

ROCK VARNISH CATION-RATIOS MAY NOT BE A RELIABLE METHOD FOR DATING LITHIC ARTIFACTS

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ABSTRACT

Previous research suggested that the chemical composition of rock varnish, a micrometer thick Si/Al/Mn/Fe coating, changed predictably through time and so could be used as a chronometer. In particular, the cation ratio, $(Ca+K)/Ti$, was posited to decrease as the varnish aged. However, many earlier varnish studies were not well documented and were based on chemical analyses now shown to be inaccurate.

This paper describes a test and the first direct comparison between two different analytic methods used previously to "cation-ratio date" archeologic and geologic materials. It provides methodology sufficiently detailed for replication of analytical and sampling techniques.

Our analyses of rock varnish from a prehistoric chert quarry in California show that the two principal methods used to "cation-ratio date" rock varnish generate consistently different elemental abundances and are therefore not comparable. Neither analytic method produced a significant time-dependent trend in varnish chemistry, suggesting rock varnish cation ratios are not a reproducible and thus probably not a reliable way to date lithic artifacts.

INTRODUCTION

Rock varnish is found most commonly on exposed rock surfaces in arid regions. It is a thin ($<200 \mu\text{m}$) coating made up predominately of Si, Al, Mn, and Fe. There is general agreement that the bulk of the varnish is derived not from the underlying substrate but from dust falling on the rock surface. There is evidence that microbes are an important factor in the concentration of Fe and perhaps Mn at abundances far greater than those in the ambient dust flux [1].

Rock Varnish Cation Ratio Dating

Rock varnish could be an important dating tool for archeologists and geologists because it is frequently found in circumstances where other dating methodologies cannot be applied. For instance, varnished artifacts are often found on the land surface with no stratigraphic context to constrain their age and many geologic deposits are not amenable to ^{14}C or K/Ar dating because of their age or composition.

It has been suggested that the chemistry of rock varnish changes predictably through time [2-4]. Specifically, the varnish cation ratio, $(K+Ca)/Ti$, appears to decrease as the age of the varnished rock surface increases. This trend has been calibrated and rock-varnish cation ratios have been used to assign numerical ages to landforms, artifacts, and rock art (see review in [3]).

There is no agreement regarding the cause of previously observed cation-ratio changes. Some [3-5] attribute the apparent time-dependent decrease in cation ratios to leaching of more "mobile" Ca and K. Others [6] find no evidence of such cation leaching and suggest that the observed decrease in cation ratios is due to inadvertent contamination of varnish analyses by the underlying rock substrate. To test these hypotheses, we specifically analyzed varnish on a chert (Si-rich, Ti-/Ca-/K-poor) substrate.

Recent publications have questioned not only the cause of reported cation-ratio changes, but their veracity. For example, many published rock-varnish chemical analyses and resultant cation ratios have been shown to be inaccurate [7, 8]. The assumption that micron-thick varnish and the underlying substrate remain stable for hundreds of thousands to millions of years is commonly not valid [9]. There are significant flaws in prior varnish sampling strategies [10] and simple statistical tests show that many archeologic conclusions previously drawn from varnish data may not be robust [11,12].

Methods Used Previously for Varnish Analysis

Most rock varnish analyses used for cation ratio dating have been conducted by one of two methods: in situ analysis or analysis of varnish scraped from the underlying substrate. In situ analysis of varnished surfaces has been done primarily by SEM/EDS [2] and PIXE/EDS [13]. Analysis of scraped samples has been done primarily by PIXE and ICP [3].

Although proponents of each method claim it minimizes the incorporation of substrate in varnish analyses [2, 3], it has not been demonstrated that either method eliminates substrate incorporation. The in situ SEM method is inherently surface biased, analyzing at most the upper few microns of the varnish coating [14]. The scraping method homogenizes the entire varnish coating and analyzes a larger volume of varnish. There is no indication, in the refereed literature, that these two disparate analytic methods have ever been applied to the same varnish sample.

This study applies both the scraping and in situ methods to similar, and in three cases, the same samples. Because the varnish we analyzed coats a chert substrate containing very low levels of Ti, K, and Ca, substrate incorporation probably does not significantly affect the cation ratios we present in this paper.

CA-KER-140 Prehistoric Quarry Site

CA-KER-140 is a Native American quarry site located in the Mojave Desert, south-central California at an elevation between 760 and 820 m (2500 and 2700 feet, Fig. 1, 2, 3). Present vegetation is sparse desert scrub and average yearly precipitation is < 25 cm (10 inches). The site consists of three buttes of predominately dark colored chert (Si-rich) mantled by colluvial debris. There are extensive alluvial fan and colluvial surfaces at the base of the buttes. Chemical analyses show that most of the chert contains <0.15% Ti, Ca, and K, the important components in varnish cation ratio dating (Table 1). Samples for this study were collected from the top of eastern butte because there was a higher density of varnished artifacts on this part of the CA-KER-140 site and because this part of the site was least disturbed by human activity.

The chert bedrock is frequently well-varnished where it crops out, especially on the eastern butte (Fig. 2). Detrital chert fragments on alluvial and colluvial surfaces are less well varnished than the bedrock, but are better varnished than artifacts. Most artifacts have only thin and patchy varnish on the worked or cultural faces and many,

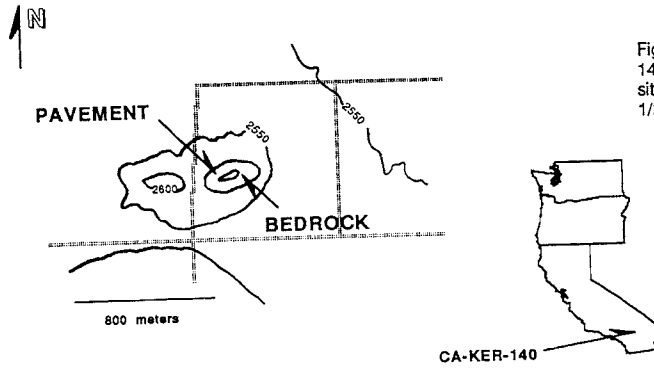


Fig. 1 Location of CA-KER-140 and specific sampling sites (USGS Galileo Hills 7 1/2 minute quadrangle).

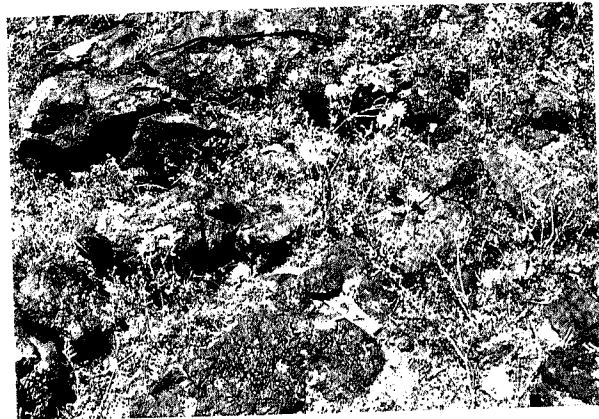


Fig. 2 Heavily varnished bedrock outcrop from which sample 1.04.4 was collected. Labeled tape in center of photograph is about 3 cm wide.

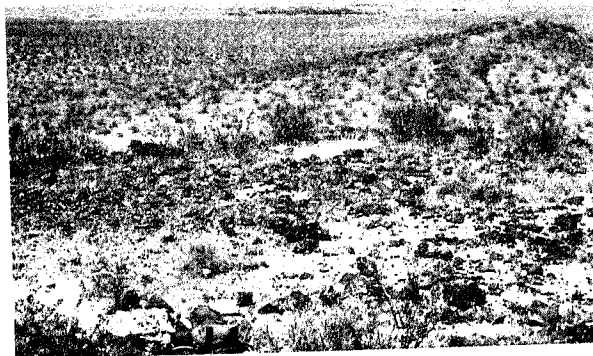


Fig. 3 Desert pavement from which artifacts were collected.

TABLE 1. Summary of Rock Varnish Analyses

Sample	N	Type	(K+Ca)/Ti	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO
<i>In Situ Substrate</i>								
KER-140	36	Mean		94.98 +/- 2.94	0.11 +/- 0.12	2.08 +/- 1.68	1.40 +/- 0.93	0.18 +/- 0.33
Substrate		Median		94.98	0.09	1.82	1.33	0.06
<i>In Situ Varnish Analyses</i>								
1.04.10	10	ROCK	9.51 +/- 1.37	27.27 +/- 2.41	0.37 +/- 0.05	19.38 +/- 1.02	12.45 +/- 0.84	30.39 +/- 3.81
1.04.08	8	ROCK	8.44 +/- 1.65	30.94 +/- 1.23	0.38 +/- 0.09	20.56 +/- 0.99	13.64 +/- 1.17	25.00 +/- 1.40
1.04.04	10	ROCK	9.71 +/- 1.81	30.50 +/- 1.80	0.42 +/- 0.09	17.76 +/- 0.97	11.77 +/- 1.37	28.83 +/- 2.13
1.03.02C	9	NCUL	6.29 +/- 1.30	29.13 +/- 3.64	0.58 +/- 0.13	15.09 +/- 1.84	12.40 +/- 1.81	32.16 +/- 5.69
1.03.02B	9	NCUL	8.21 +/- 1.21	36.79 +/- 3.81	0.55 +/- 0.11	17.54 +/- 1.97	10.98 +/- 2.06	23.47 +/- 6.24
1.03.02A	8	NCUL	7.85 +/- 1.44	32.66 +/- 2.90	0.62 +/- 0.17	16.74 +/- 2.93	13.58 +/- 2.59	26.59 +/- 3.24
1.03.03D,O	9	OMIX	8.20 +/- 1.20	33.43 +/- 4.05	0.53 +/- 0.08	18.07 +/- 1.30	14.49 +/- 1.85	23.71 +/- 2.75
1.03.03I,Y1,O	8	OMIX	16.30 +/- 5.62	34.78 +/- 3.69	0.39 +/- 0.08	9.82 +/- 1.64	4.36 +/- 0.44	34.30 +/- 3.34
1.03.03S,O	8	OMIX	9.95 +/- 1.89	28.59 +/- 3.46	0.44 +/- 0.08	14.87 +/- 1.42	9.03 +/- 0.92	34.43 +/- 3.97
1.03.03I,O	8	OMIX	10.02 +/- 1.72	30.53 +/- 2.76	0.57 +/- 0.10	14.38 +/- 0.96	11.17 +/- 0.78	31.70 +/- 3.07
1.03.03I,Y1	13	YMIX	16.03 +/- 8.85	25.80 +/- 5.22	0.29 +/- 0.09	7.92 +/- 0.62	3.53 +/- 0.41	46.58 +/- 4.32
1.03.03S,Y	10	YMIX	9.39 +/- 2.09	55.92 +/- 9.10	0.35 +/- 0.09	9.79 +/- 1.99	5.15 +/- 1.36	21.39 +/- 4.78
1.03.03I,Y2	10	YMIX	9.61 +/- 1.88	36.71 +/- 6.49	0.31 +/- 0.05	7.06 +/- 1.20	2.99 +/- 0.69	39.41 +/- 4.00
1.03.03D,Y	10	YMIX	15.35 +/- 5.95	43.48 +/- 14.62	0.24 +/- 0.05	3.98 +/- 0.93	2.68 +/- 0.49	42.66 +/- 13.19
1.03.01F	10	CULT	5.39 +/- 0.70	38.30 +/- 8.66	0.42 +/- 0.05	12.73 +/- 1.33	7.77 +/- 0.93	30.08 +/- 7.32
1.03.01E2	10	CULT	13.28 +/- 4.75	47.45 +/- 6.53	0.35 +/- 0.08	14.48 +/- 1.29	6.61 +/- 0.62	20.63 +/- 4.92
1.03.01E1	10	CULT	5.35 +/- 1.63	33.84 +/- 4.54	0.59 +/- 0.18	11.36 +/- 2.41	12.92 +/- 3.71	29.23 +/- 5.30
1.03.01B	13	CULT	8.78 +/- 2.30	39.24 +/- 5.93	0.53 +/- 0.11	15.99 +/- 2.05	8.78 +/- 1.40	24.27 +/- 6.87
1.03.01A2	10	CULT	20.65 +/- 5.33	43.48 +/- 11.56	0.25 +/- 0.05	7.53 +/- 2.00	3.68 +/- 1.01	36.80 +/- 11.03
1.03.01A1	10	CULT	9.81 +/- 1.69	36.44 +/- 13.95	0.41 +/- 0.10	12.66 +/- 1.08	5.40 +/- 0.51	32.09 +/- 10.08
<i>Scraped Varnish Analyses</i>								
1.04.10	9	ROCK	5.48 +/- 0.29	28.90 +/- 1.80	0.79 +/- 0.05	18.09 +/- 1.42	13.26 +/- 1.00	28.58 +/- 0.73
1.04.08	9	ROCK	6.06 +/- 0.55	34.28 +/- 3.11	0.70 +/- 0.05	19.72 +/- 1.68	11.22 +/- 0.73	24.81 +/- 1.06
1.04.04	5	ROCK	5.75 +/- 1.22	29.59 +/- 2.34	0.67 +/- 0.17	15.61 +/- 2.15	9.97 +/- 0.72	34.89 +/- 1.18
1.03.30,O	11	OMIX	5.59 +/- 0.50	28.97 +/- 2.57	0.88 +/- 0.04	16.79 +/- 2.76	11.84 +/- 0.45	28.85 +/- 0.60
1.03.3B,O	11	OMIX	3.79 +/- 0.80	32.85 +/- 1.03	1.08 +/- 0.24	19.03 +/- 0.91	13.05 +/- 0.49	24.54 +/- 0.31
1.03.3F,O	6	OMIX	4.36 +/- 0.45	56.16 +/- 1.09	0.59 +/- 0.05	11.72 +/- 0.51	7.66 +/- 0.23	17.31 +/- 0.59
1.03.02D	11	NCUL	3.98 +/- 0.51	47.81 +/- 4.51	0.73 +/- 0.08	17.11 +/- 1.58	11.60 +/- 1.06	16.41 +/- 1.70
1.03.3F,Y1	7	YMIX	7.34 +/- 0.51	36.69 +/- 1.43	0.65 +/- 0.03	17.15 +/- 0.49	10.74 +/- 0.59	24.63 +/- 0.72
1.03.3B,Y	9	YMIX	4.91 +/- 0.35	43.79 +/- 3.14	0.79 +/- 0.07	15.87 +/- 1.47	8.88 +/- 0.59	22.66 +/- 0.87
1.03.3F,Y2	6	YMIX	8.70 +/- 0.20	33.27 +/- 1.00	0.61 +/- 0.02	16.46 +/- 0.61	8.93 +/- 0.48	29.38 +/- 0.39
1.03.3M,Y	8	YMIX	5.97 +/- 0.44	32.78 +/- 1.71	0.67 +/- 0.02	20.24 +/- 1.52	11.48 +/- 0.55	25.51 +/- 0.59
1.03.03P	13	CULT	6.05 +/- 0.26	38.39 +/- 0.90	0.57 +/- 0.01	19.95 +/- 0.65	9.73 +/- 0.29	23.17 +/- 0.32
<i>Other Varnish</i>								
Potter and Rossman, 1979		on Andesite		21.89	1.07	21.13	23.67	16.63
Potter and Rossman, 1979		on Quartz		36.83	0.93	21.56	18.87	13.70
Potter and Rossman, 1979		on Rhyolite		35.02	0.80	20.40	12.40	23.07
Reneau et al., 1991		on Basalt		28.92	0.89	22.63	24.20	16.96
Reneau et al., 1991		on Granite		37.17	0.71	24.15	12.60	18.70
Reneau et al., 1991		on Rhyolite		37.98	1.01	24.18	17.49	11.17

Note: Type of Sample: ROCK = Bedrock, NCUL = Noncultural, CULT = Cultural
 YMIX = Mixed, young (cultural) surface, OMIX = Mixed, old (noncultural) surface.
 Uncertainties in table are one sample standard deviation about the mean and represent variability in sample or glass.
 Analytic uncertainties (counting statistics) are stated in text

MgO	CaO	Na2O	K2O	BaO	SO3	P2O5
0.34 +/- 0.29 0.27	0.08 +/- 0.24 0.01	0.15 +/- 0.07 0.13	0.05 +/- 0.20 0.01	0.09 +/- 0.12 0.07	0.06 +/- 0.07 0.03	0.43 +/- 0.20 0.35
1.80 +/- 0.22	1.49 +/- 0.18	0.36 +/- 0.04	1.20 +/- 0.10	1.94 +/- 0.42	1.03 +/- 0.20	2.38 +/- 0.30
1.91 +/- 0.12	1.39 +/- 0.28	0.31 +/- 0.06	1.02 +/- 0.05	1.41 +/- 0.20	1.16 +/- 0.15	2.27 +/- 0.23
1.95 +/- 0.13	1.78 +/- 0.22	0.40 +/- 0.05	1.32 +/- 0.10	1.93 +/- 0.46	1.36 +/- 0.25	1.98 +/- 0.19
1.44 +/- 0.18	1.24 +/- 0.10	0.28 +/- 0.04	1.45 +/- 0.12	4.51 +/- 1.11	0.51 +/- 0.17	1.19 +/- 0.22
2.31 +/- 0.35	1.61 +/- 0.21	0.41 +/- 0.07	1.81 +/- 0.27	3.48 +/- 1.59	0.30 +/- 0.06	0.73 +/- 0.05
2.19 +/- 0.23	2.03 +/- 0.47	0.45 +/- 0.10	1.62 +/- 0.21	1.45 +/- 0.21	0.77 +/- 0.12	1.27 +/- 0.25
1.84 +/- 0.10	2.04 +/- 0.33	0.25 +/- 0.05	1.32 +/- 0.12	1.40 +/- 0.19	0.58 +/- 0.09	2.30 +/- 0.23
2.12 +/- 0.38	3.86 +/- 1.25	0.34 +/- 0.05	1.04 +/- 0.23	7.66 +/- 0.79	0.23 +/- 0.08	0.94 +/- 0.66
1.82 +/- 0.24	1.89 +/- 0.14	0.42 +/- 0.06	1.44 +/- 0.13	5.15 +/- 1.46	0.66 +/- 0.23	1.25 +/- 0.38
1.91 +/- 0.14	2.74 +/- 0.38	0.39 +/- 0.06	1.67 +/- 0.15	1.82 +/- 0.24	1.33 +/- 0.22	1.77 +/- 0.23
1.55 +/- 0.22	2.50 +/- 0.40	0.29 +/- 0.07	0.73 +/- 0.08	10.38 +/- 1.06	0.13 +/- 0.03	0.28 +/- 0.11
1.79 +/- 0.29	1.08 +/- 0.28	0.40 +/- 0.10	1.35 +/- 0.28	1.94 +/- 1.25	0.15 +/- 0.05	0.44 +/- 0.07
1.34 +/- 0.26	1.68 +/- 0.76	0.36 +/- 0.04	0.73 +/- 0.16	8.68 +/- 0.85	0.21 +/- 0.07	0.35 +/- 0.10
0.91 +/- 0.23	1.28 +/- 0.54	0.49 +/- 0.29	1.44 +/- 0.67	0.88 +/- 0.32	1.20 +/- 0.42	0.64 +/- 0.11
1.47 +/- 0.14	0.76 +/- 0.12	0.36 +/- 0.03	0.98 +/- 0.15	5.64 +/- 1.41	0.36 +/- 0.08	0.93 +/- 0.17
2.40 +/- 0.22	1.69 +/- 0.32	0.36 +/- 0.09	1.62 +/- 0.20	3.61 +/- 1.18	0.14 +/- 0.08	0.48 +/- 0.15
1.25 +/- 0.31	1.08 +/- 0.10	0.29 +/- 0.10	1.18 +/- 0.18	5.71 +/- 1.15	0.66 +/- 0.12	1.70 +/- 0.42
2.19 +/- 0.43	1.59 +/- 0.37	0.30 +/- 0.06	1.91 +/- 0.39	4.40 +/- 1.79	0.12 +/- 0.03	0.56 +/- 0.12
1.34 +/- 0.22	2.33 +/- 0.81	0.50 +/- 0.19	1.66 +/- 0.38	1.23 +/- 1.23	0.64 +/- 0.43	0.52 +/- 0.15
1.84 +/- 0.17	1.43 +/- 0.27	0.32 +/- 0.06	1.58 +/- 0.21	7.03 +/- 3.37	0.19 +/- 0.03	0.41 +/- 0.10
1.48 +/- 0.12	1.88 +/- 0.09	0.09 +/- 0.01	1.51 +/- 0.10	2.97 +/- 0.17	0.11 +/- 0.20	2.33 +/- 0.16
1.78 +/- 0.13	1.77 +/- 0.09	0.13 +/- 0.01	1.52 +/- 0.13	2.36 +/- 0.20	0.13 +/- 0.10	1.78 +/- 0.14
1.11 +/- 0.18	1.54 +/- 0.12	0.14 +/- 0.02	1.34 +/- 0.04	2.42 +/- 0.14	0.37 +/- 0.32	2.34 +/- 0.17
1.46 +/- 0.17	2.40 +/- 0.15	0.12 +/- 0.02	1.50 +/- 0.16	4.14 +/- 0.29	0.02 +/- 0.02	2.02 +/- 0.14
1.73 +/- 0.11	1.50 +/- 0.05	0.16 +/- 0.02	1.53 +/- 0.10	2.62 +/- 0.13	0.12 +/- 0.06	1.79 +/- 0.09
1.22 +/- 0.09	1.38 +/- 0.05	0.09 +/- 0.01	0.65 +/- 0.05	2.42 +/- 0.18	0.04 +/- 0.03	0.79 +/- 0.06
1.57 +/- 0.17	1.26 +/- 0.15	0.16 +/- 0.07	0.99 +/- 0.12	1.03 +/- 0.11	0.06 +/- 0.07	1.28 +/- 0.11
2.01 +/- 0.07	1.79 +/- 0.09	0.11 +/- 0.01	1.94 +/- 0.25	2.96 +/- 0.25	0.08 +/- 0.11	1.24 +/- 0.05
1.81 +/- 0.12	1.36 +/- 0.04	0.22 +/- 0.03	1.62 +/- 0.11	2.20 +/- 0.17	0.05 +/- 0.08	0.74 +/- 0.03
1.66 +/- 0.10	2.72 +/- 0.12	0.08 +/- 0.01	1.50 +/- 0.09	4.25 +/- 0.14	0.13 +/- 0.06	1.00 +/- 0.05
1.82 +/- 0.15	1.65 +/- 0.11	0.10 +/- 0.02	1.48 +/- 0.15	2.14 +/- 0.15	0.14 +/- 0.11	1.99 +/- 0.09
2.22 +/- 0.09	1.04 +/- 0.03	0.08 +/- 0.01	1.60 +/- 0.08	2.56 +/- 0.14	0.06 +/- 0.06	0.62 +/- 0.02
2.21	0.72	0.12	1.36	0.76	NR	2.45
2.90	0.74	0.12	1.84	0.61	NR	1.88
2.48	1.30	0.23	1.93	1.24	NR	1.12
2.10	0.72	0.06	1.55	0.40	0.12	1.45
2.88	0.58	0.08	1.67	1.15	BDL	0.30
3.42	0.80	0.06	2.30	0.32	0.12	1.15

BDL = Below detection limit

NR = Not reported

In situ Na analyses include a machine background of 0.15 to 0.30 % as described in Bierman and Kuehner, 1992.
Analyses have been normalized to 100%.

especially those on the topographically lower sections of the buttes, are smooth and glossy but unvarnished. None of the worked faces had varnish as continuous or well developed as that on non-cultural or bedrock surfaces; this suggests that the varnish on cultural surfaces is the youngest varnish we sampled.

There are desert pavements present both on the summits of the buttes and on the fan surfaces (Fig. 3). These pavements contain a surface layer of stones and artifacts supported by an underlying matrix of silt and clay. The pavements are flat and support only scant vegetation. Recent findings suggest that stones mantling these silt-supported desert pavements float on the surface, increasing the likelihood of continuous subaerial exposure [15, 16].

SAMPLE COLLECTION AND TEST DESIGN

This study was designed to compare the two principal methods of cation ratio dating [2, 3] and to determine, using both methods, whether cation ratios of relatively younger varnish differed systematically from cation ratios of relatively older varnish. Samples were collected from the CA-KER-140 site on June 24 and 25, 1991 by the authors. Samples were assigned identification numbers in the field and were placed in plastic bags for transport. Statistical Research survey teams mapped the locations from which the samples were collected.

We collected subaerially-exposed varnished samples from both bedrock outcrops (Fig. 2) and desert pavements (Fig. 3). All of the samples collected from outcrops were dark and well-varnished and showed no evidence of human-induced flaking (Fig. 2). Bedrock samples were collected from uniformly varnished, gently sloping or flat-lying rock faces. There was no indication that these surfaces had recently eroded or that the varnish on them had not formed subaerially.

From the desert pavement, we collected samples with two types of varnished surfaces, cultural and non-cultural (Fig. 4). Cultural surfaces showed evidence of percussion and had varnish on the fresh or worked face. Non-cultural surfaces had varnished portions which showed no evidence of percussion or working. Some samples we collected had both cultural and non-cultural surfaces, both of which were varnished. We termed these "mixed" samples.

If varnish forms continuously, as suggested by [3, 4], superposition mandates that varnish on worked (cultural) surfaces is younger than varnish on unworked (noncultural) surfaces. Similarly, varnish on exposed bedrock surfaces should be older than varnish on the worked (cultural) material. On "mixed" objects, varnish on the worked (cultural) portion is no older than varnish on the unworked (noncultural) portion. Even if our decision to label a sample "cultural" is in error, a broken face should have an exposure time no longer than a natural face whether or not that break is anthropogenic. The thickness and extent of varnish coverage (bedrock>noncultural>>cultural) support the relative chronology we present and suggest that varnish on bedrock is much older than varnish on artifacts.

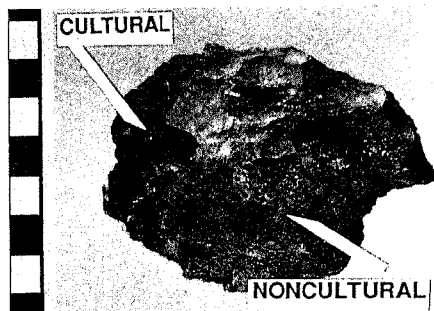


Fig. 4 Mixed sample 1.03.03 I on which cultural and noncultural varnish was analyzed by SEM/EDS. Sampling sites are labeled. Cm intervals on scale bar.

There is an uncertainty intrinsic to dating varnished artifacts which applies both to published studies [17] and to this test. Because most artifacts (and in this study, varnished stones) are relatively small (5-20 cm), they are prone to disturbance on the ground surface. For instance, animals and humans visiting this or any other quarry, kill, or habitation site may have overturned varnished materials exposing previously unexposed, unvarnished sections and burying varnished portions of an artifact.

There is also the possibility that artifacts now exposed on the surface were at some time in the past buried and then exposed by erosion. By selecting samples from desert pavements, where the material is believed to be continuously floated at or near the ground surface [15, 16], we minimized the likelihood that samples were buried and then exposed to the varnishing process long after manufacture.

SAMPLE PREPARATION AND CHEMICAL ANALYSIS METHODS

Samples were returned to the University of Washington, lightly scrubbed with a toothbrush under running water, rinsed in deionized water, and air-dried. Each sample was photographed, measured and described. A subset of samples was selected for chemical analysis based on the certainty with which the cultural and non-cultural surfaces could be identified.

All analyses were performed on a JEOL 733 superprobe equipped with four wavelength-dispersive spectrometers (WDS) and one energy-dispersive spectrometer (EDS). This instrument also functions as a scanning electron microscope (SEM) allowing us to image the sample using both secondary and backscattered electron detectors. All analyses were made using beam stabilization to minimize changes in beam current. Collection of EDS spectra and all data reduction was performed on a Tracor Northern 5500 computer.

In Situ SEM/EDS Analysis

Samples used for in situ SEM/EDS varnish analyses were, if necessary, cut to appropriate size (<4 cm) with a rock saw. These samples were again rinsed in deionized water, air dried, and then carbon coated. In situ analyses of the varnish surface were made during June and July 1991 using SEM/EDS and followed the calibration and analysis protocol detailed in [18]. Spectra were collected for 800-1000 s using a beam current of 15 nA. Uncertainties (1σ , counting statistics only) for each analysis are typically less than < 2 % for Ca, Ba, and K and < 5% for Ti.

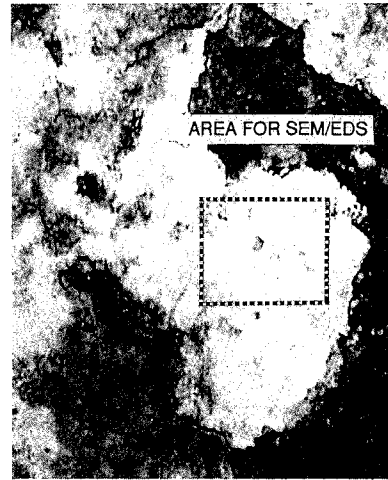
Our SEM/EDS analyses were made by rastering the electron beam using magnifications between 100 x and 3000 x, resulting in areas of varnish being analyzed between 1 and 10^{-3} mm². We chose these high magnifications in order to minimize the amount of substrate incorporated in our analyses. At lower magnifications, we were unable to select areas of varnish that did not include patches of unvarnished substrate. The specific magnification for any one sample was chosen by first scanning the entire sample and then selecting the least magnification at which we could make ten analyses free of visible substrate.

Areas for analysis were selected using both secondary and backscattered electron detectors in order to minimize the amount of substrate included in varnish analyses (Fig. 5). Areas selected for varnish analysis were specifically chosen to avoid exposed rock and microcolonial fungi visible on the varnish surface. Eight to twelve varnish analyses were made on each sample; on most samples, two substrate analyses were also made. For each varnish analysis, we recorded such

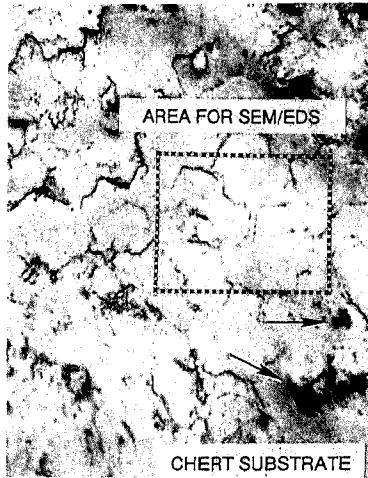
A. CULTURAL (1.03.01)
(BACKSCATTERED ELECTRONS)



B. CULTURAL (1.03.01)
(BACKSCATTERED ELECTRONS)



C. BEDROCK (1.04.10)
(BACKSCATTERED ELECTRONS)



D. BEDROCK (1.04.10)
(SECONDARY ELECTRONS)



Fig. 5

Fig. 5 Scanning electron micrographs of bedrock (1.04.10) and cultural (1.03.01) varnish. Secondary electron images show topography. Backscattered electron images show both topography and average atomic number of material; Fe-, Mn-rich varnish is light and Si-rich chert is dark. A, C, and D show approximately 2 x 2.2 mm of varnish; B shows 0.2 x 0.22 mm. A) Backscattered electron image shows thin, patchy, light colored varnish extending radially over dark gray chert cultural surface. B) Same cultural sample as A magnified 10x shows texture and relative thickness of varnish; thicker varnish is white. SEM/EDS analysis would be conducted in boxed area to minimize substrate contamination. C) Backscattered electron image of varnished bedrock surface shows almost continuous varnish cover compared to A. Outcrops of dark gray chert substrate are indicated by arrows. SEM/EDS analysis would be conducted in the boxed area. D) Secondary electron image of the same area as C shows smooth varnish in center. Furrowed area in lower left-hand corner was scraped for analyses.

characteristics as surface texture, relative brightness of backscattered electron image, and surface topography.

Our SEM/EDS technique differs from that used previously [2, 19] because these workers used lower magnification to analyze larger areas of varnish. Thus, our analyses may include a lesser contribution from substrate than previous in situ measurements, although differences in varnish age and thickness make such a comparison uncertain. Unlike [2] and similar to [19] we made our analyses using a single accelerating voltage, 15 keV.

Scraping and SEM/WDS Analysis

Samples from which the varnish was scraped received the same initial preparation. The varnish was scraped by hand from the chert substrate using a carbide drill bit provided by R.I. Dorn. Scraping was done at various magnifications under a binocular microscope avoiding the few microcolonial fungi that were present. In most cases, the varnish could be removed cleanly from the hard underlying chert. In cases where the underlying chert was weathered, separating the varnish from the substrate was more difficult and resulted in the incorporation of substantial amounts of substrate in varnish scrapings. We used a tweezers to remove visible pieces of chert substrate from the scrapings. Between 10 and 100 mm² of varnish was scraped.

Between 0.5 and 2 mg of varnish scrapings were collected on glassine paper, stored in silver crucibles, and transferred to dimpled 0.013 mm thick molybdenum strips for fusion. Samples were fused, under an argon atmosphere, by passing a current through the strip for 20 s. No flux was used and each strip was used only once. Fusion temperature was probably between 1200 and 1400 °C. The resulting glass was detached from the strip, mounted in epoxy, polished, and carbon-coated.

The fused varnish scrapings were analyzed using SEM/WDS with an accelerating voltage of 15 keV, a beam current of 20 nA, and a beam diameter of 20 µm; Bence-Albee matrix correction was used. Standards and operating conditions are reported in Table 2. Counting time for each element was set at 130 s or 2 % precision, whichever came first. Uncertainties (1σ, counting statistics only) are typically < 2 % for Ca, Ba, Ti, and K for each analysis. Five to ten analyses were made of each glass in order to reduce the dominant uncertainty in the WDS analyses, the inhomogeneity of the fused glasses. Because some of the glasses, especially those high in SiO₂, were quite vesicular, most totals ranged between 85 and 95%.

Accuracy of Analyses

To ensure the accuracy of our analyses, we utilized synthetic varnish standards. Before each analytical session, three varnish standards [8] were each analyzed repeatedly as unknowns. All varnish analyses in this report have been corrected by a factor representing the ratio of the observed and nominal compositions of these standards [8]. All corrections were < 8% (relative) of the reported values; most corrections, including Ti, Ca, and K were < 2% (relative). We believe our SEM/EDS

and WDS analyses are directly comparable because they were corrected to the same three standards, and because surface roughness appears not to bias cation ratios determined with SEM/EDS [18].

To determine whether fusion could affect the composition of varnish samples, the synthetic varnish standards were powdered and fused in a similar fashion to the CA-KER-140 varnish samples. Fusion did not alter significantly the composition of the varnish standards, nor the calculated cation ratios, so fusion presumably did not alter the composition of CA-KER-140 varnish samples.

Raw analytic data were minimally edited. Analyses with low totals (<70%), extremely inhomogeneous glasses, and samples containing extremely large amounts (>60%) of Si (presumably substrate contamination) were omitted before varnish summary statistics were calculated. No analyses were omitted because of Ti, Ca, Ba, or K "anomalies".

DATA AND DISCUSSION

CA-KER-140 varnish is chemically similar to rock varnishes from the American southwest (Table 1), suggesting that our results are probably widely applicable. CA-KER-140 varnish is dominantly Si (30-40%), Mn (20-40%), Al (10-20%), and Fe (5-12%). Ba, K, Mg, P, and Ca are usually present at concentrations between 1 and 3 wt%. Ti, S, and Na are present at concentrations < 1%. The chert substrate is almost exclusively Si (95%) containing only low levels of Fe and Al (1-3%) and Ca, Ti, and K (<0.15%). We report all analyses as oxide weights normalized to 100%.

SEM images support the initial field observation that varnish on cultural (younger) surfaces is both thinner and less extensive than varnish on either bedrock or noncultural surfaces (Fig. 5). Varnish on cultural surfaces appears to be spreading radially away from sites where it first began to form. Because the varnish is thinner and patchier on cultural surfaces, we used higher SEM magnifications to analyze cultural varnishes than we used to analyze noncultural varnishes (Fig. 5). The use of high magnifications explains, at least in part, the higher variance of in situ-measured cation ratios on cultural surfaces. Because analytic uncertainties are only a few percent, the variance in cation ratios reflects intrinsic variability in varnish chemistry.

SEM images show that scraping removed most but not all of the varnish from the scraped areas (Fig. 5). On cultural surfaces, we scraped the entire varnished surface so the mean value reported is the population mean. On noncultural surfaces, we scraped only part of the surface and so the reported mean is that of the subsample we gathered. Because we scraped all the varnish on cultural surfaces, the high variability in scraped cultural varnishes (Fig. 6B) reflects artifact to artifact variability; it is probably not the result of our analytic protocol. Means of scraped samples are less variable than those measured in situ; nevertheless, analysis of scraped samples demonstrates that varnish is chemically heterogeneous on the artifact to artifact scale and that cation ratios and attendant dates are, at best, noisy signals.

Lack of Time Dependence in Cation Ratios

Our data suggest that the in-situ SEM/EDS method is not useful for cation-ratio dating rock varnish on chert substrates at CA-KER-140. In-situ analyses cannot be used to date individual varnished samples because varnish on cultural (young) surfaces had both the highest (20.65 +/- 5.33, 1 σ) and lowest mean cation ratios (5.35 +/- 1.63, 1 σ) (Fig. 6A). Nor can in-situ analyses be used to date populations of CA-KER-140 varnished chert clasts because grand means of all analyses in an age class did not change significantly as a function of relative varnish age (Fig. 7). These findings are supported by the lack of a consistent relationship between cation ratios of relatively older and younger varnish on mixed samples (Table 1).

Similarly, analyses of scraped varnish cannot be used to date individual CA-KER-140 artifacts, because varnish on some cultural (younger) surfaces had cation ratios lower than or equal to that on older noncultural or bedrock surfaces (Fig. 6B).

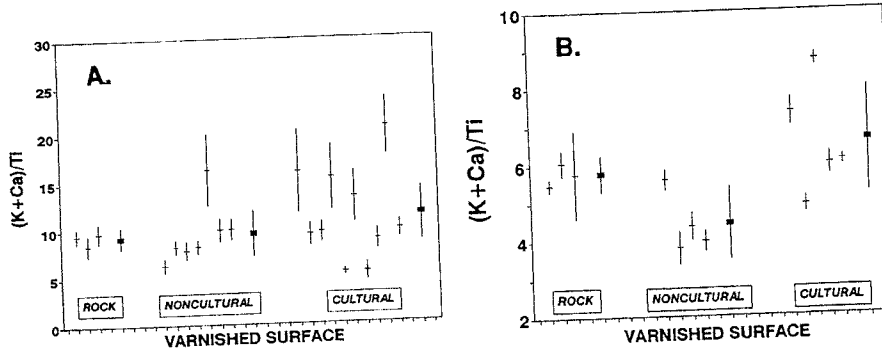


Figure 6. Mean and grand mean cation ratios for individual bedrock, noncultural, and cultural varnish samples analyzed in situ and after scraping. Thin line symbols are means for individual samples. Error bars represent 90% confidence intervals. *Rock* refers to bedrock samples. *Noncultural* refers to both varnish on pieces of unworked rock and to varnish on the unworked cortical portions of mixed samples. *Cultural* refers to both varnish on pieces of worked rock and to varnish on the worked faces of mixed samples. Grand mean for all bedrock, noncultural, and cultural analyses is shown by square with 90% confidence interval about the grand mean shown by error bars. A. In situ varnish. B. Scraped varnish fused into glass.

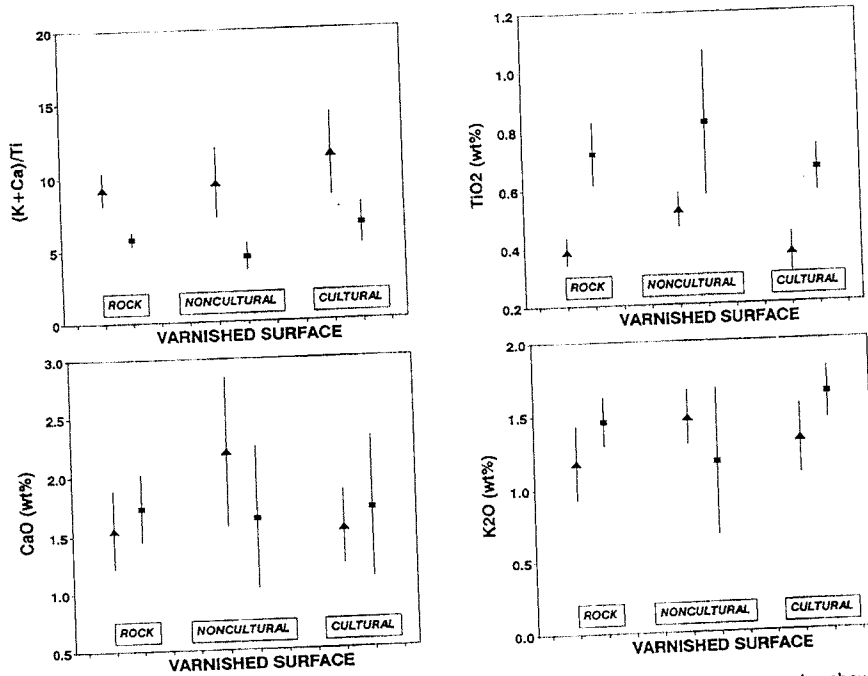


Figure 7. Grand means of Ti, Ca, K, and (K+Ca)/Ti for bedrock, noncultural, and cultural samples show difference between in situ analysis and analysis of varnish scrapings. Uncertainties are 90% confidence intervals. Triangles represent in situ analyses. Squares represent scraped varnish.

Table 2. Protocol for SEM/WDS Analysis

OXIDE	CRYSTAL USED FOR ANALYSIS	BACKGROUND OFFSET (sin θ)	PEAK	STANDARD	CONCENTRATION OF ELEMENT IN STANDARD (WEIGHT %)
SiO ₂	TAP	+/- 0.03929	k α	Basalt Glass	23.28
Na ₂ O	TAP	+/- 0.01786	k α	Albite, Tibron	8.75
Al ₂ O ₃	TAP	+/- 0.03571	k α	Basalt Glass	6.88
MgO	TAP	+0.03571 - 0.03929	k α	Basalt Glass	4.89
P ₂ O ₅	TAP	+0.01429 - 0.01071	k α	Apatite, Wilberforce	17.77
K ₂ O	PET	+0.00571 - 0.00857	k α	Orthoclase, OR-1	12.39
CaO	PET	+0.01429 - 0.02143	k α	Basalt Glass	8.08
TiO ₂	PET	+/- 0.01071	k α	TiO ₂	59.95
BaO	PET	+/- 0.00714	L α	Barite	58.84
Fe ₂ O ₃	LIF	+/- 0.02143	k α	Basalt Glass	8.53
MnO	LIF	+/- 0.02857	k α	Garnet, Nuevo	16.31
SO ₃	TAP	+/- 0.02143	k α , n = 2	Barite	13.73

Nor can analyses of scraped varnish be used to date populations of CA-KER-140 artifacts, reliably. Although the grand mean cation ratio of five cultural (younger) surfaces is marginally higher ($p=0.045$) than the grand mean of four noncultural (older) surfaces, it is not significantly higher than the grand mean of three older bedrock surfaces (Fig. 6B). On both of the mixed samples, cultural (younger) varnish had higher cation ratios than adjacent noncultural (older) varnish. However, one of the cultural (younger) surfaces had a cation ratio (4.91 ± 0.35 , 1σ) lower than the mean for adjacent older bedrock (5.76 ± 0.29 , 1σ) (Table 1 and Fig. 6B).

Comparison of In Situ and Scraping Results

Unless the varnish is extremely thin ($<1 \mu\text{m}$), in-situ and scraping methods sample different levels of the varnish coating. The in-situ SEM method is surface-biased, analyzing only the upper few microns of varnish [14]; the scraping method samples and homogenizes the entire thickness of the varnish. Therefore, measured cation-ratio differences between the two methods most likely reflect varnish thickness and differences in elemental distribution with depth.

Interpreting differences in absolute elemental abundances between the two methods is less certain because substrate (Si) contamination can affect apparent elemental abundance. If the abundance of major elements such as Si and Mn in cultural and non-cultural varnish is similar, then a Si excess or a Mn deficiency would indicate contamination by the chert substrate. For instance, cultural varnish analyzed

in situ appears to contain more Si than noncultural varnish. However, average Mn concentration is similar for cultural and non-cultural varnish. If Mn indicates the degree of contamination, then there is little incorporation of chert substrate and the apparent abundance of other elements in cultural varnish has not been lowered. If Si indicates the amount of substrate contamination, then the abundance we report of other elements in cultural varnish is uniformly 10-30% too low compared with varnish on bedrock surfaces. In either case, substrate incorporation will not affect cation ratios because there is little Ti, Ca, and K in the chert.

Cation ratios measured on scraped varnishes were consistently and significantly lower than those measured in situ (Fig. 7), suggesting that deeper layers of CA-KER-140 varnish have lower cation ratios. Since the concentrations of K and Ca measured by both methods did not differ significantly, the difference in cation ratios appears to be caused by the presence of >50% more Ti at depth than in the upper microns of varnish (Fig. 7). The inference that Ti is not uniformly distributed in varnish could imply variable rates of Ti input or incorporation or it could imply a previously unrecognized diagenetic process. This finding has not been reported before although other studies have found Ti-rich bands of detritus within varnish [20, 21]. Our findings could be explained by the presence of Ti-rich layers below the surface of CA-KER-140 varnish; layers which are too deep to be detected by in situ SEM/EDS measurements.

Cause of Previously Reported Cation-Ratio Variations

Our data suggest that substrate contamination could be a more important factor than cation leaching in previously reported cation-ratio variations because: 1) Cation ratios for varnish on CA-KER-140 chert, which contains little Ti, Ca, or K, show no consistent change corresponding to relative age. 2) Neither in-situ nor scraped varnish analyses shows a consistent and significant decrease in K or Ca with increasing relative age. 3) Comparison of in-situ and scraped varnish suggests that Ti is more abundant but K and Ca are not depleted in deeper, presumably older CA-KER-140 varnish.

CONCLUSIONS

This study used two previously proposed techniques [2, 3] to analyze the chemical composition of rock varnish at the CA-KER-140 site in the Mojave Desert, CA. The study was specifically designed both to compare and test the utility, for dating lithic artifacts, of these two cation ratio methods. Our study showed the following:

1. The composition of rock varnish at the CA-KER-140 site is similar to that of other arid-region rock varnishes. CA-KER-140 varnish is predominately Si, Al, Fe, and Mn with lesser amounts of P, Ba, Ca, K, and Mg and trace levels of Ti, Na, and S. Because the chert substrate is almost entirely Si, its incorporation should not significantly affect the varnish cation ratio, $(Ca+K)/Ti$.

2. Cation ratios determined from analysis of scraped varnish [3] and from analysis of in situ varnish [2] are significantly different indicating that these two previously proposed analytic and dating techniques are not sampling the same populations and are not directly comparable at CA-KER-140. Cation ratios measured in situ were consistently higher than those measured in scraped varnish.

3. Varnish on artifacts showed great variance in composition and cation ratios suggesting such scatter is an intrinsic characteristic of varnished artifacts from the KER 140 site and precluding simple or meaningful chronologic interpretation of cation ratio measurements.

4. Neither scraped nor in-situ analyses of varnished rock from the CA-KER-140 site show cation ratios changing predictably and consistently with time, as would be expected if rock-varnish cation ratios were a consistently reliable dating tool.

Considered along with other recent findings [6-12] these data suggest that rock-varnish cation ratios provide neither a well understood nor a consistently reproducible basis for dating subaerially exposed lithic artifacts.

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