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SCANNING ELECTRON MICROSCOPIC ANALYSIS OF ROCK VARNISH CHEMISTRY FOR CATION-RATIO DATING: AN EXAMINATION OF ELECTRON BEAM PENETRATION DEPTHS

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Abstract

Rock varnish is a microns-thick manganese- and iron-rich coating that forms on exposed rock surfaces in arid and semi-arid environments, and empirical correlations of the varnish cation ratio (K+Ca):Ti with age have been used to estimate ages of geomorphic surfaces. One method of obtaining varnish chemistry for cation-ratio dating involves scanning electron microscope (SEM) energy dispersive x-ray (EDX) analysis of natural varnish surfaces. The chemical analyses of rock varnish with SEM/EDX utilize a sequence of accelerating voltages to vary penetration depths into the sample. Using elemental x-ray maps of natural varnish surfaces obtained by SEM/EDX analysis, penetration into the substrate can be recognized at accelerating voltages where contamination with substrate is inferred from SEM/EDX chemical analyses, illustrating the ability of the SEM method to obtain varnish chemistry with minimal inclusion of substrate. Calculations of theoretical x-ray depth-distribution ($\phi(\rho z)$) curves in varnish indicate that at an accelerating voltage of 10 kV most of the emitted x-rays are generated in the upper 0.5 μm of a sample. At a higher voltage of 30 kV most of the signal is still restricted to the upper 2 μm , representing a very small percentage of total varnish volume in many cases. The ability of the SEM method to obtain empirical correlations of the chemistry of the uppermost varnish with varnish age suggests that it is not necessary to average the entire varnish coat, and that surface-biased varnish analyses provide similar results as bulk varnish analyses.

KEY WORDS: Scanning Electron Microscopy, Rock Varnish, Cation-Ratio Dating, X-ray Maps, X-ray Depth-Distribution Curves

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Introduction

Rock varnish is a microns-thick coating, composed primarily of manganese and iron oxides and clay minerals, that forms on exposed rock surfaces in arid and semi-arid environments. The varnish constituents are believed to be derived from eolian fallout and not from the underlying rock, with great enrichment in Mn relative to ambient levels in dust (e.g., Potter and Rossman, 1977, 1979; Perry and Adams, 1978; Dorn and Oberlander, 1981, 1982). Chemical composition is heterogeneous with depth, and examination of varnish cross-sections reveals that distinct layers are often present that may be relatively enriched in Mn and Fe oxides or Si- and Al-rich detritus (Fig. 1; see also Raymond et al., 1991, this issue).

Rock varnish chemical analyses have been used to estimate ages of a variety of geomorphic surfaces. Dorn and Oberlander (1981) originally proposed that an empirical correlation exists between a ratio of the cations (K+Ca):Ti in rock varnish and varnish age. They proposed that this cation ratio decreases with varnish age due to depletion of relatively mobile K and Ca ions as compared to relatively immobile Ti ions. The cation-ratio rock varnish dating method was further developed by Dorn (1983; see Dorn, 1989, for a recent discussion). Dorn uses proton-induced x-ray emission (PIXE) to analyze bulk chemistry of varnish samples scraped from the underlying rock. He attempts to minimize contamination with scraped substrate in part by removing visible rock fragments during examination under a binocular microscope.

An alternative method of analyzing varnish chemistry was proposed by Harrington and Whitney (1987). Their method involves scanning electron microscope (SEM) energy dispersive x-ray (EDX) analyses of natural varnish surfaces, with the penetration depth of the electron beam varied by varying the accelerating voltage. An important aspect of the SEM method for analyzing natural varnish surfaces is the recognition and rejection of analyses that incorporate a significant amount of substrate. As discussed by Harrington and Whitney (1987), each selected area on a varnish surface is analyzed at a sequence of accelerating voltages, and

significant penetration into the underlying rock is inferred at voltages where the analyses show that elements much more abundant in varnish, such as Mn, decrease, or where elements more common in the rock increase. However, because of variations in varnish thickness associated with substrate roughness and stratigraphic variations in varnish chemistry, such interpretations may not always be straightforward.

The purpose of this paper is to explore the relationships between surface analyses of rock varnish at varying accelerating voltages and the variable thickness and chemistry of varnish. We first present SEM/EDX maps of natural varnish surfaces, acquired at a sequence of voltages, and accompanying chemical analyses to illustrate penetration through the varnish into the underlying substrate. We then present calculated depth-distribution curves for emitted x-rays in varnish to evaluate the thickness of varnish being analyzed and variations in this thickness for different elements.

Materials and Methods

Rock varnishes discussed in this paper were collected from several sites in southern Nevada and northern Arizona, with the darkest, smoothest varnishes sampled from each locale. Sample preparation involved coring 2-cm diameter disks for analyses of natural varnish surfaces, and preparing thin sections for analyses of the chemistry through vertical cross-sections. All samples were carbon-coated before analysis.

Analyses of rock varnishes were performed with an ISI-D130 SEM equipped with a Tracor Northern Series 2 EDX analytical system and with a Cameca MBX electron probe microanalyzer (EPM) equipped with a wavelength dispersive x-ray (WDX) analytical system. X-ray maps of varnish surfaces were acquired on the SEM using Tracor Northern's EDX mapping program, and chemical analyses on the SEM utilized Tracor Northern's semi-quantitative SQ program based on internal elemental references and incorporating a ZAF matrix correction. The SEM analyses using SQ provide normalized elemental compositions and are used in this paper to compare relative elemental concentrations at different accelerating voltages. Estimates of average chemical composition of several varnish cross-sections were acquired on the EPM with the Sandia TASK8: A Subroutined Electron Microprobe Automation System program (Chambers, 1985), which incorporates a Bence-Albee matrix correction and calculates water by difference. The SEM analyses and theoretical calculations were restricted to accelerating voltages of 10-30 kV because excitation efficiencies for the elements of interest in varnish are optimum at these voltages.

Theoretical x-ray depth-distribution curves, also called $\phi(\rho z)$ curves, were obtained for eight elements of interest in rock varnish using the program PRZ85, developed by J. Doyle and based on the work of Bastin et al. (1984). The term $\phi(\rho z)$ refers to x-ray distributions calculated as a function, ϕ , of sample density, ρ , and

depth, z . Bastin et al. (1984) modified equations that had been previously developed to obtain this function, improving the agreement between theoretical $\phi(\rho z)$ curves and EPM data. The PRZ85 program calculates the intensity of both generated and emitted x-rays at a series of levels in a sample. The number and spacing of these levels, together with the sample composition and density, the accelerating voltage of the analysis, and the x-ray line of interest, are specified by the user.

Results

X-ray Maps

Elemental x-ray maps of natural rock varnish surfaces, acquired at a sequence of accelerating voltages, can display variations in sample composition with depth. By comparing maps of elements more abundant in varnish or in the substrate, areas of thinnest varnish can be identified and x-ray emission from the underlying substrate can be documented. X-ray maps of K and Mn distribution from varnish sample EYM-E, a K-rich ash-flow tuff, are shown here as a representative example.

At an accelerating voltage of 10 kV the distributions of Mn and K are fairly uniform (Figs. 2a, b), indicating that the x-rays are being emitted from material that is spatially uniform in composition. The x-ray maps acquired at 15 kV (not shown) display similar uniform distributions. With increased accelerating voltages of 20 and 30 kV, the areas of thinnest varnish can be identified by a reduction in relative Mn concentration (black areas) and by an increase in relative K concentration (bright areas), the result of significant x-ray emission from the underlying rock (Figs. 2c-f). Si x-ray maps for this area (not shown) have the same patterns as K, consistent with the higher Si content in the substrate than in the varnish.

An examination of a backscattered electron image of the same area (Fig. 2g) indicates that the thinnest varnish (highest K, lowest Mn) generally occurs on micro-topographic highs, which is consistent with observations of varnish cross-sections. Calculations discussed in the next section suggest that the varnish shown in Fig. 2 is on the order of 1- μm thick on these highs. However, varnish thickness is extremely variable, and some of the highs in Fig. 2b do not show the same high-K low-Mn concentrations on the x-ray maps. Thicknesses may reach 3-5 μm or more on these highs, still much thinner than in many depressions (often 50-100 μm or more) but thick enough so that the substrate is not clearly contributing to the analysis. Similarly, varnish is locally thin off the highs, and some high-K low-Mn spots are not on highs.

Chemical analyses for the area of rock varnish shown in Fig. 2, also acquired at a sequence of accelerating voltages (Table 1), are consistent with the incorporation of substrate into the analyses at voltages where areas of rock are recognized in the x-ray maps. At accelerating voltages greater than 15 kV, concentrations of K and Si increase as the analyses incorporate an

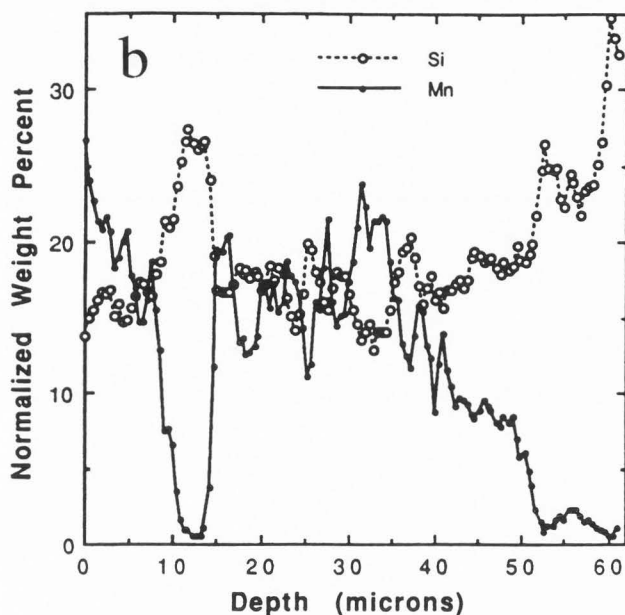
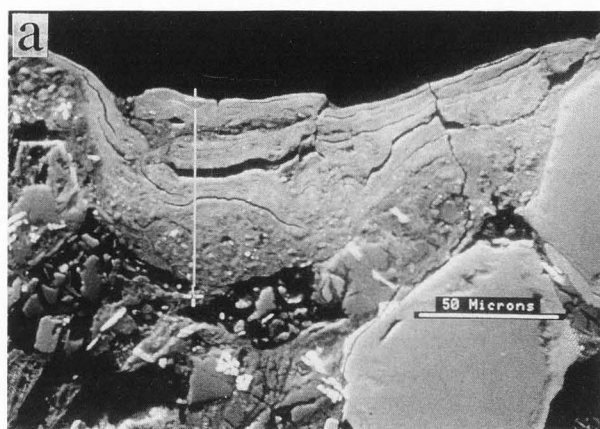


Figure 1. a) Photograph of 65- μm thick rock varnish in depression. Upper varnish is relatively Mn-rich, while lower varnish contains abundant detritus. Sample CM3-112 collected from the Cima volcanic field, California. White line in photograph indicates position of elemental line profile in Fig. 1b. Black areas within the varnish are cracks. Bar = 50 μm . b) Elemental line profiles of Mn and Si through same varnish, showing Si-rich detrital layers contrasting with Mn-rich layers. Line profile collected with the program SQ at 15 kV and with a 100 s counting time. Weight percents are normalized to 100%.

increasing volume of material and, presumably, progressively more substrate. The variation in the chemical analyses at 10-20 kV (Table 1) also reflects changes in rock varnish chemistry with depth. The chemical analyses show that this sample has a Fe-rich, Mn-poor surface layer relative to deeper layers of the varnish, which re-

Table 1. Normalized elemental weight percent at varying kV for sample EYM-3.¹

Element	10 kV	15 kV	20 kV	25 kV	30 kV	\pm^2
K	1.37	1.33	1.41	1.55	1.59	2.5%
Ca	0.56	0.47	0.42	0.41	0.35	7.6%
Ti	0.62	0.56	0.55	0.51	0.50	9.3%
Ba	BDL	0.34	0.27	0.30	0.25	34.1%
Mg	0.64	0.84	0.87	0.69	0.73	12.2%
Al	7.68	7.94	8.12	8.07	8.26	2.3%
Si	16.02	15.58	15.83	16.71	17.21	1.1%
P	0.72	0.98	0.69	0.61	0.81	12.2%
S	0.46	0.50	0.50	0.51	0.36	20.4%
Mn	12.06	13.63	14.11	14.06	13.25	1.8%
Fe	19.80	17.68	17.02	16.37	15.53	1.8%

¹ Data acquired on SEM with SQ program. 200 s counting time. BDL = below detection limit.

² Mean of analytical uncertainty for each element, based on counting statistics. Uncertainty typically least at 15-20 kV.

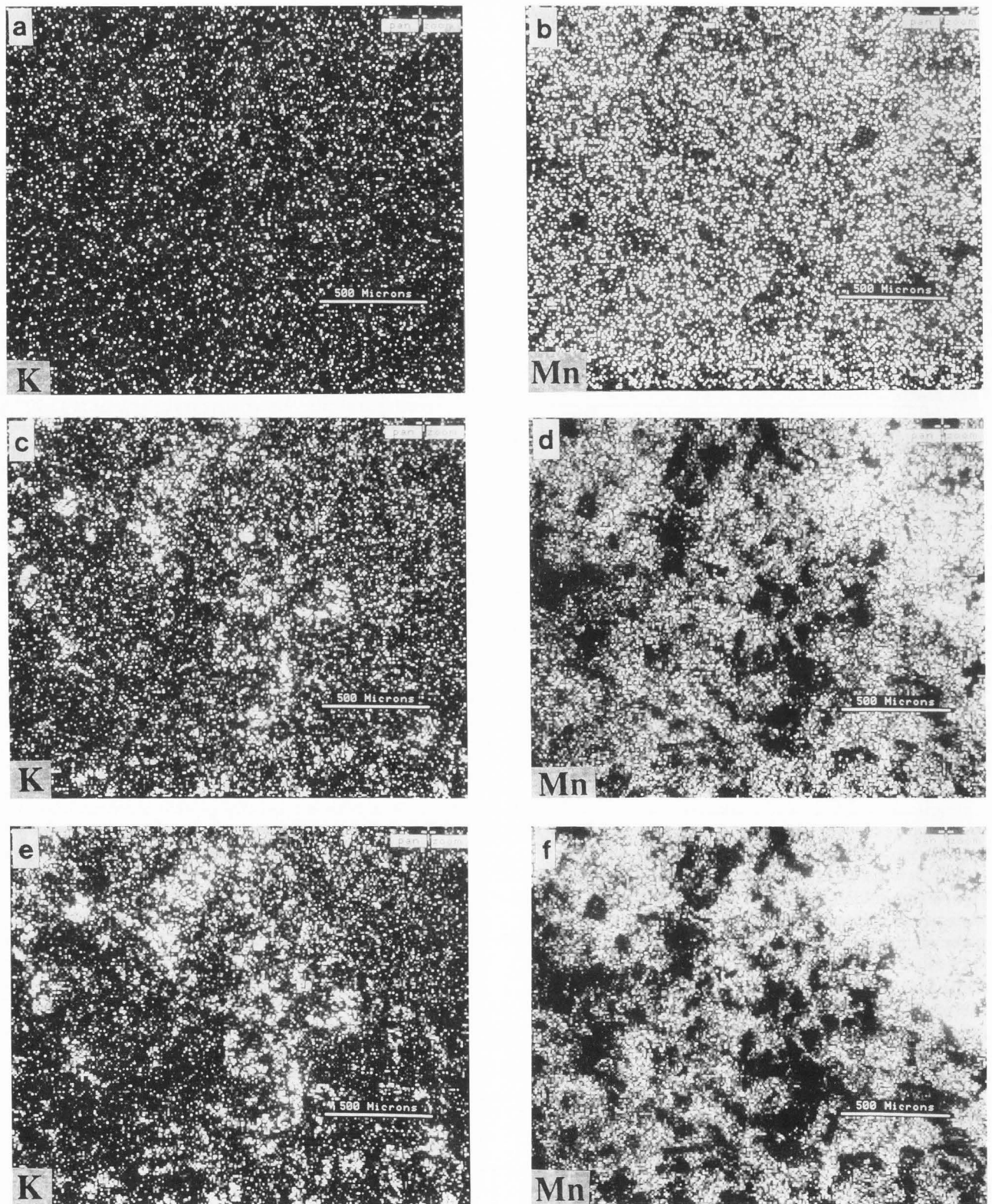
sults in an increase in Mn concentration and a decrease in Fe concentration as the accelerating voltage is increased from 10 to 20 kV. Similar surface layers relatively Fe-rich and Mn-poor have been identified in many varnish cross-sections. Significantly, the peak in Mn concentration at 20-25 kV (Table 1) is at voltages where substrate is recognized on the x-ray maps, indicating that Mn concentration alone may be a poor measure of whether the analyses are entirely in varnish.

X-ray Depth-Distribution Curves

Depth-distribution curves of x-ray generation for any element are dependent on the density and the chemical composition of the sample and the accelerating voltage of the electron beam. The influence of these three factors are discussed below in relation to understanding SEM analyses of rock varnish. Although x-ray depth-distribution curves are usually plotted as x-ray intensity versus ρz , or mass-depth, in this paper the ρz axis is replaced by depth alone to allow comparison with observations of varnish thickness as seen in cross-section.

In order to evaluate the effect of sample composition on x-ray depth-distribution curves, several trial calculations were made with the PRZ85 program using average mass absorption coefficients calculated for three varnish samples from southern Nevada and northern Arizona, shown in Table 2, and three additional varnish samples analyzed by Potter and Rossman (1979). The range in mass absorption coefficients resulting from variations in chemistry for these varnish samples results in less than a 1% variation in calculated x-ray generation depth. This indicates that within the compositional range of typical varnishes, variations in varnish chemistry have only a minor effect on calculated x-ray depth-distribution curves.

Sample density is a more important variable controlling the depth of x-ray generation than sample composition. The x-ray generation depth is inversely proportional to the density of the material, with x-ray generation being shallowest in the densest varnish (Fig. 3);



Figures 2a-f. X-ray maps of K (a, c, e) and Mn (b, d, f) concentration in rock varnish acquired at 10 (a, b), 20 (c, d), and 30 kV (e, f). Bright areas identify highest elemental concentrations in each field of view. Bars = 500 μm .

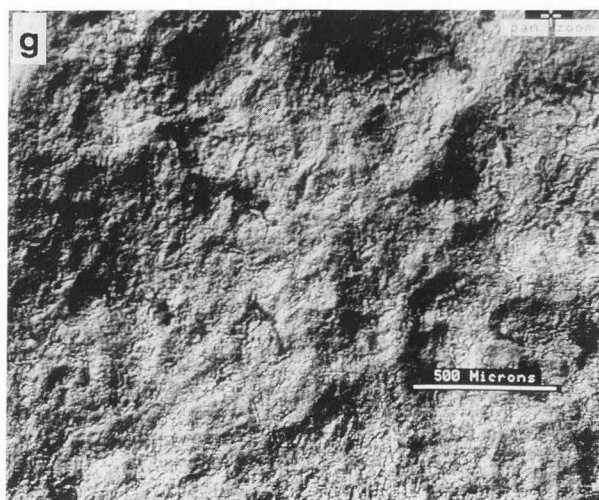


Figure 2g. Backscattered electron image of same area as Figs. 2a-f. Sample EYM-E collected from Yucca Mountain, Nevada. Substrate is an ash-flow tuff.

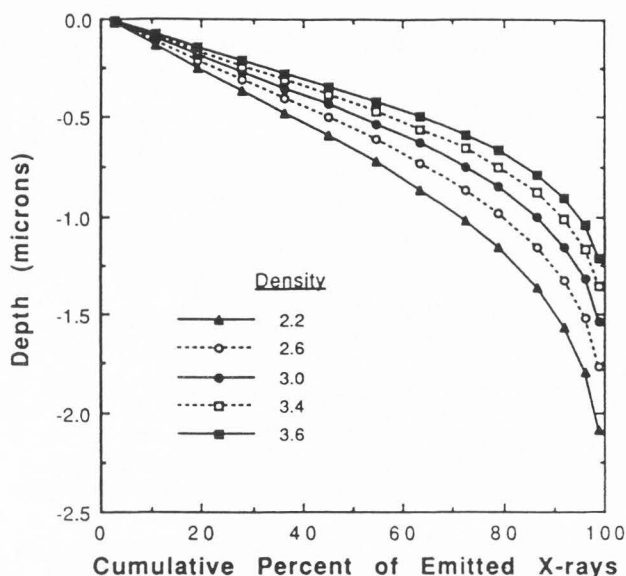


Figure 3. Cumulative depth-distribution curves of emitted K-K α x-rays in a homogeneous rock varnish at an accelerating voltage of 15 kV and a range of potential varnish densities. Average varnish composition used in developing these curves was obtained from 17 separate 200- μm^2 EPM analyses of sample BM-3 (Table 2).

an increase in density of 10% results in a 10% decrease in the depth of x-ray generation. Unfortunately, varnish density is poorly known and probably varies significantly both within a sample and between samples. The highest varnish densities likely occur in areas of low porosity and high Mn and Fe concentration, and the lowest densities in areas of high porosity and low Mn and Fe concentration. Because of uncertainties in varnish density the depth values used in this paper should be considered first

Table 2. Average rock varnish composition.¹

Sample	BM-3 ²	PW3-25 ³	LB10-3 ⁴
K ₂ O	1.32	1.38	1.86
CaO	0.61	0.48	0.65
TiO ₂	0.76	0.59	0.82
BaO	0.34	0.95	0.26
Na ₂ O ₃	0.05	0.07	0.05
MgO	1.78	2.38	2.77
Al ₂ O ₃	19.23	19.94	19.59
SiO ₂	24.57	30.69	30.77
P ₂ O ₅	1.23	0.25	0.93
SO ₃	0.10	BDL	0.10
MnO	14.41	15.44	9.05
FeO	18.52	9.37	12.77
H ₂ O	17.06	18.61	20.39

¹ Values are oxide weight percents. Data acquired on EPM at an accelerating voltage of 15 kV and a beam current of 15 na. BDL = below detection limit.

² Sample collected from Buckboard Mesa near Yucca Mountain, Nevada. Substrate is basalt.

³ Sample collected from Petroglyph Wash near Lake Mead, Arizona. Substrate is of granitic composition.

⁴ Sample collected from Lava Butte near Las Vegas, Nevada. Substrate is rhyodacite.

approximations, to be revised when reliable density measurements are available, although their general magnitudes are accurate.

X-ray depth-distribution curves illustrate the increased depth of electron beam penetration with increased accelerating voltage, and in addition clearly illustrate the surface-bias inherent in SEM and EPM analyses. In the example shown in Fig. 4a, for a theoretical homogeneous varnish, the depth in a sample where the highest percentage of emitted K-K α x-rays (hereafter referred to as K x-rays) are generated increases from about 0.13 μm at an accelerating voltage of 10 kV to about 0.85 μm at 30 kV. Similarly, the 50% level in curves of cumulative x-ray emission (where 50% percent of the emitted signal is generated at or above this depth in the sample) increases from about 0.2 μm at 10 kV to about 1.6 μm at 30 kV (Fig. 4b). The increase in the intensity of x-ray emission with increasing depth in the uppermost part of a sample (Fig. 4a) is due to increased scattering of electrons with depth. The decrease in x-ray emission intensity with depth in the lower part of a sample is due to both the decreased number of electrons reaching each successively deeper level and to the decreased probability that x-rays will escape the sample because of increased absorption.

In a sample of given chemical composition and density, at a given accelerating voltage, each element has a different x-ray depth-distribution curve due to their differing excitation energies. Because of these variations among elements in a sample with a specific average atomic number, analyses for each element are to some degree biased towards different levels (Fig. 5). It

is convenient that the three elements used in cation-ratio dating of rock varnish, K, Ca, and Ti, have similar depth-distribution curves due to their similar excitation energies. However, the lighter elements Al and Si, and the heavier elements Fe and Mn, have significantly different depth-distribution curves. At 10 kV, the 50% level of Si-K α (similar to Al-K α) is about 20% deeper than the 50% level of K (Fig. 5), resulting in a thicker layer of varnish being analyzed for Si than for K (in turn similar to Ca and Ti). In contrast, at low accelerating voltages of 10-15 kV, Mn-K α x-rays (and similarly Fe-K α x-rays) are emitted from significantly shallower depths than K x-rays (Fig. 5), resulting in a thinner layer of varnish being analyzed for Mn at these voltages. The curves for K and Si are similar at 15 kV, whereas at higher accelerating voltages Si x-rays are emitted from progressively shallower depths in relation to K. At 30 kV, the 50% level of Si is only about 60-65% the depth of the 50% level of K. At accelerating voltages of 20-30 kV, the x-ray depth-distribution curves for Mn are similar to those for K (Fig. 5).

The positions of Mn and Si curves at 10 to 30 kV in Fig. 5 invert in relation to K because of a trade-off between the probabilities of x-ray generation and x-ray emission from different depths for each element. When a Mn x-ray is produced, it has a higher energy than a Si x-ray and therefore has a higher probability of reaching the sample surface than a Si x-ray generated at the same depth. However, Si x-rays can be generated from deeper levels than Mn x-rays because of the lower excitation energy of Si. At an accelerating voltage of about 18 kV these effects balance and Si and Mn have similar x-ray depth-distribution curves. In contrast, at lower accelerating voltages the deeper generation of Si x-rays is relatively more important and Si x-rays are thus, on average, emitted from deeper levels than Mn x-rays. At higher voltages the greater energy of Mn x-rays is relatively more important and Mn x-rays are emitted from deeper levels than Si x-rays (Fig. 5).

Conclusions

Chemical analyses of rock varnish using SEM/EDX are strongly surface-biased. At an accelerating voltage of 10 kV most of the emitted x-rays are generated in the upper 0.5 μm of a sample. At a higher accelerating voltage of 30 kV most of the x-rays are still emitted from the upper 2 μm , with only a small percentage of x-rays emitted from depths greater than 5 μm . Rock varnish commonly attains thicknesses much greater than 5 μm , especially in small-scale depressions on rock surfaces. Therefore, SEM/EDX analysis of rock varnish using the method of Harrington and Whitney (1987) consistently samples only the uppermost layers of varnish where it is thick, although the entire varnish may be sampled where it is thin.

Rock varnish thickness can be extremely variable, and SEM analyses of natural varnish surfaces have the potential to incorporate varying amounts of substrate depending on the thickness of varnish on micro-topographic highs and the accelerating voltage of the analysis. As part of SEM analyses of varnish chemistry for cation-ratio dating, variations in the chemistry of a spot as seen at different voltages have been used to infer when substrate is being included (Harrington and Whitney, 1987), although,

because of stratigraphic variations in chemistry, the reliability of such interpretations is not always clear. X-ray maps of varnish surfaces can be used to document the incorporation in analyses of x-rays emitted from the underlying substrate, allowing these interpretations to be tested.

Due to the heterogeneous nature of rock varnish and the characteristics of x-ray depth-distribution curves, quantitative analyses of varnish chemical composition using natural varnish surfaces do not provide true average varnish chemistry. In addition to the analyses being biased toward the chemistry of the upper layers of varnish, somewhat different thicknesses are typically sampled for different elements. Conveniently, the elements used in cation-ratio dating of rock varnish (K, Ca, Ti) all have similar x-ray depth-distribution curves and so the sampled thickness of varnish is similar for each of these elements. However, depth-distribution curves for the major cations in rock varnish (Mn, Fe, Si, Al) are significantly different from curves for K, Ca, and Ti due to their differing atomic numbers and excitation energies. Because of these differences, Mn, Fe, Si, and Al concentrations should be used cautiously as indicators of varnish thickness with reference to acquiring K, Ca, and Ti concentrations of rock varnish.

The SEM method of Harrington and Whitney (1987) for chemical analysis of rock varnish for cation-ratio dating is substantially different from the other commonly used method. Whereas the SEM method produces analyses that are inherently surface-biased, analyses by Dorn (1983, 1989) of scraped varnish attempt to average the entire thickness. Although there is thus no reason to expect the different techniques to yield the same elemental concentrations for a given sample, it is significant that both methods have reported success in establishing empirical correlations between the ratio (K+Ca):Ti of varnish samples and the age of the underlying geomorphic surface. It seems that analysis of the entire varnish coat is not essential to obtain useful empirical correlations. For example, in the successful application of SEM-based cation-ratio dating by Dethier et al. (1988), analyses were restricted to an accelerating voltage of 15 kV and most of the x-rays were therefore emitted from the upper micron of the samples. The reason for the similarity in empirical trends of varnish chemistry and age obtained by such different methods is uncertain, although resolution of this uncertainty promises to provide a greatly improved understanding of cation-ratio dating.

Acknowledgments

The authors thank Peggy Snow for assistance with the EPM analyses. This work was conducted under the auspices of the U.S. Department of Energy through a Director's-funded postdoctoral fellowship from Los Alamos National Laboratory and under contract W-7405-ENG-36 with Dr. George Kolstad of the Office of Basic Energy Sciences.

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Penetration Depths in SEM Analysis of Rock Varnish

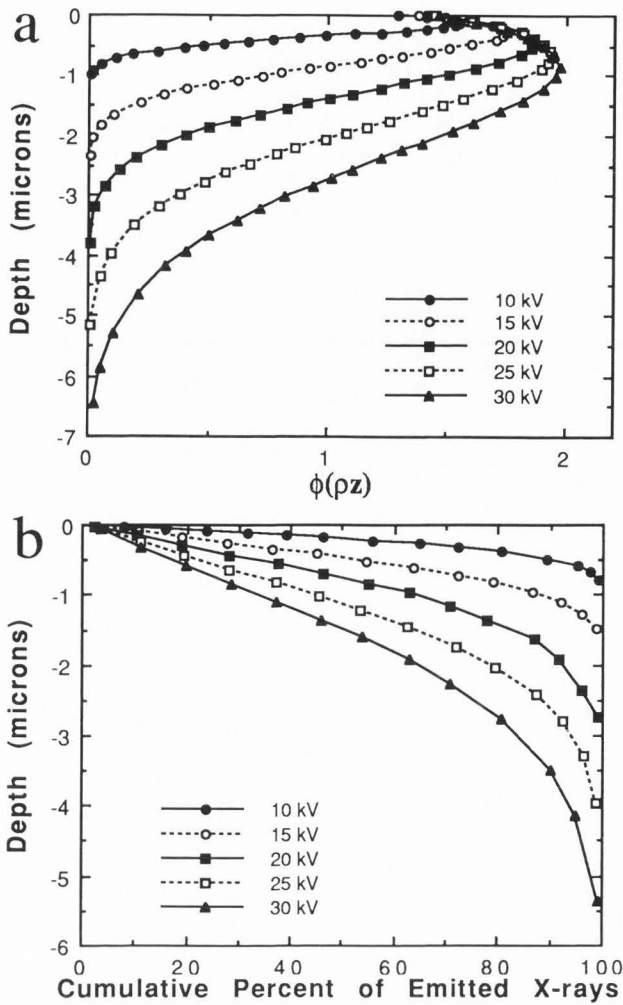


Figure 4. a) Depth-distribution curves of emitted K-K α x-rays in a homogeneous rock varnish, at 10 to 30 kV. The $\phi(\rho z)$ scale is a relative intensity of emitted x-rays. b) Cumulative depth-distribution curves of emitted K-K α x-rays at 10 to 30 kV. Density of varnish set at 3.1, and average varnish composition same as used in Figure 3.

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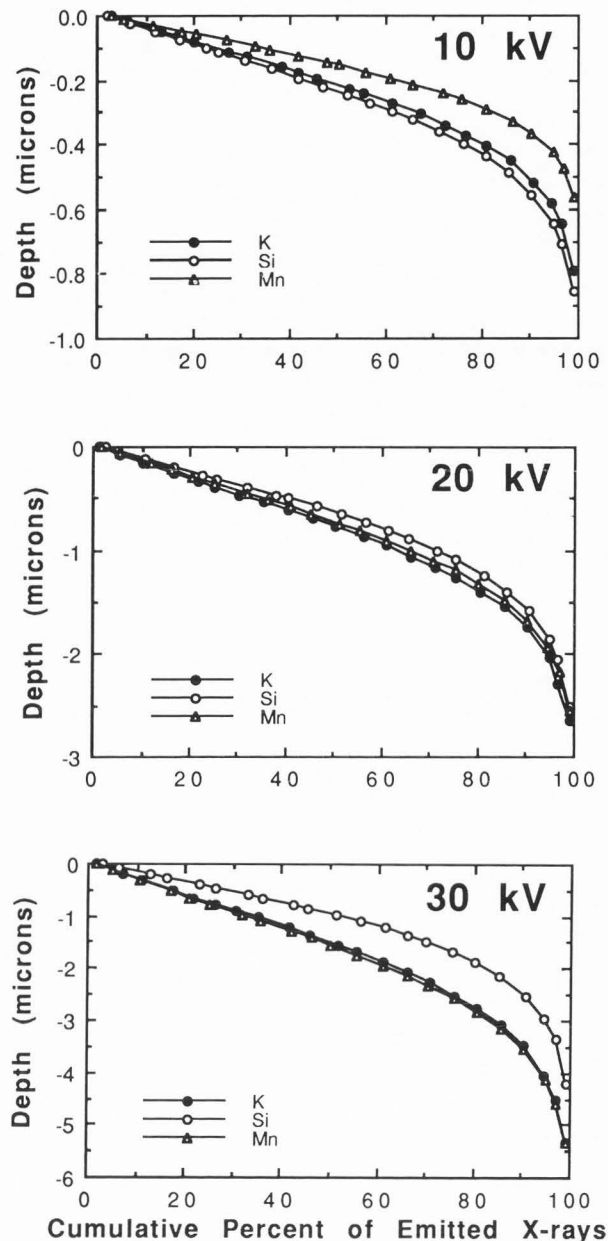


Figure 5. Cumulative depth-distribution curves of K-K α , Si-K α and Mn-K α x-rays in a homogeneous rock varnish, at accelerating voltages of 10, 20 and 30 kV. Curves for Ca-K α and Ti-K α are similar to K-K α ; Fe-K α is similar to Mn-K α ; and Al-K α is similar to Si-K α . Varnish characteristics same as in Figure 4.

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Discussion with Reviewers

J. Back: Although analyses in Table 1 do show increasing K and Si concentrations with increasing accelerating voltage (depth), K values are well within the range of reported analyses for rock varnish (e.g., see Perry and Adams, 1978; and Potter and Rossman, 1979). Although Si concentrations are on the high end of whole-varnish analyses reported in the two above articles, Table 1 Si concentrations are considerably less than those found in ash-flow tuffs (typically > 70 wt% SiO₂), and even less than found in clay minerals (which you note is a common component of rock varnish).

Authors: Because the electron beam has to first pass through a layer of varnish, the varnish will always contribute substantially to the analyses and it is unlikely that Si concentrations would approach that of the substrate. Similarly, although clay minerals are a common component of varnish, they are diluted by the Mn and Fe components. In addition, although the K concentrations in Table 1 are within the range typical for varnish, our interpretation that the increasing K and Si concentration with increasing depth reflects incorporation of substrate is supported by the recognition of substrate on the x-ray maps at these same voltages.

J. Back: The authors do not explain why differences in K and Mn x-ray maps with increasing accelerating voltage are not due solely to lateral and vertical inhomogeneities that are characteristic of rock varnishes. In particular, the greater Mn intensities in the upper right portions of the 20 and 30 kV maps imply chemical inhomogeneity in the varnish.

Authors: To some degree, the variations in elemental concentrations in the x-ray maps probably do reflect variations in varnish chemistry. Specifically, the high-Mn area in the 20 and 30 kV maps may reflect higher Mn concentrations within the varnish where the varnish is much thicker than elsewhere on the surface. In this area distinct linear ridges are present which are the surface expression of deformational features that develop within thick varnish in depressions (Raymond et al., *Geol. Soc. Am. Abstract*, 1989). Our chemical analyses of varnish cross-sections indicate that the highest Mn concentrations are often attained in these depressions. However, we feel it unlikely that the distinct high-K low-Mn patches seen at 20-30 kV, but not at 10 kV, primarily reflect subsurface varnish layers rich in K but low in Mn. As seen in cross-section, such high K (and high Si) detritus-rich layers, as shown in Fig. 1, are generally restricted to substrate depressions, which in turn are usually identifiable as surface depressions. The occurrence of most of the high K spots at surface highs argues against varnish heterogeneity being the cause of these.

J.J. McGee: What effect does the sample topography have

on the SEM and EPM analyses? Have you compared data for varnishes from the topographic highs with data from the thicker depressions, and can you determine if the varnish composition varies with topography?

Authors: Our analyses of varnish cross-sections reveal that local rock surface topography has a significant effect on varnish composition, and SEM and EPM analyses of highs will thus usually be different from analyses of lows. Varnish in the micro-topographic depressions is much more variable in composition than on the highs, and the depressions can include both the "dirtiest" and the "cleanest" varnish layers. Low-Mn high-Si layers that include a variety of detrital components occur in the depressions, especially towards the base, but the depressions also commonly contain the layers with the highest concentrations of Mn. Varnish on the highs is less variable in composition and, because of the general absence of thick detritus layers, typically has higher average concentrations of Mn than varnish in the depressions if the entire thickness is averaged. The SEM and EPM analyses reported in Tables 1 and 2 include both highs and lows in an attempt to average out these variations.

R.H. Packwood: Are your predicted $\phi(\rho z)$ curves the generated x-ray intensity ratios, or are they the observed x-ray intensity ratios with depth?

Authors: All of the $\phi(\rho z)$ results reported in this paper are the x-ray intensity ratios that would be observed at the sample surface, and thus, as a result of absorption, are less than the actual generated x-ray intensity ratios.

P.R. Bierman: Could you propose a physical/chemical model to explain why measurements made in the upper few micrometers of varnish with the SEM show similar trends with time to PIXE measurements made of the entire varnish coat?

Authors: The entire question of what controls varnish chemistry and what changes may occur over time is too complex to go into here in detail, and much remains to be resolved. However, our recent analyses of varnish cross-sections support other workers who have reported the absence of systematic changes in the ratio (K+Ca):Ti with depth (see Raymond et al., 1991). Ongoing work by our research group also reveals that, although the chemistry of the upper few micrometers is not identical to the chemistry of the entire varnish, they are related. Where the ratio (K+Ca):Ti of the upper few micrometers is relatively high or low, this cation ratio in the entire varnish is generally high or low, respectively.

R.I. Dorn: The authors specify they sample the darkest, smoothest varnishes from each locale. Is this one criterion used in collecting samples analyzed for cation-ratio dating with the SEM method?

Authors: Yes, this is one of several criteria used. Because of erosion of different parts of a geomorphic surface, and often local erosion on single clasts, there is typically a wide range in age of varnish at each locale. The darkest varnish is sampled because, in comparing spots with similar settings, relative darkness may be the best field criteria for relative age. The smoothest varnishes are sampled to minimize surface roughness effects in SEM analyses of natural varnish surfaces. Other criteria used are discussed by Harrington and Whitney (1987).