahal Efe	31° 4.77'N, 35° 9.02'E	Flat spur	Kuijt and Goring-Morris (2002)
Mazad Mazal	30° 59.35'N, 35° 18.86'E	Remnant lacustrine surface	Schyle (2007)
Nahal Boker	30° 54.56'N, 34° 47.42'E	Flat hilltop	Noy and Cohen (1974)
Lavan Elyon I	30° 50.42'N, 34° 42.42'E	Low terrace	Goring-Morris and Rosen (1987)
Divshon I	30° 50.59'N, 34° 47.13'E	Low hills	Cohen and Yizraeli (1969); Servello (1976)
Nahal Hava I	30° 40.32'N, 34° 51.16'E	Flat spur	Guvrin (2009)
Beer Ada	30° 19.90'N, 34° 54.34'E	Elevated terrace	Goring-Morris (1993)
Nahal Ketura	30° 2.19'N, 35° 3.53'E	Low terrace	Kuijt and Goring-Morris (2002)

(~9000 yr). The soil samples were first wet-sieved through a 20 μm sieve to extract only the fine fraction, then, samples were treated with sodium peroxide and chemically analyzed using an ICP-MS at the geochemistry laboratory of the Geological Survey of Israel. The results were converted from wt% of oxides to atomic % of elements for compatibility with the probe results of the varnish. To compensate for the possible differential leaching of Ca as a function of rainfall amounts, and due to the very little Ca in the varnish, the chemical composition of the soil samples was recalculated excluding Ca.

Results

Appearance in the field

In the field, rock varnish forms black–brown clusters primarily in micro-topographic depressions (~100 μm wide and ~50 μm deep), probably formed during the knapping of the artifact. Visually, varnish

distribution varies considerably across the surface of single artifacts, and from artifact to artifact from the same location.

Most of the field-observed varnished micro-basins exhibit various degrees of erosion (i.e. the upper surface is not flat and certain areas seem “peeled off”), irregularities or lichens on the surface of the varnish. Therefore, they are not suitable for varnish research according to the criteria listed above. Only ca. 5% of the micro-basins observed were suitable for detailed varnish research.

Light-microscope inspection

Observation of the varnish under a light microscope reveals two structure genera; a) the common is an aggregation of nanometer scale pods into light clusters (yellow and orange) and dark clusters (e.g. Fig. 3E–left side), this appearance was termed “rubbly” by Garvie et al. (2008). This structure does not form a coherent pattern of any sort. Therefore, this form of structure was not used for further analysis, b) the second structure is composed of nanometer-scale pods which aggregate into a

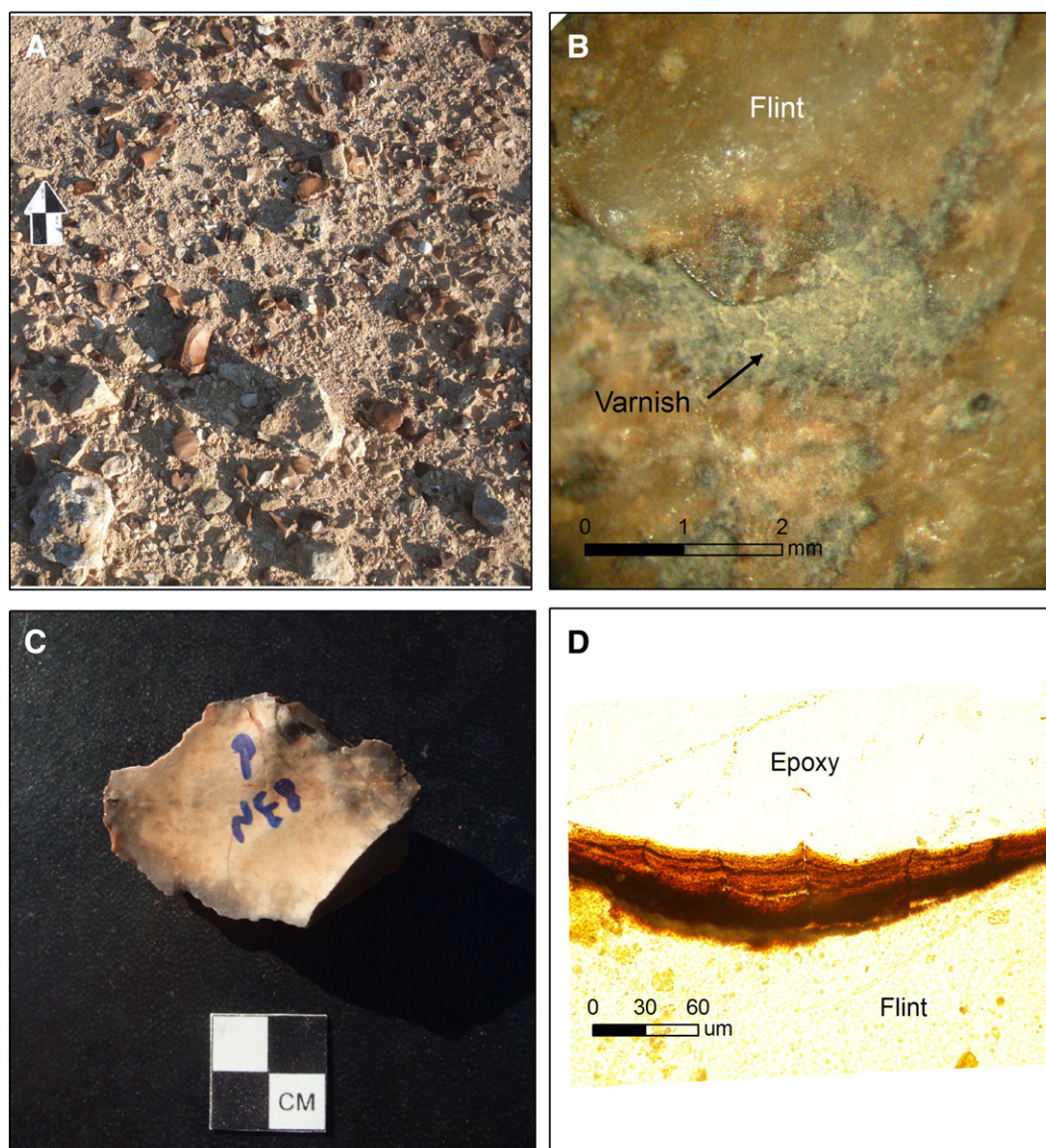


Figure 2. Examples of sampling criteria: (A) Undisturbed area in site Lavan Elyon I. (B) Micro-basin in flint sample Nahal Efe 9 showing a flat elongated surface with “mud-cracks”. (C) Red patina on the bottom side of an artifact from Nahal Efe 8. (D). Sample Nahal Efe 11_2 showing laminated varnish in an ultra-thin section.

laminated pattern of light and dark laminae (e.g. Fig. 3A, C, F, G). The laminae are $\sim 0.5\text{--}1\ \mu\text{m}$ thick, and extend across tens of μm within a micro-basin. General qualitative observations indicate that the best-developed laminated structures are in micro-basins that morphologically are shallow and elongated, whereas “rubbly” varnish forms in deeper,

less elongated and smaller micro-basins. This varnish morphology is also evident within a single micro-basin. When the varnish first began accumulating and the bottom of the micro-basins was narrow and steep, “rubbly” varnish formed; when the micro-basin began filling up and its morphology became less steep, laminated varnish formed (e.g. Fig. 3A,

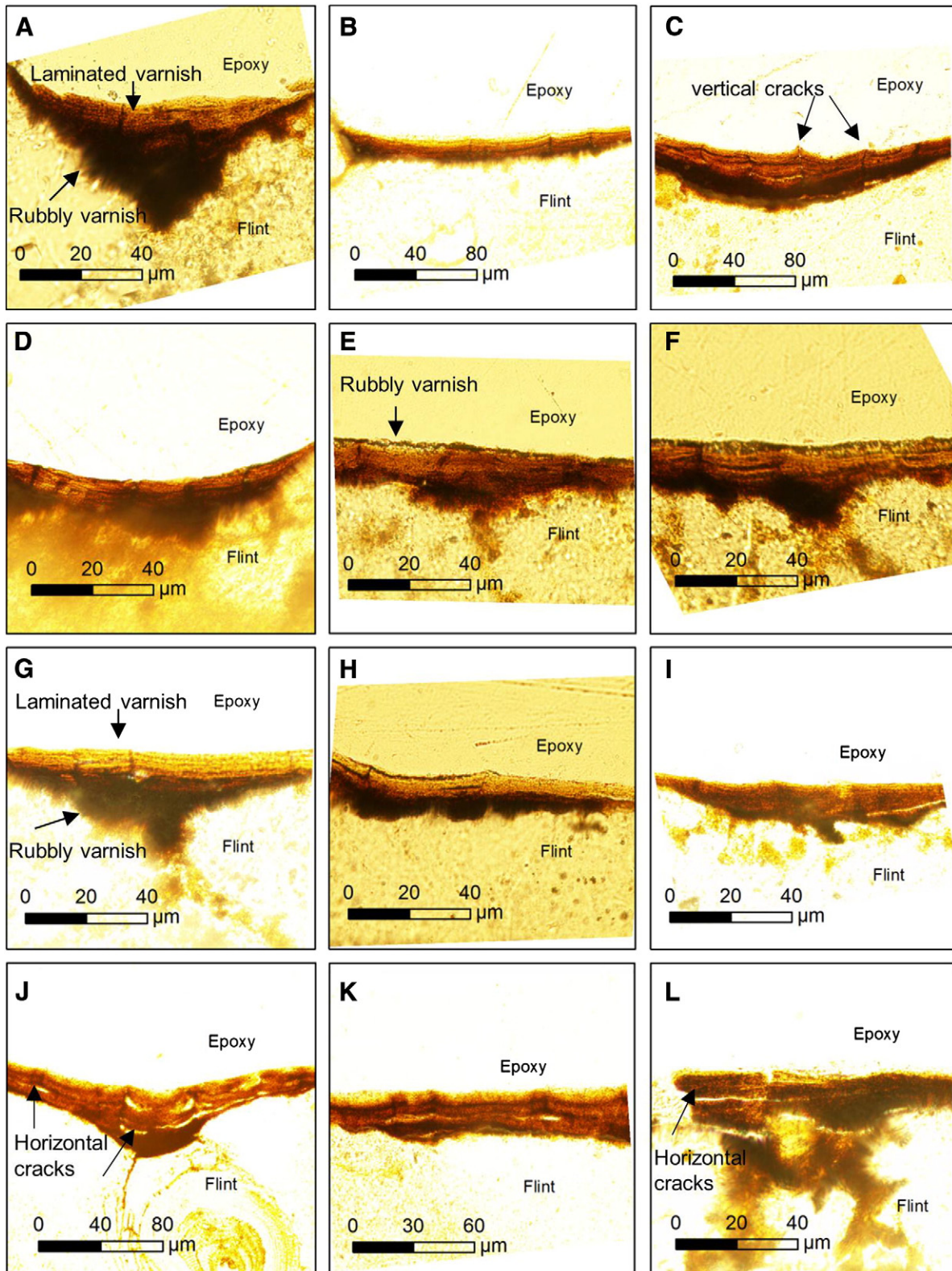


Figure 3. Light microscope images of selected ultra-thin sections through rock varnish. A. Nahal Boker 10. B. Nahal Efe 9. C. Nahal Efe 11-2. D. Nahal Hava 6. E. Nahal Hava 7-1. F. Nahal Hava 7-2. G. Lavan Elyon 1. H. Divshon-1. I. Mazad Mazal 8. J. Beer Ada 3. K. Beer Ada 3. L. Nahal Ketura 11-2.

G). This causes the laminated structure to be better developed in the upper parts of the micro-basins.

Other features evident in the varnish are horizontal and vertical cracks, which, respectively, are parallel and perpendicular to the varnish surface. The vertical cracks seem to penetrate from top to bottom into the micro-basins (e.g. Fig. 3C), and therefore postdate the formation of the entire varnish sequence. These cracks are likely an artifact of the preparation of the ultra-thin sections; they may not be an intrinsic feature of the varnish. The horizontal cracks are a more complicated phenomenon (e.g. Fig. 3J, L): they are sub-parallel to the laminations, but at times cut through and do not fully follow the laminations. Thus, these cracks probably formed during the accumulation of the varnish.

Devising a meaningful composite profile based on laminae color is necessary if varnish stratigraphy is to be used for paleoenvironmental inference, but we found this impossible on the individual micro-basin scale, let alone for all samples together. The problem is the diffusive contacts between the laminae in our samples, which prevent an unequivocal separation between laminae. When comparing the varnish sequences produced in this work with those presented by Liu (e.g. Liu, 1994; Liu and Dorn, 1996), it seems that the laminations in their work are more accentuated than the ones we studied. The reason for this is unclear. One possible explanation is that our samples have lower Mn contents relative to those presented by Liu (~12% vs. 15–25%, respectively); presumably, this may cause a less distinct color pattern. A second possible explanation could be that we sampled artifacts that were positioned close to the ground; therefore, the accumulation of the varnish might have been affected more by the local environments than Liu's samples which were located higher off the ground.

Chemical composition

Microprobe analyses of the profiles perpendicular to the varnish surface show that the ten most abundant elements in the varnish

are Si > Al > Mn > Fe > Mg > K > Ca > Ti > P > Cl. The average element concentrations (atomic %) and standard errors of the mean in the varnish are: Si: 42 ± 0.26 , Al: 22 ± 0.14 , Mn: 13 ± 0.23 , Fe: 10 ± 0.14 , Mg: 5 ± 0.07 , K: 3 ± 0.04 , Ca: 3 ± 0.09 , Ti: 2 ± 0.08 , P: 1 ± 0.06 , and Cl: 0.5 ± 0.01 .

Plotting major element vs. Mn concentrations for all samples shows a weak correlation between Mn and the other elements (Fig. 4). Qualitatively (ellipses in Fig. 4), it seems that there are weak inverse relationships between Mn and Si and perhaps between Mn and Al and Mn and Fe. A weak positive correlation exists between Mn and Ti (Fig. 4). Reneau et al. (1992) presented similar results that are more conclusive and display higher correlations ($r^2 = -0.90$). These results point to a scenario in which Mn, Si, Al and perhaps Fe are the major contributors to the variance in the chemical composition of the varnish; when Si, Al and Fe content are relatively high, Mn content is low, and vice versa. Ti seems to couple with Mn, and both Al and Fe couple with Si. However, Al and Fe seem to be relatively constant within the range of 4–8 at.%.

Average chemical variations within a micro-basin and at an archeological site

To assess the variations in element content across different micro-basins on a single flint artifact and at a geographic site, six microprobe chemical profiles were analyzed from the Nahal Efe (NE) site. These analyses are from three different micro-basins located on two different lithic artifacts. Comparison of the average concentrations of all elements from these six profiles (Fig. 5A) shows that there are minimal variations in the contents of most of the elements, although Mn, Fe and perhaps Ti stand out as exceptions varying at the sample level. The mean Mn content for all six samples ranges between 11 and 15 at.%, and is basically the same within 1- σ uncertainty (Fig. 5B). To what extent this range is significant is unclear, although it must be accounted for when trying to calculate general correlations using the mean Mn content.

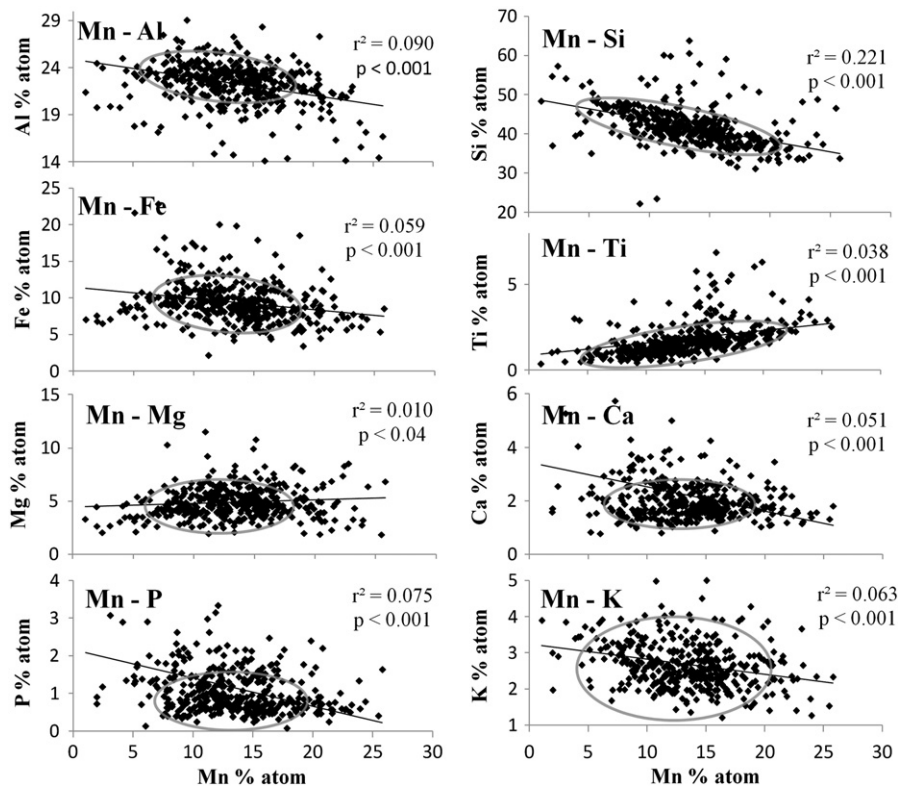


Figure 4. Major element vs. Mn concentrations for all varnish samples ($n=398$). To avoid measurements of cracks, the data plotted include only measurements for which the summed concentrations exceed 30% (cracks give low totals due to high carbon content in the epoxy). Ellipses indicate the main clusters around the regressed lines. In accordance with Bierman and Gillespie (1991), Ti and Ba were not differentiated, all energy peaks in this range were tentatively attributed to Ti.

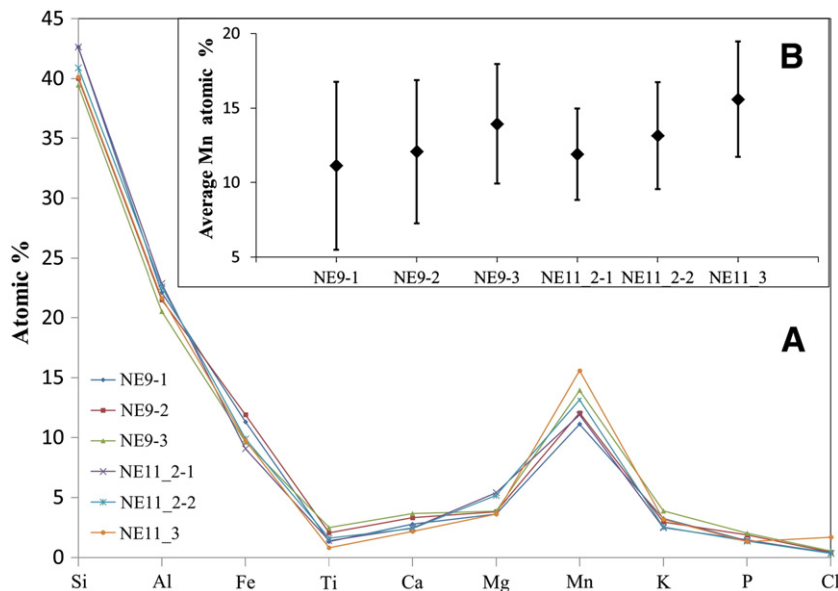


Figure 5. A) Average element concentrations for six varnish profiles from Nahal Efe (NE) sites (Fig. 1), B) average Mn content and standard deviations for six varnish profiles from Nahal Efe (NE) (Fig. 1). All Mn concentrations are the same at the 1- σ level.

The variance in the Mn content does not seem to affect the pattern of the fluctuations at the micro-basin level (Fig. 6A). The two profiles with the thickest varnish (NE11_2-1, NE11_2-2) display six distinct fluctuations in Mn content with depth (Fig. 6A). The remaining four profiles are thinner in depth and display only four peaks, although when plotting all profiles beginning with the uppermost lamina of each profile (i.e. without any sort of distance/depth rescaling) it is evident that a similar pattern of Mn content arises, excluding the two peaks from the base of the section. The amplitudes of the Mn peaks vary among micro-basins on the same artifact and among artifacts from the same archeological site. However, the overall pattern of Mn concentration, and possibly the distance between peaks seem to be similar in the upper four peaks and characterize all six profiles. This observation may support proposals by Liu (1994) that although the specific Mn concentration (i.e. the amplitude of the peaks) varies, the pattern of fluctuations in the Mn content (i.e. the number of peaks and the distance between them) seems more consistent from sample to sample. This may reinforce Liu's notion that the criteria for obtaining the longest varnish sequence is only possible by examining many varnish profiles.

Mn-content variations among sites

The vertical sections from all the analyzed varnish samples from all sites exhibit 4–6 distinct peaks in the Mn concentration (Fig. 6B). The number and pattern of such peaks seems to be in agreement within a single micro-basin (Fig. 6A), and possibly even among micro-basins from different geographic sites across the Negev, regardless of specific annual rainfall amounts (Fig. 6B). This recurring systematic pattern indicates that the fluctuations in Mn content in varnish profiles might be related to a regional environmental forcing.

Outermost Mn-poor lamina

As mentioned above, a few previous studies show that the Mn content in the outer few μm of the varnish is much lower than in the rest of the varnish (Liu and Dorn, 1996; Zerboni, 2008; mp in Fig. 6A). In our results, the Mn values of the uppermost few μm are <1 at.%. They increase gradually downward to depths of 3–6 μm , where they reach the more typical average values for the vertical varnish transect (~ 10 –15 at.%). Fe does not display this feature, with typically high concentrations even in the uppermost μm . This uppermost layer, which is always uniquely and

anomalously low in Mn (1–2 at.%) relative to the rest of the varnish appears in all samples, those which originated from areas characterized by mean annual rainfall of 30 mm or four times this amount (120 mm; Fig. 6A, B).

The Mn-poor outer lamina was termed “the orange/yellow (Mn-poor) uppermost layer” by Liu and Dorn (1996: 190–193). They claimed that the top layer is commonly depleted in Mn in respect to other layers in the varnish. This observation is the key to the hypothesis proposed by these authors that variation in varnish laminae composition is correlated with climate fluctuations. If Liu and Dorn's (1996) interpretation that this Mn-poor layer represents the current arid climate is correct, then, we would have expected to see systematically higher Mn content in the upper lamina of the varnish from areas receiving increasingly higher rainfall amounts. This is not the case in the Negev samples or from what emerges from previous work. Therefore, our spatial, across-climate observation indicates that the cause for the uppermost Mn-poor layer reflects, at least in the Negev desert, an ongoing internal mechanism of varnish formation unrelated to mean annual rainfall amounts. This mechanism is currently under research with some initial observations in Goldsmith (2011).

The lowermost Mn-rich lamina

In several of the samples, the Mn content in the bottom few μm , just above the flint-varnish contact, is extremely high, and reaches 40–50% (samples NE9-1, NE9-2, NE11_3 in Fig. 6A). This seems to occur in micro-basins having high width/depth ratio. In addition, in such micro-basins the varnish is thinner than in micro-basins with lower width/depth ratios. We speculate that the accumulation of the varnish sediment in micro-basins with a wide morphology differs from varnish which accumulates in morphologically narrower micro-basins. This might indicate that the size and shape of the micro-basin affects the formation of the varnish, therefore, very wide micro-basins might not be suitable for varnish research.

To conclude, the important results from our analyses are: (a) within the range of 30–120 mm/yr the total range of average Mn in the Negev rock varnish is 10.7–15.6 at.%, (b) in all sites, we observe 4–6 peaks in the Mn content, regardless of mean annual rainfall amounts, and (c) in all sites, the outermost layer is always uniquely and anomalously low in Mn (1–2 at.%) relative to the rest of the varnish (~ 10 –12 at.%).

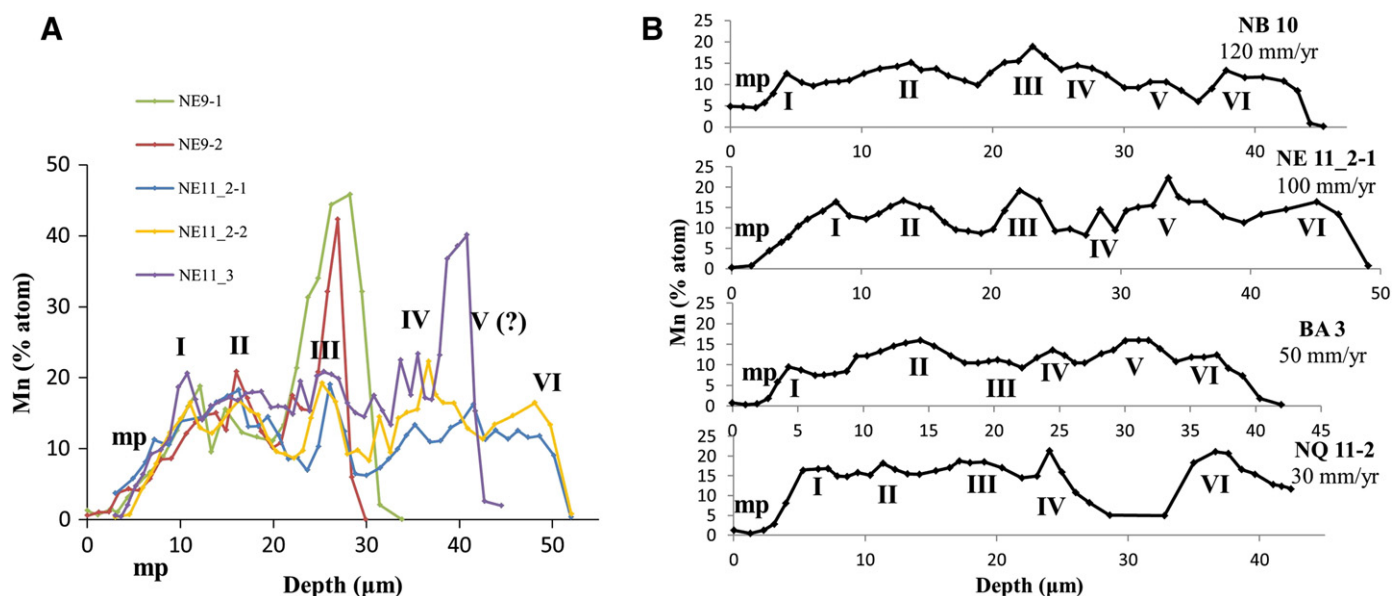


Figure 6. A) Variations in Mn composition in five varnish profiles from a single site, Nahal Efe (NE) (Fig. 1). The profiles have been aligned as a function of depth according to the upper most layer (without any sort of normalization). Roman numerals represent peaks in Mn concentrations. B) Stratigraphic variations in Mn composition in selected samples from four sites: Nahal Boker (NB) 10, Nahal Efe (NE) 11_2-1, Beer Ada (BA) 3 and Nahal Ketura (NK) 11_2. All samples are aligned as a function of depth (μm). Roman numerals represent peaks in the Mn concentrations. mp represents the upper Mn-poor layer. Average amounts of rainfall are cited on the right (for results from other sites see: Goldsmith, 2011).

Discussion

The systematic sampling of coeval laminated varnish formed along a rainfall transect enables testing of the basic hypothesis of rainfall amounts influencing formation of varnish, as proposed by Liu and Dorn (1996). We examined two additional factors that we suspected could possibly affect the Mn content in the varnish: the chemistry of the settling dust, proposed as the ultimate source of varnish (e.g. Bao et al., 2001; Fleisher et al., 1999; Hodge et al., 2005); and micro-basin size.

Dust

The chemistry of the fine fraction of the soil sediment (which will be regarded hereinafter as settling dust) from the different sites is homogenous (Table 2 and elaboration in Goldsmith, 2011). The settled dust is mainly composed of quartz, calcite and clay minerals. Chemically, the settling dust (excluding Ca) is dominated by Si (~50%) and Al (~20%) (Table 2). Relative to the settling dust, the average Mn content in the varnish is enriched by two orders of magnitude (~100 \times). The average Fe content is only slightly enriched (factor of ~1.4), limiting the importance of Fe in the formation of the laminated varnish. The average Si content in the varnish is reduced by a factor of ~0.8 relative to the settling dust. The slightly higher amount of Si in the dust relative to the Si content in our varnish can be attributed to additive quartz in the dust that is not incorporated in the varnish. The average concentrations of Al in the varnish and in the settling dust are quite similar. The Si/Al ratios in the settling dust and the average varnish are ~2.6 and ~2, respectively (Table 2). These results and their

accordance with Garvie et al. (2008) results point to a significant component of clay minerals in the varnish as well as in the dust. Large quantities of Al and Si are also presented in Perry's (2004: p. 78) microprobe results. In addition, clay minerals can also be deduced from Perry's XRD results before grain size separation (Perry, 2004: p. 100). These observations may point to significant amounts of clay minerals in the varnish.

A weak positive correlation exists between the average concentration of Mn and Si in the varnish and their respective concentrations in the dust (Fig. 7). A weak inverse correlation exists between Fe and Al in the varnish and dust (Fig. 7). Although the dust is the source for the sediments in the micro-basins, it seems that the chemical composition of the local settling dust is not the main control on the final chemical composition of the varnish. Rather, it is a product of selective geochemical processes that seem to be operating primarily on the Mn. Si, Al and Fe are only minimally affected by this process and do not hold a bearing on the final composition of the varnish.

Total accumulated volume of varnish sediment

The volume of accumulated varnish is not uniform (even between micro-basins on the same lithic artifact) and might affect the Mn composition. The volume of the accumulated material was measured using binocular microscope and light-microscope images of the varnish in plan-view and section-view, respectively. The volume of the accumulated material was approximated using the section views as a half ellipsoid ($2/3 \cdot \pi \cdot m_1 \cdot m_2 \cdot m_3$) or an elliptical surface with a cylindrical shape ($1/3 \cdot \pi \cdot m_1 \cdot m_2 \cdot m_3$). Where (m_1, m_2, m_3) represent the different radii of the shape (Table 3). Figure 8A shows that despite the large

Table 2

Average element content of the fine soil fraction (>20 μm) compared to the average varnish element content from all sites.

% atom	Si	Al	Fe	Ti	Mg	Mn	Na	K	P	Si/Al	Si/Fe	Al/Fe
NE	55.79	20.29	6.61	1.24	11.29	0.15	1.00	3.07	0.56	2.75	8.45	3.07
LE	54.85	19.67	8.37	1.18	9.48	0.12	1.92	3.55	0.87	2.79	6.55	2.35
NB	52.40	20.34	6.49	0.97	10.17	0.08	5.05	3.84	0.66	2.58	8.07	3.13
NH	56.46	22.25	7.03	1.10	8.48	0.12	0.79	3.11	0.67	2.54	8.03	3.17
BA	56.51	20.27	6.30	1.01	9.36	0.12	1.35	3.56	1.52	2.79	8.97	3.22
NK	52.96	20.35	7.35	0.97	9.24	0.11	5.09	3.11	0.82	2.60	7.21	2.77
MM	48.42	16.91	5.48	0.93	11.49	0.11	11.19	3.83	1.64	2.86	8.84	3.09
Avg varnish	42.21	22.41	9.20	1.81	5.00	12.98	NA	2.65	1.13	1.13	1.13	1.13

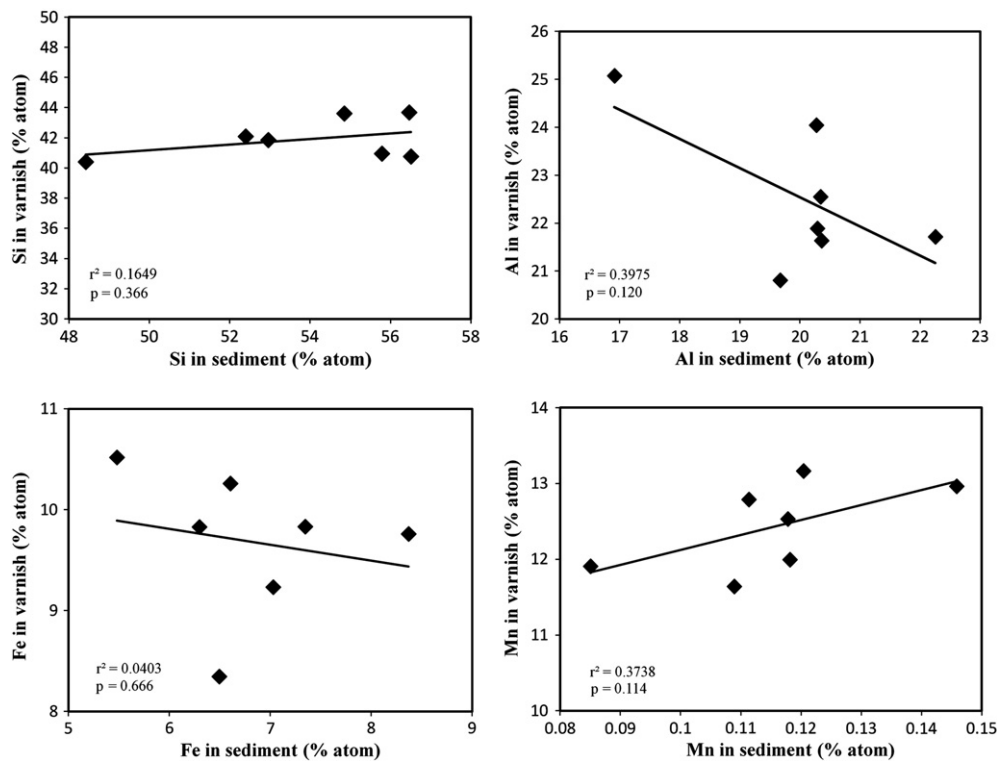


Figure 7. Comparison of average concentrations of Si, Al, Fe and Mn in varnish and in sediment, for seven sites.

differences in volume, the average Mn composition is relatively constant, and is not affected by the volume of varnish sediment accumulated. Therefore, the vertical sediment accumulation rate, and not the volume of accumulated material (i.e. the horizontal distribution), affects the Mn content.

Rainfall and dew

It has been proposed that the fluctuations in the varnish composition are environmentally driven (Broecker and Liu, 2001; Perry and Adams, 1978; Zerboni, 2008). To evaluate whether a correlation exists between the mean annual rainfall and average Mn content, we used a GIS rainfall model derived from the Israeli Meteorological Service rainfall data (Fig. 1). The average Mn content (atomic %) was calculated, excluding the analysis from the cracks and the upper Mn-poor layer. The average Mn content and the mean annual rainfall amounts are not statistically correlated (Fig. 9A), though; in the range of

30–120 mm yr⁻¹ the average Mn contents do cluster within a relatively narrow range between 10.7 and 15.6 at.%.

We plotted (Fig. 9B) our data on earlier results presented by Broecker and Liu (2001) by converting our results to oxide wt%. The mean Mn contents in the varnish from our sampling sites across the 30–120 mm yr⁻¹ are 9.2–13.9 wt%. These mean values fall almost entirely within 1 σ on the annual rainfall–Mn content line predicted by Broecker and Liu (Fig. 9B), although within the 9.2–13.9 wt% they have a wide spread. As our data clusters around the trend-line and is within the 1 σ , the correlation for the combined data slightly increases to $r^2 = 0.54$ from $r^2 = 0.46$ in Broecker and Liu's plot (2001). The combined results across a wide rainfall range, including non-desert regions, point to a higher Mn content with increasing rainfall amounts, but annual rainfall explains only ~50% of the Mn variance in the combined data (see also discussion by Broecker and Liu, 2001, p.8.). Annual rainfall from our eight sites (30–120 mm yr⁻¹) is within the range of this scatter, which may explain the absence of a significant dependence on rainfall in our data alone (Fig. 9A).

To evaluate whether rainfall amounts affect the amount of varnish material accumulated within the micro-basins, we used the calculated total volume of the accumulated material plotted vs. rainfall amounts. A positive exponential correlation ($r^2 = 0.6$) exists between the two (Fig. 8B). This suggests that the mean annual rainfall affects, to some extent, the amount of accumulated varnish sediment.

What controls Mn content in the varnish?

Neither the chemical content of the dust nor the size of the micro-basins can explain the Mn content in the varnish. For Mn to become mobile and for varnish to form, moisture must be present. Annual rainfall explains only ~50% of the Mn variance; therefore, other moisture must contribute to the Mn content. Here we propose that the amount of wetting events and not the mean annual rainfall might be the main variable controlling the Mn content in the varnish (see also Farr and Adams, 1984).

Table 3

Accumulated varnish material. Where c stands for half ellipsoid ($2/3 \cdot \pi \cdot m_1 \cdot m_2 \cdot m_3$), ce stands for an elliptical surface with a cylindrical shape ($1/3 \cdot \pi \cdot m_1 \cdot m_2 \cdot m_3$) and m_1, m_2, m_3 represent the different radii of the shape. The average Mn from each sample is stated in the right column.

Site	Shape	m1 (μm)	m2 (μm)	m3 (μm)	Vol (mm^3)	Mn (% atom)
NB10	ce	220	85	48	0.94	11.9
NE9	e	150	125	30	1.18	12.4
NE11_2	e	125	125	50	1.64	13.5
NE11_3	ce	125	125	42	0.69	14.8
NH6	e	85	90	30	0.48	11.5
NH7	ce	130	100	36	0.49	12.5
LE8	ce	100	100	39	0.82	13.3
DIV7	e	90	100	20	0.38	11.6
MM8	ce	75	40	22	0.14	12.0
BA3	ce	75	85	42	0.28	12.8
NK11_2	e	80	50	42	0.35	15.5

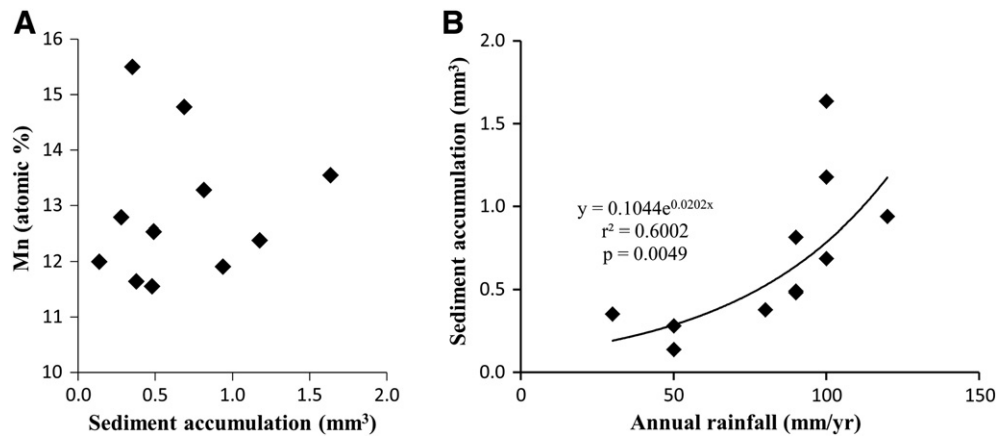


Figure 8. A) Volume of accumulated varnish material vs. Mn content, showing that there is no correlation between the two. B) Volume of accumulated varnish in micro-basins vs. annual rainfall.

An additional moisture source other than rain affecting the Mn content in the varnish was proposed by Broecker and Liu (2001). They claimed that due to a non-zero y-intercept of the trend line in Figure 9B (i.e. MnO ~9 oxide wt%, when rainfall is zero) moisture sources other than rainfall must affect Mn accumulation in the varnish. In this work, we extended the minimum rainfall range from 50 mm yr⁻¹ in Broecker and Liu (2001) to 30 mm yr⁻¹, where the mean Mn value is 10–11 wt%, thus strengthening Broecker and Liu's claim. If moisture is actually the main control on Mn accumulation in the varnish, then in the Negev, dew and light rain are the most plausible additional sources of moisture. Out of ~200 wetting days/yr in the Negev highlands, 160 days are the result of dew (Zangvil, 1996), 30 days are the result of light rain (<1 mm), and only 10 days have rainfall >1 mm (Fig. 10). The 10 individual large rainfall events contribute ~75% of the total depth of cumulative annual rainfall (Fig. 10). Thus, the majority of wetting events are not sufficiently represented by the mean annual rainfall depth data. If dew and light rain are sufficient to form varnish, then the number of wetting events (primarily dew events) are the important factor controlling the Mn content in the varnish and not the annual rainfall.

The Mn content of all Negev samples is close to the y-intercept in Figure 9B (i.e. the mean Mn values in our samples are ~11 oxide wt%,

a value very close to the 9% intercept). If we take the moisture-control assertion a step further, it seems that approximately 80% of the total Mn content in our Negev samples could have formed by dew or light rain, and only approximately 20% by the majority of rain that falls during a small number of days. These results reinforce the significant effect of dew and light rain on the Mn content in the varnish.

If the number of moisture events and not annual rainfall amounts affect the Mn content in the varnish, then this might explain why rainfall amounts in our and Broecker and Liu (2001) results explain only ~50% of the variance (Fig. 9B). To test this assumption, rigorous direct measurements of dew amounts are needed; unfortunately, these are very limited in the Negev (or other deserts). Therefore, at this point, it is not possible to directly test the relation between Mn content in the varnish and dew amounts.

Conclusions

We systematically sampled and investigated the chemistry of rock varnish that accumulated in micro-basins since the early Holocene on flint artifacts. The artifacts were sampled along a north–south annual

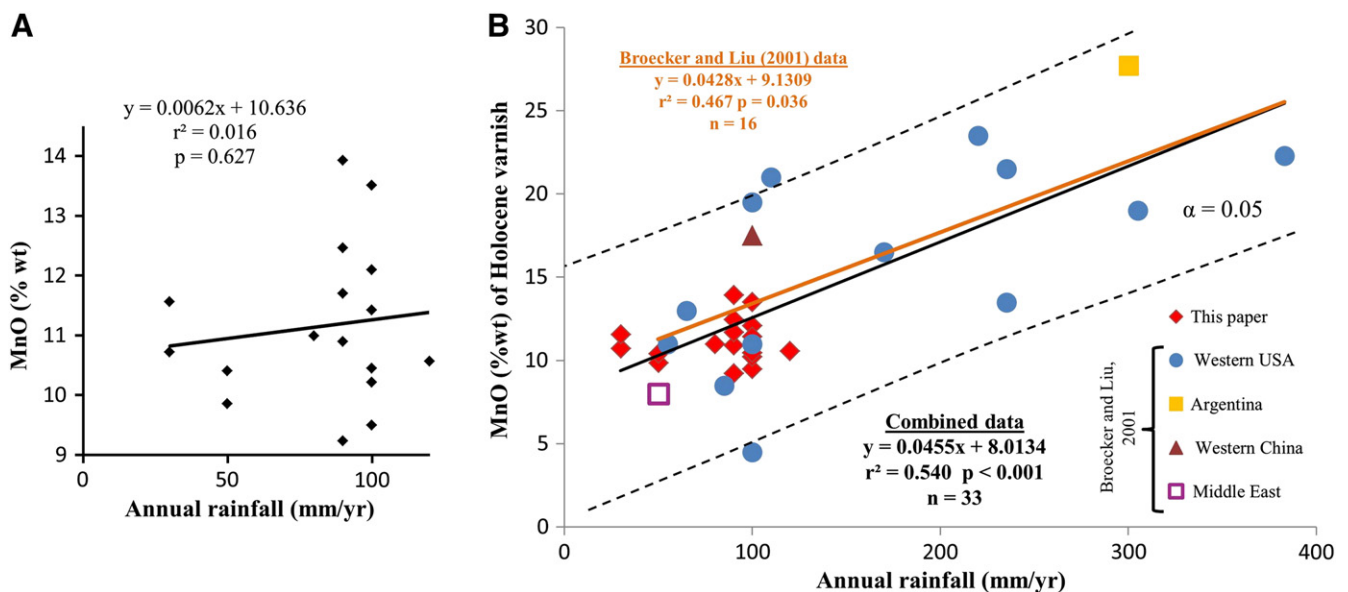


Figure 9. A) Current research results of average MnO content as a function of annual rainfall (mm/yr). B) A plot of MnO (wt%) as a function of annual rainfall (after Broecker and Liu, 2001). The red points are our data; the rest are data collected by Broecker and Liu (2001). The orange line ($R^2 = 0.467$) is calculated from Broecker and Liu's data. The black line ($R^2 = 0.540$) is for Broecker and Liu's data together with ours. The dashed lines represent $\pm 1\sigma$ around the black trend line (combined data).

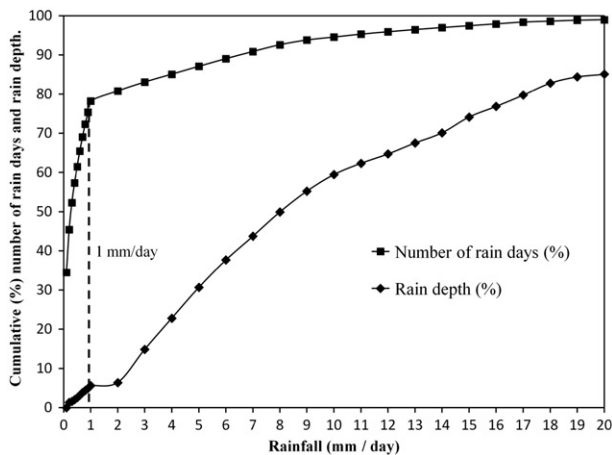


Figure 10. Cumulative percentages of total rainfall depth and number of rainfall days for 56 yr (1952–2008) in Sde Boker. This figure emphasizes the large number of light rain days (~80%) that have little effect on the total depth of rainfall in Sde Boker: i.e. all days with ≤ 1 mm are $<10\%$ of the total rainfall depth in Sde Boker over the 56 yr record but are ~75% of the wetting events.

rainfall transect, ranging between 120 and 30 mm yr⁻¹. The main results are as follows:

- The Negev rock varnish is composed mainly of clay minerals with a two-order of magnitude enrichment of Mn relative to the chemical composition of the fine-grain mode ($<20 \mu\text{m}$) of local settling dust. The concentrations of all other elements composing the varnish (e.g. Si, Al, and Fe) mimic the fine-grain fraction composition of the settling dust. The chemical content of the major elements in the varnish is a product of selective geochemical processes that seem to be operating primarily on the Mn and not on the Fe.
- Over the past ~10 ka the varnish displays 4–6 distinct peaks in the concentration of Mn, Si and Fe, regardless of the local annual rainfall amounts, dust chemistry, or micro-basin size. This may indicate that the fluctuations in chemical content of the varnish portray a regional pattern.
- In all the Negev samples, the Mn content in the outer yellow lamina is enriched from 0% at the outermost surface to ~10% at depth of ~5 μm , regardless of current local rainfall amounts. Earlier studies used this Mn-poor yellow-colored outer lamina as the basis for associating lamina color sequence with changing climate conditions. Our data indicate that the outer yellow lamina is most probably the result of an ongoing internal mechanism of varnish formation unrelated directly to mean annual rainfall amounts.
- Each of the varnish profiles showed laminae with higher Mn content that formed during the Holocene below this outermost lamina, across the range of regional annual rainfall of 30–120 mm.
- The average accumulation rates of Mn and sediment accretion show, respectively, linear and exponential positive correlations with annual rainfall amounts. Moisture seems to affect the rate of clay-mineral accretion more than the rate of Mn accumulation.
- The correlation between Mn content and annual rainfall is currently not strong enough to rigorously use varnish data as an annual rainfall recorder in the Negev. Though, if the main parameter controlling Mn accumulation is the amount of moisture days, then the correlation to annual rainfall amounts might be misleading as the amount of dew days is not represented. Therefore, only more rigorous dew measurements will help determine whether rock varnish can serve as a recorder of the amount of paleomoisture events.

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