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ELEMENTAL RELATIONSHIPS IN ROCK VARNISH AS SEEN WITH SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE X-RAY ELEMENTAL LINE PROFILING

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Abstract

The heterogeneous nature of rock varnish requires a thorough understanding of elemental and mineralogic compositions before chemical variability of rock varnish may be confidently related to varnish age or to past geochemical environments. Elemental relationships in rock varnish were examined using scanning electron microscopy in conjunction with an elemental line profiling routine using semi-quantitative, energy-dispersive x-ray analysis. Results of our analyses suggest: 1) variations in cation concentrations used in varnish cation-ratio dating relate more specifically to variations in detritus concentration within the varnish than to element mobility as defined by weathering indices; 2) Mn:Fe ratios may be a poor indicator of paleoclimatic fluctuations; and 3) the Mn-oxide phase existing in varnish is most likely a Ba-enriched phase rather than birnessite. An examination of data collected from elemental line profiling offers great potential for gaining insights into geochemical processes affecting the deposition and diagenesis of rock varnish and for testing hypotheses relating to its chemical variability.

KEY WORDS: Rock varnish, electron microscopy, line profiling, energy dispersive analysis, varnish cation ratios, Mn:Fe ratios, birnessite.

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Introduction

Rock varnish is a ubiquitous, dark coating commonly occurring on rock surfaces in semiarid and arid environments. Rock varnish is inherently heterogeneous, containing various percentages of Mn and Fe oxides and clay- to silt-sized detritus. Included in several extensive reviews on rock varnish are discussions of the use of electron microanalysis to study elemental and textural characteristics in varnish cross-sections (Elvidge, 1979; Perry, 1979; Dorn and Oberlander, 1982; Whalley, 1983). Specific examples include the use of an electron probe microanalyzer (EPM) to show variations in elemental concentrations with depth (Hooke et al., 1969), combining electron-probe microanalysis and elemental x-ray maps to distinguish varnish horizons from both weathered and unweathered rock surfaces (Hooke et al., 1969; Allen, 1978), and combining electron-probe microanalysis with energy-dispersive x-ray (EDX) analysis to delineate cyclic Mn-Fe banding in some varnishes (Perry and Adams, 1978). Dorn and Oberlander (1982) and Dorn (1984) more extensively documented Mn-rich and Mn-poor layers in rock varnish using an EPM and proposed that microchemical laminations defined by varying Mn:Fe ratios reflected past fluctuations in the level of eolian alkalinity. Dorn and Oberlander (1982) also reported the existence of a relationship between some specific elements and surface age of varnished rocks (e.g., increasing Cu with increasing age) as measured with scanning electron microscopy (SEM) and EDX analysis. Dragovich (1988), in contrast, examined the concentrations of 12 common elements with an EPM and reported no systematic differences between the upper and lower layers of varnish that would reflect an age dependency. Smith and Whalley (1988) combined EPM and SEM analyses with x-ray maps to demonstrate the effect that varnish substrate can exert on the nature and occurrence of varnish.

Most researchers studying rock varnish believe that rock-varnish constituents are usually of allochthonous origin, deposited by eolian or aqueous processes and then cemented in place by Mn- and Fe-oxides (Potter and Rossman, 1977, 1979; Allen, 1978; Perry and Adams, 1978; Dorn and Oberlander, 1981a, 1982;

Moore and Elvidge, 1982; Whalley, 1983; Dorn, 1986). Thus, rock-varnish accumulation should follow patterns similar to other sedimentary accumulations, and layers of differing composition should primarily reflect depositional stratigraphy and, only secondarily, subsequent diagenesis. Combining SEM with x-ray diffraction (XRD) analysis has provided insight into the deposition of rock varnish. For example, Raymond et al. (1989) reported from SEM observations that depositional basins (pits) on substrate surfaces on the order of millimeter(s) in diameter are preferentially filled with rock varnish relative to surrounding highlands (Figure 1A). These micro-basins contain stratigraphic horizons representative of regional or local depositional events not preserved in varnish deposited outside of the basins, such as detrital horizons lacking in Mn but rich in Al and Si that may record a large dust influx. By evaluating rock varnish using XRD, Raymond et al. (1988) reported that regional eolian influx may provide nearly an identical baseline of silicate minerals within varnishes over broad geographic areas, and that the weathered products of surrounding or substrate geology play a secondary, though important, role as a source for additional detrital material. Thus, as inferred above, the elemental chemistry of varnish appears to be controlled initially by sedimentologic processes although subsequent diagenetic changes may affect the concentrations of some elements.

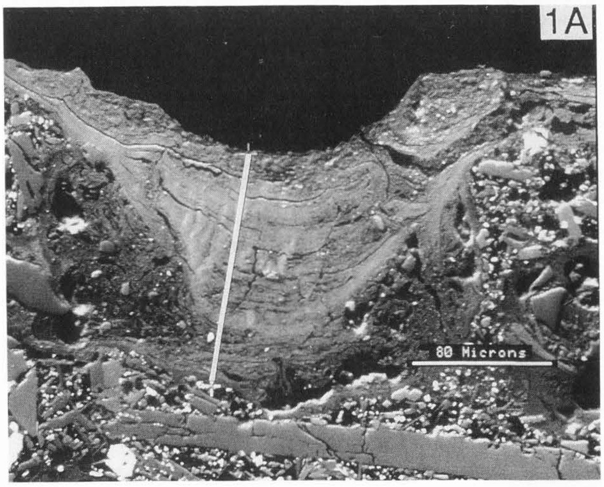

Figure 1. Rock varnish from a lava flow ca. 15-20 ka old (Wells et al., 1990). Sample CIA-16. **A)** Backscattered electron SEM photomicrograph showing brighter Mn-rich varnish and darker, detritus-rich varnish with visible foreign grains. The varnish is filling a depression on the substrate surface and is about 20x thicker in the depression than on the surrounding highs.

Until the late 1970s geochronologic interest in rock varnish was restricted to its potential as a relative age discriminator among different geomorphic surfaces by utilizing differences in darkness and color of the varnish. Recent work, however, has suggested the potential for using rock varnish to date geomorphic surfaces based on the ratio of several minor elements, (K+Ca)/Ti, within the varnish (Dorn and Oberlander, 1981a; Dorn, 1983; Harrington and Whitney, 1987). The main assumptions of the varnish cation ratio (VCR) dating method are that the initial cation ratio of airborne fallout incorporated into varnish is similar for the period of time under examination and that rock varnish serves as a cation-exchange complex where relatively mobile K and Ca are depleted over time as compared to relatively immobile Ti (Dorn 1983, 1989). If these assumptions are valid and if depth serves as a proxy for age, cation-ratio trends with depth should reflect the relative greater mobility of K and Ca compared to Ti and (K+Ca)/Ti measurements should decrease with increasing varnish depth. However, although only analyzing small volumes of rock varnish, recent EPM studies of varnish cross-sections have reported a lack of elemental trends with depth that would support the assumed changes over time (Dragovich, 1988; Krinsley and Anderson, 1989).

The heterogeneous nature of rock varnish requires a thorough understanding of elemental and mineralogic compositions before researchers may confidently interpret chemical variability of rock varnish in terms of past geochemical environments and in terms of time-dependent changes. The purpose of this paper is to document the utility of SEM/EDX elemental line profiles across varnish cross-sections for understanding the chemical variability of varnish and for testing hypotheses relating elemental variations to varnish histories. Data are presented that are relevant to interpreting variations in Mn:Fe ratios and to understanding variations in cation ratios, and that yield insight into some elemental relationships within varnish.

Methods and Materials

Rock-varnish samples reported in this paper were collected from the Cima volcanic field in the Mojave Desert of California. Cores through the varnish and into the substrate were drilled in the field from basaltic outcrops possessing the darkest, most consistent varnish at each site. Small slabs of rock 15-20 mm long and 5 mm thick were cut through the rock varnish and approximately 5-10 mm of substrate, stabilized with epoxy, ground to obtain a flat cross-section and mounted onto rectangular glass slides. The samples were then polished with 0.05-μm Al_2O_3 paste to provide smooth cross-sections of the varnish suitable for quantitative x-ray microanalysis. Samples were carbon coated prior to analysis.

Areas of the cross-sections lacking visible unconformities in varnish stratigraphy were identified in the SEM for analysis. Elemental line profiles of rock varnish were acquired on an ISI, DS-130 SEM equipped with a Tracor Northern 5500 EDX analyzer. Elemental profiles were acquired using the Tracor Northern Microimage program, which uses a standardless semi-quantitative routine, SQ, to analyze, decompose, and report

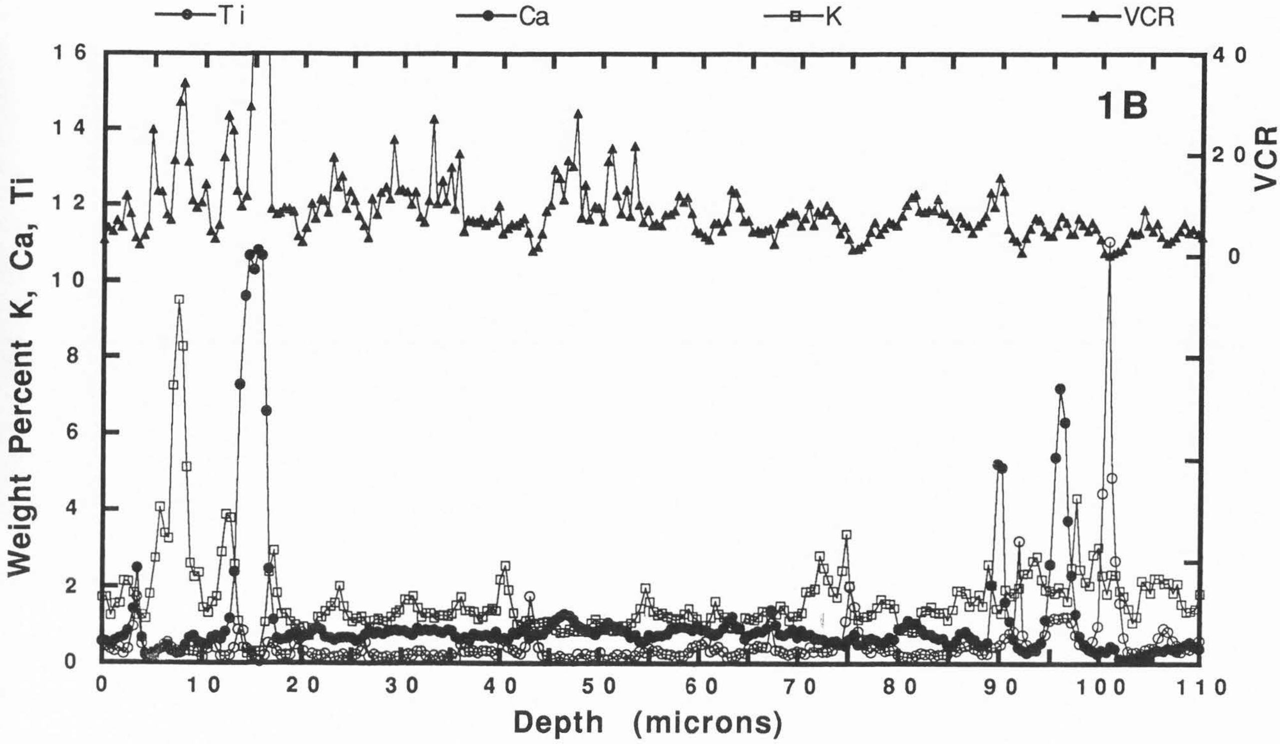

Figure 1B. K, Ca, and Ti concentrations (left Y axis) and VCR [(K+Ca)/ Ti] (right Y axis) plotted versus depth. Uncertainties for average values: K (3.4%), Ca (5.6%), Ti (7.3%).

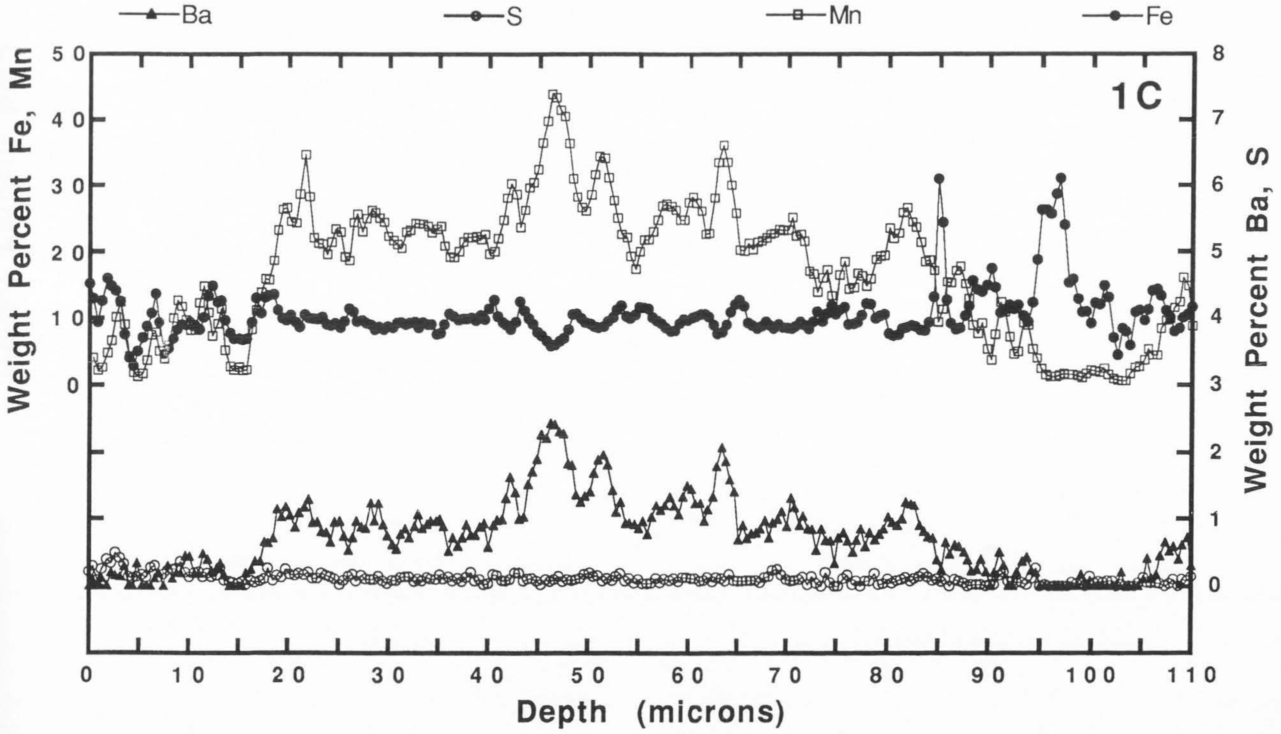

Figure 1C. Fe and Mn (left Y axis), and Ba and S (right Y axis) concentrations plotted versus depth. Uncertainties for average values: Fe (2.4%), Mn (1.0%), Ba (13.8%), S (66.8%).

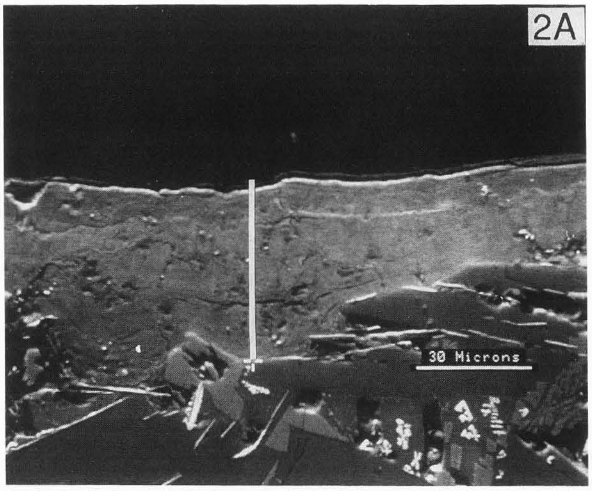

Figure 2. Rock varnish collected from a ca. 90 ka old lava flow (Turrin et al., 1985). Sample CIU-47. **A**) Backscattered electron SEM photomicrograph showing a consistently thick coat of varnish with a uniform surface. Note how relative thickness of varnish is related to the microtopography of original substrate surface.

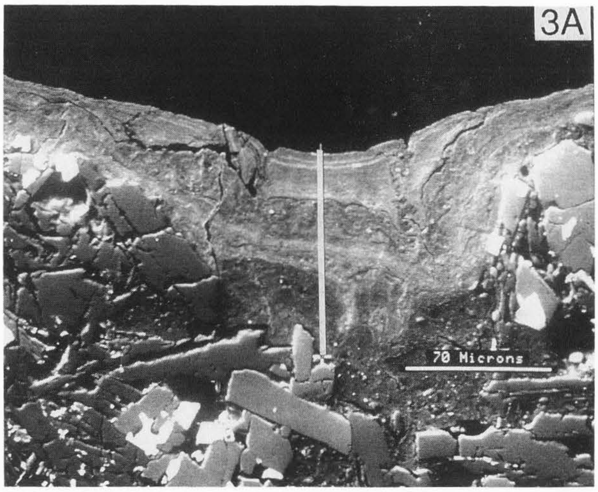

Figure 3. Laminated rock varnish collected from a ca. 320 ka old lava flow (Turrin et al., 1985). Sample CM3-109. **A**) Backscattered electron SEM photomicrograph showing brighter, banded Mn-enriched varnish and darker, more poorly-laminated, detritus-enriched varnish.

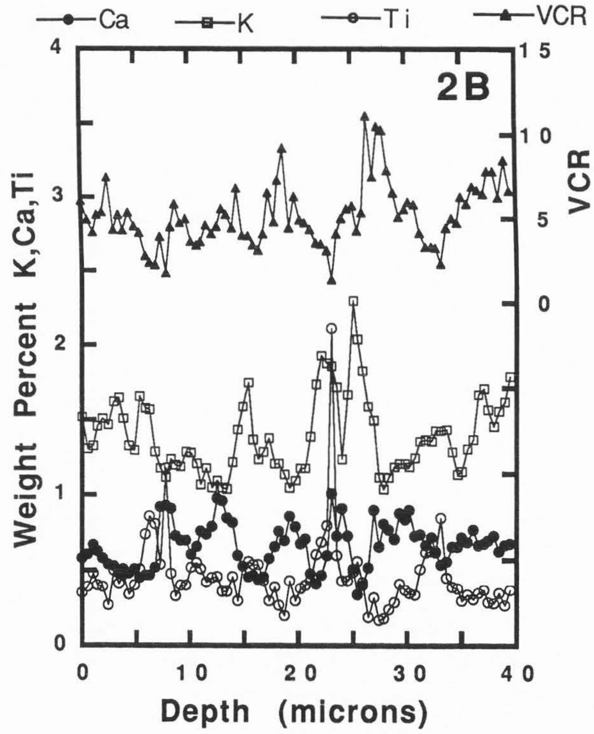

Figure 2B. K, Ca, and Ti concentrations (left Y axis) and VCR [(K+Ca)/Ti] (right Y axis) plotted versus depth. Uncertainties for average values: K (2.7%), Ca (10.2%), Ti (8.5%).

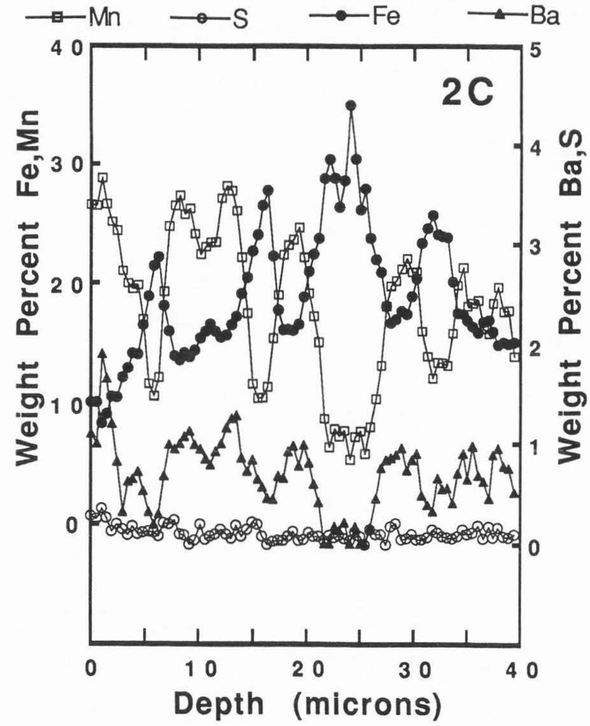

Figure 2C. Fe and Mn (left Y axis), and Ba and S (right Y axis) concentrations plotted versus depth. Uncertainties for average values: Fe (1.5%), Mn (1.3%), Ba(16.1%), S(80.8%).

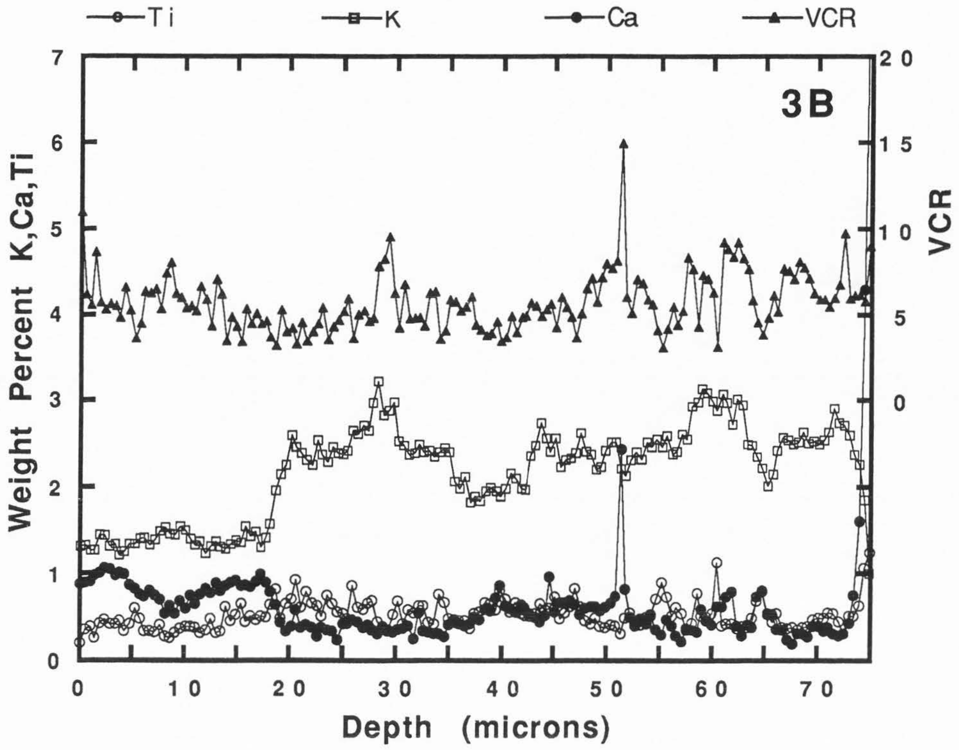

Figure 3B. K, Ca, and Ti concentrations (left Y axis) and VCR [(K+Ca)/Ti] (right Y axis) plotted versus depth. Uncertainties for average values: K (3.9%), Ca (8.6%), Ti (9.4%).

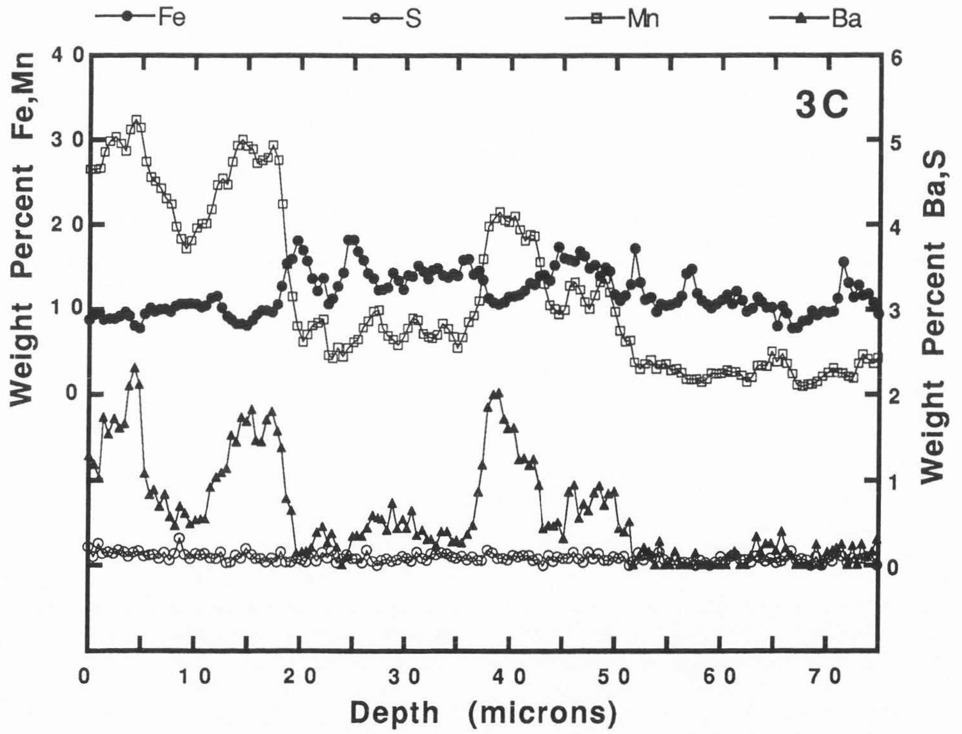

Figure 3C. Fe and Mn (left Y axis), and Ba and S (right Y axis) concentrations plotted versus depth. Uncertainties for average values: Fe (1.2%), Mn (1.0%), Ba (14.3%), S (60.4%).

elemental data. Concentrations of eleven cations were determined in this study: Mg, Al, Si, S, P, K, Ca, Ti, Mn, Fe, and Ba. Analytical points were spaced at 0.5-μm intervals and acquisition time for each point was 100 seconds. The electron beam was automatically repositioned by the Microimage program between analyses. An accelerating voltage of 15 kV provided an average penetration depth of about 1 μm (Reneau et al., 1991, this issue) and therefore an excitation volume approximating 1 μm in diameter, providing 0.5-μm overlap of sample points. Location of analytical profiles were recorded on backscattered electron images (Figures 1A, 2A, 3A).

Results

Backscattered scanning-electron micrographs and respective elemental-line and VCR [(K+Ca)/Ti] profiles are presented in Figures 1-3. Although only three cross-sections and their elemental profiles are presented in this paper, the trends discussed (or lack thereof) are generally consistent with those of 50 elemental line profiles from Cima samples and for samples from several locations in southern Nevada and northern Arizona.

Figure 1 is of rock varnish that occurs within a depression on a rock surface. The rock varnish exceeds 100 μm in thickness in depressions, but is generally less than 5μm thick on the topographically high areas (not shown in Figure 1). Distinct detritus-rich horizons occur within both the upper and lower parts of the varnish cross-section within the depression. Except for peaks in concentration associated with detritus-rich horizons (e.g., K peak at 8 μm, Ca peak at 15 μm), K appears to increase with depth while the concentration of Ca is lowest near the top and bottom of the varnish. Ti concentrations are highest near the top and bottom of the profile in areas containing abundant detritus. The VCR generally decreases from an average of 8 near the surface to approximately 5 near the varnish base, although it shows significant fluctuations. There is a positive correlation between Ba and Mn and a lack of correlation between Fe or S with either Ba or Mn. Mn concentration is lowest in the darker, less laminated, detritus-rich areas.

The second sample possesses a rock varnish of fairly uniform thickness (Figure 2). Variations in varnish thickness relate directly to microtopography of the substrate surface. No detritus-rich horizons are apparent here. The VCR varies non-uniformly with depth, ranging from about 2 to 12, although a slight increase with depth is suggested. K, Ca, and Ti concentrations also vary non-uniformly with depth, although K and Ca show a strong inverse relationship. Ti varies independently of K and Ca. Fe and Mn are inversely related; Ba correlates positively with Mn; and S shows no correlation with Fe, Mn, or Ba. Mn, though fluctuating greatly in concentration, may decrease slightly with depth.

The third sample is of a laminated varnish that began to develop in a small depression on the rock surface (Figure 3). K and Ca vary inversely while Ti concentrations again vary independently of K and Ca. VCRs, on average, remain essentially constant or increase slightly with depth. Again, Ba correlates positively with Mn; a slight inverse relationship may exist between Fe and Mn; and S does not correlate with either Mn, Fe, or Ba. Mn concentrations appear to decrease with depth as they do in Figure 2C.

Discussion

No consistent trends in K, Ca, or Ti concentration with varnish depth exist in any of the three profiles. Since varnish age increases with depth, there likewise is no consistent trend in K, Ca, and Ti relative to varnish age within these cross-sections. Trends of K, Ca, and Ti with varnish depth appear to be dominated by occurrences of K-, Ca-, or Ti-rich detritus horizons (e.g., Figure 1B). Where detritus-rich horizons are absent within the varnish, an inverse correlation is generally present between K and Ca (Figures 2B and 3B). Variations in K, Ca, and Ti concentration appear, therefore, to be related specifically to variations in the distribution of detritus within the varnish. Similarly, varnish cation ratios show no consistent trends with varnish depth for the Cima samples (Figures 1B, 2B, and 3B). Ignoring peaks in concentration due to the occurrence of detrital grains rich in K, Ca, or Ti, VCRs for the samples discussed above both decrease (Figure 1B) and increase slightly (Figures 2B and 3B) with varnish depth.

The decreases in K and Ca predicted by the premises of cation-ratio dating, specifically that K and Ca are preferentially depleted from varnish over time relative to Ti, are not substantiated within the analyzed Cima varnish samples. If K and Ca were being leached as predicted by their weathering indices as proposed by Dorn (1983) and described by Colman (1982) for weathering of andesites and basalts [$Ca \geq Na > Mg > Si > Al \geq K > Fe > Ti$], Ca should be depleted much more rapidly than K relative to Ti. Such leaching of Ca relative to K should remove the observed relationship between K and Ca with depth that apparently reflects original detrital input. Relationships seen at the surface should become less clear with depth. In contrast, the consistent inverse relationship throughout cross-sections documented in Figures 2B and 3B and to a lesser extent in Figure 1B is more suggestive of variations in chemistry related to variations in detritus distribution within varnish. In addition, the lack of any consistent trends of decreasing VCR with depth within our elemental profiles, consistent with observations of Dragovich (1988) and Krinsley and Anderson (1989), suggests that the main premise of cation-ratio dating, relative element mobility, needs reevaluation.

The observed relationships between Fe and Mn have implications for the paleoenvironmental interpretation of varnish stratigraphy. Dorn (1984) discussed several lines of evidence to support the hypothesis that Mn-poor and Mn-rich laminae in varnish are related to regional alkalinity levels in the environment, with peaks and troughs in line profiles of Mn:Fe ratios proposed as recording climatic fluctuations. Using Mn:Fe ratios as an indicator of climatic change implies that concentrations of both elements are related to regional alkalinity trends. However, our data (Figures 1C, 2C, and 3C) suggest that different geologic and/or geochemical conditions control the distributions of Fe and Mn. Where strong inverse correlations of Mn to Fe occur (Figure 2C), the relatively high Mn concentrations correspond with the occurrence of stromatolite-like structures (Raymond et al., 1989). As well as supporting the proposed association of bacteria with Mn concentration in varnish (Dorn and Oberlander, 1981b), the stromatolitic structures in turn may reflect a direct exclusion of Fe by bacteria. The lack of any correlation between Mn and Fe in Figure 1C suggests an inorganic factor, such as the input of Fe-rich eolian detritus, may account for high Fe concentration. Since Fe concentration may vary dependently or independently of Mn, interpretations of paleoenvironments using Mn:Fe ratios may be misleading.

Also noteworthy in our analyses is the positive correlation of Ba with Mn and the absence of a consistent correlation of Ba with S. In a few cases, the presence of micron-sized barite grains ($BaSO_4$) is indicated by positive correlations between discrete Ba and S peaks (see Harrington et al., 1991, this issue), but Ba occurrence as barite in rock varnish is apparently much less common than its occurrence in association with Mn. Potter and Rossman (1979) have also noted the association of Ba with Mn in rock varnish. While suggesting that birnessite $[(Na,Ca,K)Mn_7O_{14} \cdot 3H_2O]$ is the dominant Mn-bearing mineral in rock varnish, Potter and Rossman (1979) further noted that certain Ba-Mn-oxide minerals including romanechite and the hollandite series have similar infrared lines and could be responsible for some of the infrared absorption they reported as a measure of birnessite occurrence. The direct correlation between Ba and Mn (Figures 1C, 2C, and 3C) lend additional support to the interpretation that the Mn-oxide phases existing in varnish are most likely Ba-enriched phases rather than birnessite. This has particular significance when attempting to define geochemical parameters of rock varnish formation based upon known Eh-pH conditions of authigenic Mn- and Fe-rich minerals, or when comparing synthetic laboratory varnish (Dorn, 1986) with reported birnessite mineralogy to true desert varnish.

Lastly, although Dorn (1989, p. 566) has suggested that "there is a great hazard in trying to generalize from data acquired by micron-scale measurements to bulk chemistry of rock varnishes", we feel the consistency in elemental relationships within rock varnish as acquired with micron-scale measurements indicates that the approach presented here better identifies true chemical variations in varnish than an approach that relies on bulk analyses. Specifically, we feel that numerous uncertainties are introduced in using bulk analyses of varnish because such analyses disproportionally mix stratigraphic intervals of different age and composition, and the generality of the bulk analyses is unclear.

Conclusion

SEM/EDX elemental profiles can be used to document relationships between element concentrations and depth within rock varnish. As such, an examination of data collected with elemental line profiling provides great potential for gaining insight into the geochemical processes affecting the deposition and diagenesis of rock varnish and for testing hypotheses relating to its chemical variability. This approach should yield an improved understanding of the basis for the empirical cation-ratio dating method, the nature and significance of stratigraphic layers within varnish, and the nature of the different mineralogic phases within varnish.

Acknowledgments

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Discussion with Reviewers

W.B. Whalley: Do you know if profiles on the same samples (e.g., 10 μm away) give similar results?

Authors: Yes they do. Where we have acquired closely-spaced profiles, the stratigraphy is generally continuous over such short distances, providing similar results. Typically, the more stratigraphically uniform the varnish the more uniform the results. Well-laminated varnishes (see next question) tend to give almost identical elemental profiles. Varnishes with abundant detritus-rich horizons, microstromatolites, and inter-stromatolite regions tend to be more variable. However, even these varnishes with irregular stratigraphy commonly show similar elemental trends.

W.B. Whalley: Is there any sort of correspondence between elemental variation and the apparent laminations seen (esp. Fig. 2A and the top of Fig. 3A)?

Authors: Yes, most definitely. The highly-laminated, detritus-poor varnishes that appear brighter in backscattered electron microscopy are relatively enriched in Mn and Ba. Within these laminated varnishes we also find the best defined inverse relationships between Mn and Fe.

W.B. Whalley: You mention stromatolite-like structures and Mn:Fe ratios (Raymond et al., 1989). Could you perhaps illustrate this with another micrograph and/or position on a linescan?

Authors: Figure 4 shows backscattered electron micrograph of the microstromatolites and Mn and Fe elemental x-ray maps of the same area for Sample BM-3. Areas of brighter intensity within the Mn x-ray map define the occurrence of the stromatolite structures. The Fe x-ray map, in contrast, rather than correlating with the stromatolites has the greatest intensity in detritus-rich areas containing Fe-rich mineral grains. Mn and Fe x-ray maps are scaled independently and their relative intensities are not directly correlative.

L.F. Ruppert: How did you separate the compositions of the detritus-rich horizons from the composition of the varnish?

Authors: Relatively detritus-rich and detritus-poor varnish was distinguished based on both visual observations of backscattered images and on the line profiles. Detritus-poor rock varnish is brighter, appears very fine-grained, has a massive or finely laminated nature, and shows the least chemical variability (see the middle of transect 1A, most all of transect 2A, and the top 1/3 of transect 3A). In contrast, detritus-rich rock varnish is darker gray, usually possesses distinct large particles, and shows much greater chemical variability on the line profiles (see the top of transect 1A and the middle 1/3 of transect 3A).

L.F. Ruppert: Do you have surface effects in your analyses and, if so, what are they?

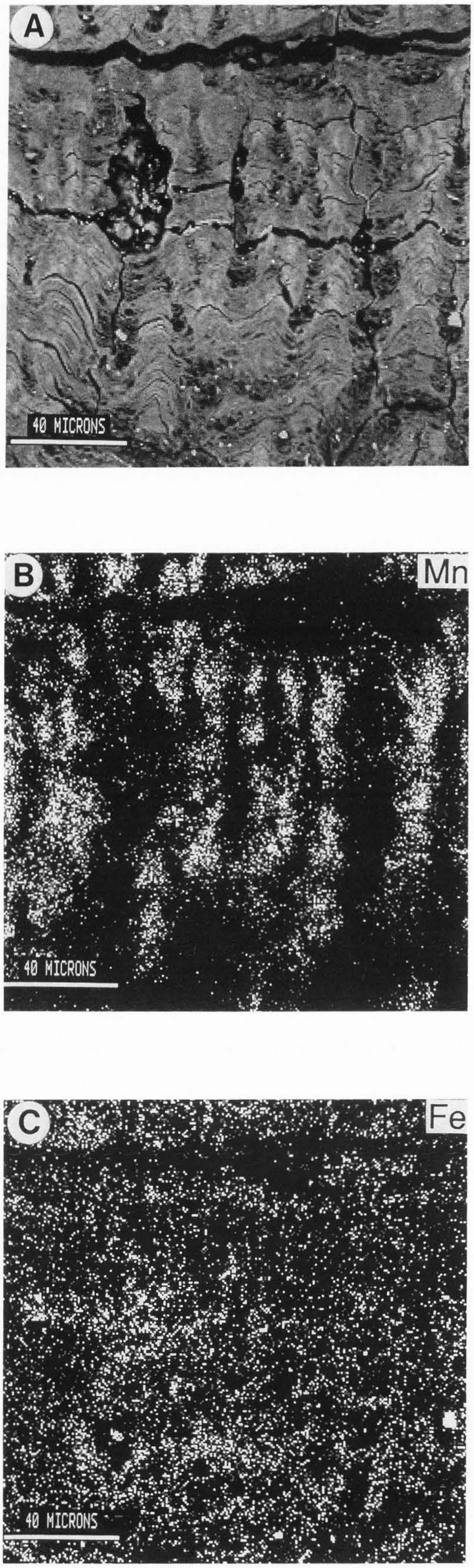

Figure 4. **A**) Backscattered electron micrograph of the microstromatolites and Mn and Fe elemental x-ray maps (**B** and **C**) of the same area for Sample BM-3.

Authors: The varnish cross-sections were polished with a 0.05 μm paste that removed most relief and provided a relatively flat surface. Thus, there should be no major shadowing of the EDS detector during any of our analyses. Minor effects due to surface irregularities in detritus-rich areas may slightly affect chemical data along elemental profiles, but since the volume of excitation of the electron beam is approximately 1 μm in diameter, most of these effects should be insignificant.

L.F. Ruppert: Would you elaborate on the factors controlling Fe concentrations in the varnish? Can eolian detritus be the sole source of Fe in the varnish?
Authors: The factors controlling Fe concentration are still poorly known. As with other elements in varnish, Fe may be present in multiple forms. For example, it is always present in our samples with at least several weight percent, suggesting it is an integral component of even the purest varnish. The highest Fe concentrations may be associated with Fe-rich eolian detritus, such as volcanic ash. Available evidence indicates that no source besides eolian, and local aqueous transport, is required to supply constituents found in varnish. An eolian source for the Fe is the only possibility for rock varnish formed on substrates with essentially no Fe (e.g., silicified carbonates, quartzites). For varnish on Fe-rich substrates, no evidence exists for interchange between substrate and varnish.

P.R. Bierman: What are the chemical or physical processes which result in the correlation between Ba and Mn abundance?
Authors: The association of Ba and Mn probably results from Ba being an integral part of the predominant Mn-phase in varnish. Although no Mn-bearing mineral phases are present in rock varnish that may be defined by x-ray diffraction, utilizing transmission electron microscopy we have defined an amorphous Mn phase with dark field imaging that in addition to Mn contains minor amounts of Ba, Fe, Al, Ca, and P. We do not yet understand the processes that control the deposition, occurrence, or chemical variations of this phase but are working on the problem.

P.R. Bierman: How do you explain the change in cation ratios with time if you believe that the varnish chemistry you measure is depositional rather than diagenetic?
Authors: We are presently testing alternative hypotheses that could give similar empirical relationships but have not yet been able to substantiate any single cause. Possible mechanisms include gradual changes in the composition of the accreting varnish as depressions fill and surface roughness decreases, and decreases in the amount of substrate incorporation into analyses as

varnish thickens.

P.R. Bierman: Can sedimentary analogs be applied on a micrometer scale when the physics of sediment transport are a function of length scale? What evidence do you have that varnish age increases with depth in the varnish and that elements are not remobilized as the varnish ages?

Authors: As the material being accreted as rock varnish generally consists of sub-micron particles brought to the site by eolian transport and individual varnish laminae are generally microns in thickness, we see no inherent size limitations on the use of sedimentary analogs. In addition, numerous features have been observed that argue for standard superposition of layers including microstromatolites, erosional unconformities, imbricated clasts within detritus-rich horizons, and detrital clasts throughout varnish cross-sections. Although there is not space in this paper to fully discuss the topic of remobilization, a thorough examination of our data reveals no evidence that systematic depletion or enrichment of any of the minor elements relative to correlative major elements occurs in the varnish cross-sections we have examined.

R.I. Dorn: I have gone over many of my EPM data with a new set of eyes, and I find similar results for much of my data from the same region. I would like to stress, however, that before any micron-scale analyses can be generalized, multiple probe transects must be conducted on a given thin section, with similar replications from thin-section to thin-section on a given boulder, and replicated this same way from boulder to boulder in a particular area.

Authors: The three elemental profiles presented in this paper were chosen because they represented general trends seen within more than 50 profiles from the Cima volcanic field that we have collected to date. Within this group of profiles we have multiple acquisitions from within single pits on individual thin sections, from multiple places on the same sections representing both topographic lows and highs, from multiple outcrops of the same volcanic flow, and from multiple lava flows. The generalizations we have reported are based on this larger data set, and we have seen the specific elemental associations we discussed occur repeatedly. We have also seen similar relationships in varnish collected from other areas, suggesting that they are also not unique to the Cima volcanic field.