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## BARIUM CONCENTRATION IN ROCK VARNISH: IMPLICATIONS FOR CALIBRATED ROCK VARNISH DATING CURVES

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### Abstract

Cation-ratio dating of rock varnish is a recently developed technique for obtaining surface exposure ages of a wide variety of geomorphic surfaces. As originally proposed, the technique utilizes a ratio among minor cations [(K+Ca)/Ti] in rock varnish. Although this varnish cation ratio is related to the Ti concentration, it can also be affected by the presence of Ba that may be partially included in the analyzed concentration of Ti. Barium is a minor constituent found in virtually all rock varnishes sampled from the Lake Mead area, Las Vegas Valley, and the Crater Flat region of southern Nevada. Barium is heterogeneously distributed in rock varnish, associated predominantly with Mn and secondarily with sulfur (detrital barite). Barium concentrations are apparently greater in varnishes found on young surfaces (< 100 ka) than in varnishes found on older surfaces (> 500 ka), and they are apparently greater in varnishes on low elevation surfaces than in varnishes on hill-slope or ridge deposits.

In energy dispersive spectroscopy (EDS), Ba  $L_{\alpha}$  and  $L_{\beta}$  peaks overlap with Ti  $K_{\alpha}$  and  $K_{\beta}$  peaks. Unless decomposed, the overlapping peaks may yield erroneously large values for Ti. We have compared the effect of Ba concentration on calculated varnish cation ratios using: (1) quantitative EDS with the scanning electron microscope (SEM) that decomposes Ti and Ba peaks; (2) quantitative wavelength-dispersive spectroscopy (WDS) with an electron probe microanalyzer (EPM); (3) semi-quantitative EDS with the SEM that decomposes Ti and Ba peaks; and (4) semi-quantitative EDS with the SEM that does not decompose Ti and Ba lines. Results suggest small amounts of Ba relative to Ti will not significantly change the value of the calculated varnish cation ratio with or without decomposition. However, if Ba concentrations are high relative to Ti, the effect on cation ratios is pronounced, resulting in anomalously low cation ratios. As younger varnishes and varnishes on topographically lower surfaces apparently have higher Ba concentrations, the effect of Ba on cation ratios calculated for younger rock varnishes and lower surfaces will be greater.

**KEY WORDS:** Rock varnish, cation-ratio dating, barium, barium-titanium decomposition, Southern Nevada, scanning electron microscopy.

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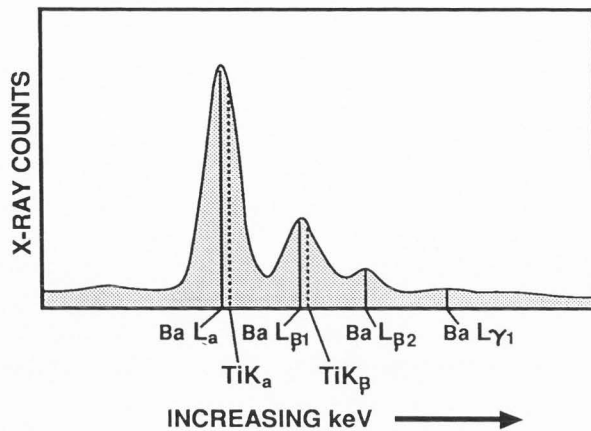
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### Introduction

Rock varnish is a Mn- and/or Fe-rich coating commonly found on rock exposures in arid and semiarid regions. Dorn (1983) proposed a technique for using rock varnish to estimate the age of geomorphic surfaces utilizing a ratio of minor elements in the varnish [(Ca+K)/Ti] calculated for specific geographic areas. This ratio is thought to decrease with varnish age and has been calibrated using isotopically dated surfaces to construct rock varnish dating curves (plots of cation ratio versus log time). The importance of the rock varnish dating technique lies in the wide variety of young (< 1 Ma) geomorphic surfaces that possess rock varnish on surface clasts and thus could potentially yield surface exposure ages derived from rock varnish analysis.

It is now commonly accepted that rock varnish components are of detrital origin, with 30% to 70% of the varnish composed of eolian transported clay minerals (e.g., Potter and Rossman, 1979). Manganese and Fe are markedly enhanced in the varnish over levels within eolian detritus. Barium has been reported to be a minor constituent of rock varnishes (Engle and Sharp, 1958, Potter and Rossman, 1979), but the prevalence and distribution of Ba in rock varnish, either geographically or within a single sample, has not been previously described. Furthermore, the relationship of Ba incorporated in rock varnish to the regional dust composition and proximity to Ba sources has not been addressed. In this paper we discuss two aspects of Ba as a constituent of rock varnishes: (1) the distribution of Ba in rock varnishes from southern Nevada; and (2) the effect that this occurrence of Ba has on measuring Ti concentrations and therefore on calculated cation ratios used in rock varnish dating curves.

Low concentrations (< 2 wt%) of Ba in the presence of Ti are difficult to detect when the analysis is by energy-dispersive spectroscopy (EDS). The  $K_{\alpha}$  and  $K_{\beta}$  lines for Ti occur at nearly the same energies (within ~ 50 eV) as the  $L_{\alpha}$  and  $L_{\beta}$  lines for Ba, resulting in the overlap of these peaks in an EDS analysis (Fig. 1). The problem of peak overlap of Ba and Ti occurs in any analysis that uses EDS, whether in conjunction with a scanning electron microscope (SEM), an electron probe



**Figure 1.** SEM EDS spectra of material containing both Ti and Ba illustrating the overlap of Ti  $K_{\alpha}$  and  $K_{\beta}$  and Ba  $L_{\alpha}$  and  $L_{\beta}$  peaks.

microanalyzer (EPM), or a proton probe utilizing proton induced x-ray emission (PIXE). If the peak overlaps are not decomposed following analysis, then a portion of the Ba concentration will be misidentified as Ti. This will result in an erroneously high Ti concentration, and consequently, a cation ratio that is erroneously low.

In earlier analyses of rock varnishes from southern Nevada, Harrington and Whitney (1987) used a Tracor Northern standardless semi-quantitative EDS program (SSQ) that performed no decomposition of peak overlaps during SEM analysis. Based on our present understanding of Ba occurrence in rock varnishes in this region, we believe the Ti concentrations that were calculated during these earlier analyses erred towards overestimation, yielding cation ratios that were lower than would be calculated using Ti concentrations unaffected by Ba occurrence.

Dorn (1989b, p. 575) has stated that "Energy-dispersive X-rays analyzed with a SEM cannot separate barium from titanium when they are in similar concentrations at levels around 1%". In this paper we document that, in fact, such separation of Ba from Ti is possible using both quantitative (MICRO Q) and semi-quantitative (SQ) Tracor Northern EDS analytical programs, each of which decompose overlapping Ti and Ba peaks. We also document that SEM EDS analyses yield similar results to wavelength dispersive spectrometer (WDS) analyses of the same varnish using an EPM. Comparison of our SEM and EPM results with reported proton probe PIXE analyses of rock varnish on the same geomorphic features (Dorn, 1989a), indicates a systematic difference in Ba values for similar aged rock varnish and suggests the lack of adequate separation of Ba from Ti during the reported PIXE analyses.

### Materials and Methods

The data discussed in this paper were acquired on an ISI-DS 130 SEM and a Cameca MBX EPM. Both

were equipped with Tracor Northern 5500 EDS systems. EDS analyses utilized three programs of which one was quantitative (MICRO Q), and two were semi-quantitative (SQ and SSQ). WDS analyses on the EPM provides quantitative data. SEM and EPM analyses were made both on rock varnish surfaces and cross-sections of rock varnish. SEM cation ratio analyses of varnish surfaces follow the procedure described in Harrington and Whitney (1987) and Harrington and Raymond (1989). We analyze the varnish on 2 cm diameter, 0.5 cm thick disks made from cores drilled through the varnish and rock substrate on each varnished clast. A low magnification ( $\sim 30\times$ ) is used to obtain a relatively large surface area ( $\sim 12 \text{ mm}^2$ ) in each analysis. The SEM analysis is performed using a working distance of 30 mm, a takeoff angle of 40 degrees, and a counting time of 100 to 150 s with 20% to 30% dead time. We use progressively increasing accelerating voltages to obtain deeper penetration into the varnish. SEM analyses of cross-section transects utilized the same working distance and take off angle, but maintained a spot size acquisition mode, and accelerating voltage of 15 kV, and an acquisition time of 100 s.

EPM analyses of varnish surfaces and cross-sections utilizing Bence Albee corrections are based on standards and use a preset counting precision of 1% with a default maximum time of 40 seconds for each element analyzed. Analyses of Ti and Ba in rock varnish seldom achieve the 1% counting precision and, instead, are terminated at the 40 second default time. Counting precision for these elements is generally  $< 7\%$ . Analyses are also frequently defaulted at 40 seconds in the analysis of Ca and K with a counting precision generally  $< 3\%$ . Each EPM analysis of Ba for surface samples represents the average concentration for three  $400 \mu\text{m}^2$  rastered area analyses on a varnished disk. Cross-section analyses were acquired in a spot mode.

Using the EDS program MICRO Q, all x-ray peak intensities are  $\phi(\rho Z)$  (PRZ) corrected before elemental weight percents are calculated for varnish constituents. MICRO Q utilizes sets of elemental reference standards to perform quantitative analyses. This program allows these reference standards to be input at each of the accelerating voltages at which analyses will be run. Additionally, MICRO Q performs a decomposition of peak overlaps resulting in Ti values unaffected by the presence of Ba within the varnish (Table 1). In standards that contain either Ba or Ti, but not both, generally only the element present was recorded in the analyses at concentrations above detection limits.

In addition to MICRO Q, a second SEM program, SQ, has been used to decompose overlapping Ba-Ti peaks. SQ analyzes x-ray spectra using a library of references stored on disk. Since standard data are retrieved from storage rather than acquired prior to analysis, the SQ program is considered semi-quantitative. The program uses multiple least squares analysis and a PRZ matrix correction procedure to calculate elemental concentrations.

Barium Concentration in Rock Varnish

Table 1. MICRO Q and SQ analyses of standards

Standard	Concentration in Standard (wt%)	Concentration (wt%) WDS-Microprobe	MICRO Q Analyses (wt%)	SQ Analyses (wt%)
Barite			N=5	N=5
BaO	65.43		65.17±0.03	55.34±0.63
TiO <sub>2</sub>	≤0.00		0.60±0.38	BDL
Augite			N=10	N=10
BaO	≤0.00		BDL**	0.02±0.06
TiO <sub>2</sub>	0.74		0.88±0.06	0.83±0.05
Benitoite			N=12	N=12
BaO	37.05		37.38±1.60	37.31±1.14
TiO <sub>2</sub>	19.35		19.29±3.16	18.51±2.59
Synthetic Varnish*		N=5	N=5	N=15
BaO	0.62	0.60±0.13	0.80±0.05	0.62±0.12
TiO <sub>2</sub>	1.84	1.73±0.08	1.77±0.03	1.73±0.06

\* Synthetic varnish is sample FV-1 from Bierman and Kuehner (to be published).

\*\* BDL below detection limit (detection limit for Ba and Ti is 0.1 wt%).

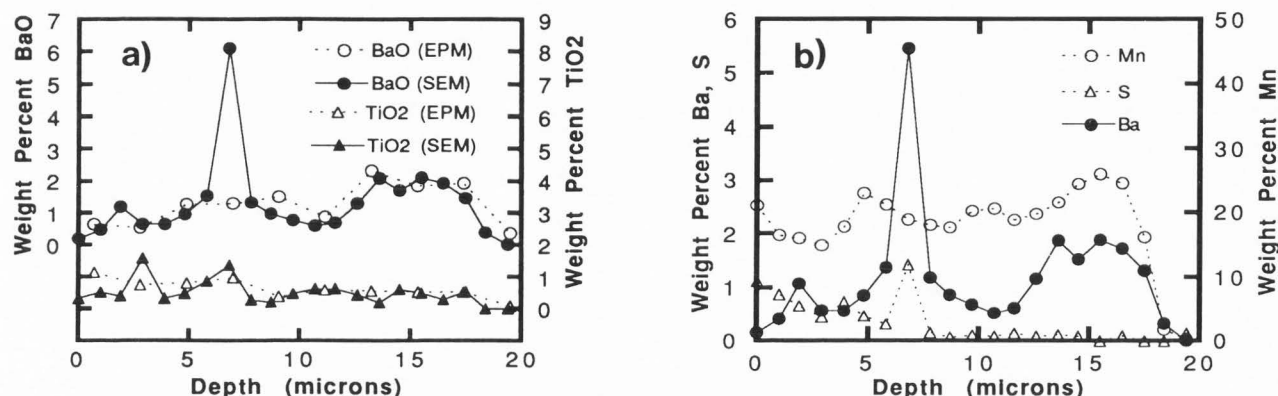


Figure 2a (at left). Replicate line transects of BaO and TiO<sub>2</sub> obtained by SEM EDS analysis using the program SQ and by EPM WDS analysis. Transect 3 on rock varnish sample PW3-25, from Petroglyph Wash, AZ, near Lake Mead, NV. Analytical uncertainty for each EPM analysis is generally about 9-18% for Ba and 10-20% for Ti. Analytical uncertainty for each SEM analysis is generally about 6-20% for Ba and 7-28% for Ti.

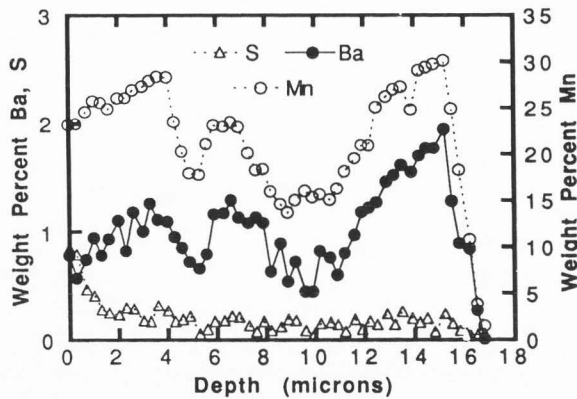
Figure 2b (at right). SEM EDS line transects of Ba, S, and Mn in rock varnish cross-sections. Transect 3 on sample PW3-25, from Petroglyph Wash, AZ, near Lake Mead, NV. Transect acquired at 15 kV with 100 second count times, and reduced using SQ program. Analytical uncertainty for each analysis is generally about 1% for Mn, 6-20% for Ba, and 13-37% for S.

A third SEM program, SSQ, uses a standardless technique that applies peak integration with Krome's Law background modelling to calculate elemental concentrations. SSQ does not decompose Ti and Ba peaks. The SEM is configured in the same manner for MICRO Q, SQ, and SSQ.

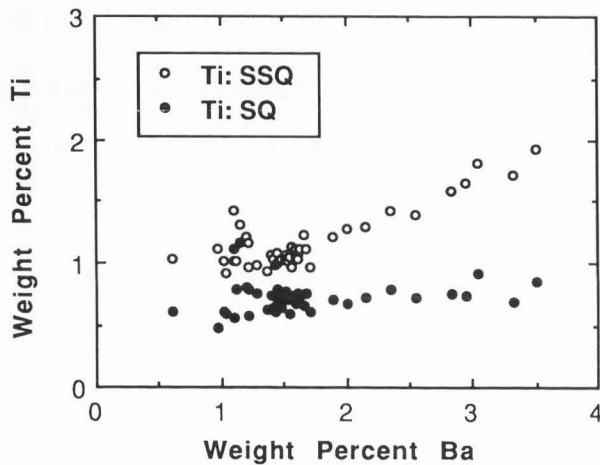
Results

One method of checking the ability of SQ to successfully decompose overlapping Ba-Ti peaks is by comparing SEM SQ line transects through varnish cross-sections with EPM WDS analysis transects at approximately the same locations. Although comparisons are limited by the absolute siting of analytical points in the EPM due to poorer image resolution and larger electron beam

diameter, general trends in Ba and Ti along transects may be compared. In Figure 2a, TiO<sub>2</sub> values obtained on the SEM using SQ and on the EPM using WDS analysis are similar, and both show decrease in TiO<sub>2</sub> concentration with depth. In addition, BaO values from the two instruments are generally similar, including a broad peak in BaO at a depth of about 13 to 18 μm. A major BaO peak recorded on the SEM at 7 μm, but not measured on the EPM apparently represents a micron-sized detrital barite grain, evidenced by a peak in sulphur at the same spot in the SEM transect (Fig. 2b), that did not fall within the volume of x-ray excitation of the EPM transect. Other than the correlation of Ba with S due to occasional barite grains, the primary correlation of Ba in analyzed rock varnish cross-sections is with Mn (Fig 2b, Fig. 3).

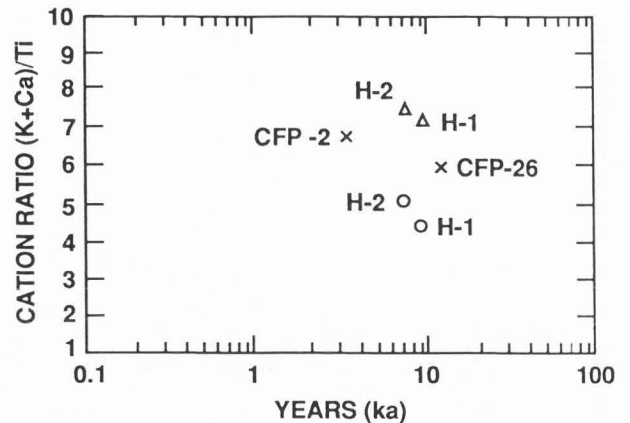


**Figure 3.** SEM EDS line transects of Ba, S, and Mn in rock varnish cross-sections. Transect 4 on sample LB10-3, from Lava Butte near Las Vegas, NV. Transect acquired at 15 kV with 100 seconds count times, and reduced using SQ program. Analytical uncertainty for each analysis is typically about 1% for Mn, 6-20% for Ba, and 40-60% for S.

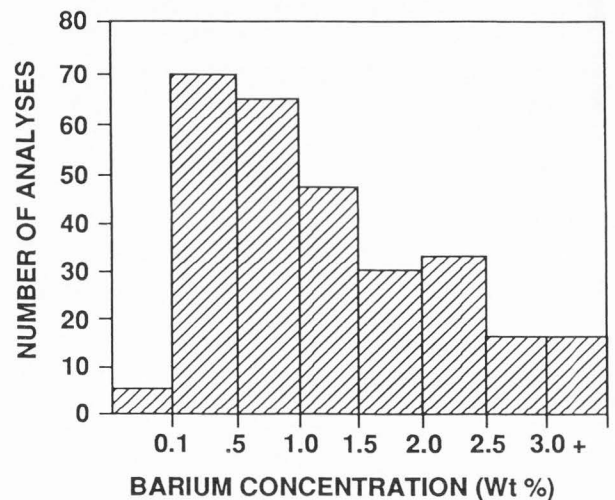


**Figure 4.** Comparison of SSQ derived Ti concentrations with SQ derived Ti concentrations. Rock varnish samples LB10-3 and LB11-2, from Lava Butte near Las Vegas, NV. Replicate SSQ and SQ analyses acquired at 10, 15, 20, 25, and 30 kV for nine 0.2-12 mm<sup>2</sup> spots, with 200 seconds counting times. Analytical uncertainty for each analysis is 1-3% for the reported SSQ Ti values, 5-15% for the SQ Ti values, and 4-24% for the SQ Ba values.

The inadequacy of SSQ, the EDS program without Ti and Ba decomposition, to provide reliable Ti concentrations in the presence of Ba can be illustrated by comparing spot analyses replicated with SQ and SSQ. Titanium concentrations obtained with SSQ are consistently greater than Ti values from SQ (Fig. 4) due to overlap of the Ba L<sub>α</sub> peak with the Ti K<sub>α</sub> peak. The Ti values using SSQ are highest where Ba concentrations are highest.



**Figure 5.** Cation ratios from Holocene surfaces in southern Nevada. Points H-1 and H-2 are from Las Vegas Valley, NV. (Δ) are mean cation ratios calculated with Ba-Ti decomposition performed using SEM EDS MICRO Q analyses. (O) are mean cation ratios calculated using SEM EDS SSQ analyses with no Ba-Ti decomposition. (X) are mean cation ratios of Dorn (1989a) by PIXE analysis.



**Figure 6.** Ba concentrations in rock varnish samples from southern Nevada. Data obtained by EPM analyses using 400 μm<sup>2</sup> spot sizes and SEM analyses of 12 mm<sup>2</sup> areas. Minimum detection limits for Ba are 0.1 wt%.

The effect of Ba on calculation of rock varnish cation ratios if Ba and Ti peaks are not decomposed can be illustrated by comparing cation ratios calculated from SEM analyses of varnish disks using SSQ (non-decomposed) with cation ratios calculated from SEM analyses of the same disks using MICRO Q (decomposed). For rock varnish collected from two Holocene surfaces in Las Vegas Valley, cation ratios using SSQ are more than 30% lower than cation ratios calculated using MICRO Q (Fig. 5).

## Barium Concentration in Rock Varnish

Table 2. Barium concentrations in rock varnish for selected deposits from the Crater Flat area, Nevada

Site	Estimated Age(ka)**	Average Ba Concentration (wt%)	Number and Type* of Analyses
Black Cone (lava flow)	1100±200	0.55±0.09	9(P)
		0.34±0.26	5(MQ)
		0.00	5(PI)
Red Cone (lava flow)	1100±135	0.58±0.17	10(P)
		0.00	5(PI)
Lathrop Wells Cone (lava flows)	uncertain	0.48±0.20	5(MQ)
		0.00	15(PI)
Alluvial Surfaces (Crater Flat and Forty mile Wash)			
Q2C	255±15	0.97±0.24	13(P)
JWB-20	190±45	0.00	5(PI)
Q2B	160±20	1.02±0.53	11(P)
CFP-29	137±25	0.00	10(PI)
CF-3	40±10	1.74±0.67	11(P)
		1.75±0.52	15(MQ)
CFP-32	30±0.5	0.00	5(PI)

\* (P) = Microprobe (This Paper); (MQ) = SEM using MICRO Q (This Paper); (PI) = PIXE (Dorn, 1989a).

\*\* Age estimates are detailed in Harrington and Whitney (1987) and Dorn (1989a).

Based on over 250 SEM and EPM spot analyses and numerous elemental line scans on varnish cross-sections, the following observations can be made concerning Ba occurrence in rock varnish samples from southern Nevada and adjacent areas:

(1) Barium was detected in 98% of rock varnishes analyzed from the Lake Mead area, from Las Vegas Valley, NV, and from the Crater Flat area in Nye County, NV (Fig. 6). Sampled varnished surfaces range in age from < 10 ka to over 1 Ma; topographic positions of varnish collection sites range from the lowest parts of intermontane basins, at or just above local base levels, to > 300 meters above the basin floors. Rock varnishes from the Cima volcanic field, California (Raymond et al., 1991, this issue) and from New Mexico yielded similar percentages of Ba.

(2) Barium concentrations recorded for southern Nevada varnishes were as high as 3.8 wt% for a varnish surface spot analysis and average > 1.5 wt% for all varnish surface analyses. Concentrations are commonly 1-2 times that of Ti.

(3) Barium concentrations can vary by more than a factor of two both laterally and vertically within rock varnish on a single clast. Average Ba concentrations among a suite of clasts taken from a single geomorphic surface also commonly vary by more than a factor of two.

(4) Barium apparently occurs in higher concentrations in younger varnishes than in significantly older varnishes in the Crater Flat area of southern Nevada. Average Ba concentrations of 0.55 and 0.58 wt% were measured in varnishes on 1.1 Ma lava flow surfaces at

Black and Red Cones, whereas average Ba concentrations of 0.97 to 1.75 wt% were measured on nearby alluvial surfaces with estimated ages of 255-40 ka (Table 2).

(5) Barium occurs in higher concentrations in varnishes formed on surfaces at lower elevations in basins than in varnishes on surfaces high on hillslopes or ridges. For example, rock varnish on a hillslope boulder deposit on Little Skull Mountain, NV, has lower Ba values (average concentration 0.23 wt%) than rock varnish occurring 170 meters lower in the basin at Black Cone (0.55 wt%, Table 2). Both varnishes have similar estimated ages, about 1 Ma. Similarly, rock varnish on a boulder deposit on the crest of Yucca Mountain yields lower Ba concentrations (0.47 wt%) than rock varnish with a similar estimated age 400 m lower on an alluvial surface in Crater Flat (1.26 wt%).

### Discussion

The ubiquity of Ba within investigated rock varnishes from Nevada and adjacent regions suggests the possibility that Ba may be universally present in rock varnishes of the southwestern U.S. Thus, most Ti values measured using EDS, if uncorrected for the presence of Ba, will be erroneously high and calculated cation ratios will be too low. Since Ba concentrations are heterogeneous at all scales, cation ratios from an area, previously obtained with programs performing no Ba-Ti decomposition, can not be satisfactorily adjusted for Ba occurrence by applying a single correction factor. Instead, in constructing rock varnish dating curves, cation ratios should be used for which individual analyses incorporate a Ba-Ti decomposition. The apparent relationship of Ba concentration to varnish age may partially reflect apparent

topographic relationships in that younger surfaces generally lie closer to the local base level and therefore lower in the basin than do older, generally higher surfaces. Therefore, Ba concentrations in rock varnish may most influence cation ratios calculated for younger varnishes forming in low-lying basin environments in close proximity to sources of Ba.

Rock varnish dating curves have been constructed for the Crater Flat area by Harrington and Whitney (1987), and by Dorn (1989a). Barium concentrations reported from PIXE analyses of rock varnish by Dorn (1989a, Table 6) differ markedly from our analyses (Fig. 6). Of 117 PIXE analyses of varnish reported by Dorn (1989a) only six include the presence of any detectable Ba. For the other 111 samples, representing 95% of the total analyses, no Ba greater than .01 percent is reported. In addition, we have found Ba in rock varnish on all geomorphic surfaces examined in the Crater Flat area. These sites include several lava flows and colluvial boulder deposits in addition to sites on more than a dozen alluvial surfaces. Dorn (1989a), in contrast, reported Ba in samples from only two of 17 geomorphic surfaces in Crater Flat, and for these two surfaces only half of the total samples were reported to contain any Ba. Sites reported by Dorn (1989a) to contain no Ba include three lava flows where we found average Ba concentrations of approximately 0.5 wt% and three alluvial surfaces of similar estimated age to surfaces where we found pervasive Ba (Table 2).

The lack of reported Ba in the varnish analyses of Dorn (1989a) from the same region where we show an almost universal presence of Ba strongly suggests that Ba was not quantified and that decomposition of Ba-Ti peak overlaps was not adequately performed for his PIXE analyses. Therefore, we believe that the Dorn (1989a) data are biased by erroneously high Ti values in much the same manner as were our earlier SSQ analyses.

Barium in rock varnish seems to be generally associated with Mn, shown by strong positive correlations of Ba and Mn in line transects through varnish cross-sections (Figs. 2b and 3; see also Raymond et al., 1991, this issue). Although in some analyses barite ( $\text{BaSO}_4$ ) grains are evidenced by a coincidence of distinct Ba and S peaks (Fig. 2b), Ba and S concentrations commonly have no distinct correlation in line transects (Fig. 3). Thus, Ba concentrations can not be correlated directly with barite occurrence. Rather, Ba content is typically correlative with Mn concentration.

### Conclusions

In environments such as southern Nevada, Ba occurrence in rock varnish is apparently ubiquitous. If Ba and Ti peak overlaps are not adequately decomposed during chemical analyses of rock varnish, any rock varnish dating curve calibrated using such erroneously high Ti values will be lower than curves developed using Ti values decomposed from Ba. Therefore, we emphasize the need to re-evaluate all rock varnish dating curves

and to refine them as appropriate.

The inadequacy of SSQ to provide reliable Ti concentrations in the presence of Ba suggests the need for re-analysis, using either MICRO Q or SQ, of the rock varnish samples used in the calibration of the rock varnish dating curve of Harrington and Whitney (1987). Similarly, the absence of Ba in PIXE analyses reported by Dorn (1989a), despite the widespread occurrence of Ba in rock varnishes of this region and in other parts of the Southwest, suggests the need for a re-evaluation of his rock varnish chemical data. In particular, we suggest that the rock varnish dating curves generated from these reported PIXE data are suspect, as are any rock varnish dating curves derived from chemical data obtained in a similar fashion.

Finally, available data suggest a correlation of Ba concentration with varnish age. This in turn suggests the possibility that Ba might be useful as a standard elemental component in cation ratio calculations for rock varnish dating.

### Acknowledgments

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#### Discussion with Reviewers

**J.A. Minkin:** In PIXE analysis the penetration of the beam into the target is much greater than for SEM or EPM (probably up to 20 times as great), and thus the volume sampled in each analysis is much greater in PIXE. Do you think this can account for the discrepancies in the amount of Ba detected by the different methods?

**Authors:** It should be noted that the PIXE analyses of Dorn (1989a) are made of powdered rock varnish that has been scraped off the substrate on which it was accreted, whereas our varnish analyses are made of in situ rock varnish obtained by coring through the varnish into the substrate (see Materials and Method section). Although we find the concentration of Ba to be variable in analyses of both varnish surfaces and cross-sections, it is consistently present at higher concentrations than reported in Dorn (1989a). Therefore, we believe that the lower Ba concentrations reported by Dorn are not due to analyzing a larger volume of rock varnish.

**J. A. Minkin:** Are the cation ratios for Dorn's PIXE analyses in Fig. 5 determined for the same samples as those represented by your SEM analyses? If so, can you suggest what significance there may be to the fact that the two PIXE analyses lie between your SEM data corrected and uncorrected for Ba?

**Authors:** The samples used for Dorn's PIXE analyses are not the same as those used for our SEM analyses. However, the samples used for the PIXE analyses were obtained from similar types and ages of surfaces within the same geographic area (Crater Flat) of southern Nevada as were the bulk of the samples we analyzed by SEM. We suggest that the discrepancies between our cation ratios, calculated using Ti and Ba values where decomposition has been performed, and the PIXE analyses, may indicate that even if Ba-Ti decomposition is being performed with the reported PIXE analyses, this decomposition is not adequate and the reported Ti concentrations are still erroneously high.

**R.I. Dorn:** There is a misunderstanding of how to read Table 6 in Dorn (1989a). Table 6 is a direct output of my computer data file. 0.00 was entered if the element is below the limit of detection or if elements were not specifically requested by the user. I forgot to specifically request Ba and many other elements in the output reported in Table 6. Even though Ba was not specifically requested, the laboratory analyzing the samples reported anomalously high levels of Ba in six samples; only anomalously high results were reported in the hard copy

output sent to me and these were included in Dorn, 1989a. More typical values were not sent and therefore were not included. I apologize for a confusion that is my fault.

**Authors:** Indeed it is difficult to compare data when values reported as 0.00 in fact represent values that are anything less than "anomalously high" (< 0.51 wt%, minimum concentration of Ba reported in Table 6, Dorn, 1989a). We note that the average Ba concentration for our 250 analyses was > 1.5 wt% (see text, Fig. 6), higher by a factor of three than the values reported as "anomalously high" by Dorn. In addition, the average Ti concentration within our samples is 0.38 wt% compared to an average value of 1.66 wt% for the samples of Dorn (1989a). Thus, our Ti concentrations are lower by a factor of > 4. We feel, therefore, that until it has been demonstrated that the PIXE analyses incorporate a reliable Ba-Ti decomposition that any curves derived from such data should still be considered suspect.

**R.I. Dorn:** The authors stress a significant difference between the amount of Ba found by Dorn (1989a) and their results. Because I agree this is an issue that needs to be resolved, it is imperative that the authors clearly present their criteria for (a) how they select varnish to be sampled in the field and (b) whether they analyze every sample collected in the field; if not, how they select the field samples to analyze. Selection criteria that I use are detailed in Dorn (1989a), Krinsley et al. (1990), and Dorn et al. (1990). The authors do not specify in this paper how the 10 to 12 clasts measured from each site are selected. I suspect that different types of samples are being compared, because I get anomalously high barium results if samples are collected differently (Dorn et al., 1990) and because comparisons of PIXE with ICP-AES and wavelength dispersive microprobe on the same samples yield similar (K+Ca)/Ti ratios (Dorn, 1989b; Dorn et al., 1990). Their claims can not be assessed properly unless the authors are as explicit as possible on how they decide which varnishes to analyze.

**Authors:** We note that the implied high accuracy of Ba measurements by PIXE analyses has never been demonstrated. Before the role of sampling protocol can be considered as a factor in producing variations in the chemical constituents of rock varnish, the accuracy of measurements by analytical systems and procedures need to be established.

The ubiquitous presence of Ba in our rock varnish samples that were collected over a period of three years argues strongly that our chemical data are not simply an artifact of a sampling bias. Analyzed samples were collected from alluvial surfaces, lava flows, hillside boulder deposits, and debris flow lobes from southern Nevada, southern California, northern Arizona, and New Mexico, and from a variety of orientations and topographic positions on sampled surfaces. In addition to criteria outlined in Harrington and Whitney (1987), the samples were collected consistent with most of the



criteria discussed by Dorn (1983). Thus, we suggest that the near universal presence of Ba within our samples implies a widespread and common occurrence of Ba in rock varnishes of the southwestern U.S.

**J.A. Minkin:** I think deconvolution is a more suitable word than decomposition, as used numerous times in this paper. Decomposition has a strong chemical connotation, whereas deconvolution is, I believe, more generally used with reference to curve stripping (which is indeed what you are doing).

**Authors:** In previous versions of this paper we used "deconvolution" instead of "decomposition" until a colleague pointed out to us that, by a strict mathematical definition, elemental peak stripping routines used in energy dispersive analyses are not deconvolutions. Standard peak stripping routines use a multiple least-squares curve fitting procedure. In contrast, a convolution is the product of Fourier transforms of two functions and true deconvolutions consist of a more involved mathematical procedure. We have chosen to use decomposition as a more generic term for any peak stripping routine. We see no problem with the chemical implication associated with the term decomposition, for indeed we are determining the chemistry of the analytical point.

**J.A. Minkin:** What are the minimum detection limits (MDL's) for your SEM analyses? Are the weight percents of TiO<sub>2</sub> (Fig. 2a) and S (Fig. 2b) really above the MDL's?

**Authors:** MDL's for our SEM analyses were calculated as three standard deviations above the intensity (measured as count rate) of the background. MDL's for elements in our rock varnish analyses vary between 0.13 wt% and 0.08 wt% as counting dead time varies between 15% and 40%. Thus, the trends defined by TiO<sub>2</sub> and S in Figs. 2a and 2b reflect analyses above MDL's.

**P.R. Bierman:** Are there peak overlaps other than Ti-Ba which could result in poor accuracy when using an EDS to gather x-ray spectra?

**Authors:** In an EDS analysis of rock varnish there is also an overlap of the K K<sub>β</sub> peak with the Ca K<sub>α</sub> peak. The effect of this overlap, if not decomposed during analysis, would be to increase the concentration of Ca relative to its true value and thus result in cation ratios that were erroneously high. The Tracor Northern programs MICRO Q and SQ perform a decomposition of the Ca-K overlap during analyses in the same manner as the Ba-Ti peak overlap and yield slightly different values for K and Ca than are obtained using the Tracor SSQ program in which no decomposition is performed.

**P.R. Bierman:** What physical or chemical factors could change the concentration of Ba in varnish with age and with topographic position?

**Authors:** Although little is yet known regarding the factors that control Ba concentrations in rock varnish, it is logical to assume that Ba is brought to the rock varnish as part of the eolian detrital contribution. As such, factors that control or affect the nature and supply of eolian detritus (e.g., climatic changes within the source region for the eolian detritus) likely play an important role in controlling Ba supply to varnish surfaces through time. In addition, as Ba is apparently associated with the Mn component of varnish, as yet undetermined factors that affect Mn concentration may also affect Ba concentration.

#### Additional References

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