

Accuracy of rock-varnish chemical analyses: Implications for cation-ratio dating

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ABSTRACT

To compare methods of rock-varnish chemical analysis and cation-ratio determination, we prepared three glass standards, synthetic analogues of rock varnish. Analysis of these standards demonstrates that material of varnishlike composition can be accurately and precisely analyzed by means of quantitative, energy-dispersive electron microscopy (SEM-EDS). However, a blind interlaboratory comparison and reexamination of published data show that most published cation ratios of varnish are probably inaccurate because the technique used most frequently to determine rock-varnish composition, proton-induced X-ray emission (PIXE), did not accurately measure the concentration of Ti in the presence of Ba, a ubiquitous component of rock varnish. This inaccuracy suggests that the premise of cation-ratio dating and dates generated by this method should be reevaluated.

INTRODUCTION

Rock-varnish cation-ratio dating of geomorphic surfaces was first proposed nine years ago (Dorn and Oberlander, 1981) and is based on the premise that in rock varnish, the ratio (Ca + K)/Ti decreases with exposure age. Numerical ages have been generated by using calibration curves constructed from cation-ratio determinations made on independently dated surfaces.

The method has been used, almost exclusively by R. I. Dorn and co-workers, to date a variety of Pleistocene and Holocene arid-region surfaces including lava flows, shorelines, alluvial fans, glacial moraines, artifacts, petroglyphs, and colluvial deposits (Dorn, 1983, 1989a, 1989b; Dorn and Oberlander, 1981; Dorn et al., 1986, 1987, 1990; Nobbs and Dorn, 1988). Results of rock-varnish cation-ratio dating have been used to revise the Sierra Nevada glacial chronology (Dorn et al., 1990), to challenge accepted petroglyph chronologies (Nobbs and Dorn, 1988) and to characterize seismic and volcanic hazards near the proposed Yucca Mountain high-level waste repository (Dorn, 1989a). Harrington and Whitney (1987), Pineda et al. (1988), Dethier et al. (1988), and Liu and Zhang (1990) have observed temporal changes in what were presumed to be three-element rock-varnish cation ratios. Of these other workers, only Dethier and Harrington have used cation ratios to date geomorphic surfaces.

Most published cation ratios (those of R. I. Dorn and co-workers) have been determined by proton-induced X-ray emission at the University of California, Davis (PIXE UCD). Cation ratios

have also been determined by electron microscopy using energy-dispersive (SEM-EDS, also referred to as SEM-EDAX) and wavelength-dispersive spectrometers (SEM-WDS) (Harrington and Whitney, 1987; Dethier et al., 1988; Dragovich, 1988; Dorn, 1989a, 1989b; Dorn et al., 1990). Dorn (1989b) and Dorn et al. (1990) determined ratios by inductively coupled argon-plasma spectroscopy (ICP). Dorn (1983) determined ratios by using X-ray fluorescence (XRF—unspecified detector).

Meaningful cation-ratio dates will be generated only if the three-element ratio (Ca + K)/Ti is accurately determined. However, the accuracy of methods used to determine this ratio has never been demonstrated by analysis of standards of varnishlike composition. Of particular concern is the accurate measurement of Ti because (1) if Ba is also present, the concentration of Ti is difficult to measure by energy-dispersive (EDS) X-ray fluorescence (XRF) techniques such as SEM-EDS, XRF-EDS, and PIXE (Fig. 1; Cahill, 1975; Harrington et al., 1990; Dorn, 1989a, 1989b; Dorn et al., 1990) and (2) published analyses of rock varnish, made by methods known to measure Ba and Ti accurately, indicate that they are both present in varnish at concentrations of 5000 to 15000 ppm (Engle and Sharp, 1958; Bard, 1979; Dragovich, 1988; Harrington et al., 1990; Dorn, 1980, 1989b; Dorn et al., 1990; Raymond et al., 1990). Ba does not affect Ti measurements made by neutron-activation analysis (NAA), ICP, SEM-WDS, and XRF-WDS.

Because we are using SEM-EDS (Bierman et

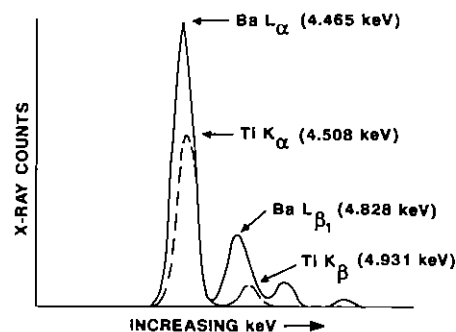


Figure 1. Ti K and Ba L peaks overlap in energy-dispersive X-ray spectra. If Ba peaks are not deconvolved, apparent Ti K_{α} (4.508 keV) and K_{β} (4.931 keV) peaks shift to lower energies as they are superimposed upon Ba L_{α} (4.465 keV) and L_{β} (4.828 keV) peaks.

al., 1991) to determine varnish chemistry and because the accuracy of SEM-EDS measurements of Ti has been questioned (Dorn, 1989a, 1989b; Dorn et al., 1990), we prepared standards of specific composition to test the accuracy of our analyses. To allow meaningful comparison of our SEM measurements of varnish chemistry with those made by other methods, we conducted a blind interlaboratory test. We used synthetic varnish standards because, in contrast to natural varnish, these standards are of known composition.

METHODS

Using reagent-grade chemicals, we prepared three glass analogues of rock varnish spanning

Note: Additional material for this article is Supplementary Data 9108, available on request from the GSA Documents Secretary (see footnote 1).

the range of Ba/Ti and cation ratios measured in natural varnish. In a blind test, aliquots of the glasses were analyzed by XRF-WDS, ICP, PIXE UCD, and PIXE microprobe (PIXE MCP). We analyzed other aliquots at the University of Washington (UW) by quantitative SEM-EDS and SEM-WDS.¹ Varnish standards are available from Bierman.

ANALYTICAL RESULTS AND DISCUSSION

The chemical composition and cation ratios of synthetic rock-varnish standards determined

¹Detailed Methodology, GSA Supplementary Data 9108, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301.

by quantitative, standard-based SEM-EDS agree with known compositions and are similar to those determined by most other methods (Table 1, Fig. 2).

However, our interlaboratory comparison shows that cation ratios and concentrations measured by PIXE UCD are inaccurate (Table

1, Fig. 2). There are two sources of error in PIXE UCD cation-ratio determinations, (Ca + K) and Ti. The error in (Ca + K) is similar for all three synthetic varnishes, is not correlated with Ba content, and averages 16%; in contrast, the

Figure 2. SEM-EDS cation ratios are accurate and comparable to those measured by all other methods except PIXE UCD. PIXE UCD error increases with Ba/Ti ratio, suggesting that Ba, included in Ti abundances, lowers cation ratio. Uncertainties, calculated according to Bierman et al. (1991), are shown if they exceeded width of symbol. Ratios in same order for FV-1 and FV-3 as for FV-2. CR = cation ratio, (K + Ca)/Ti.

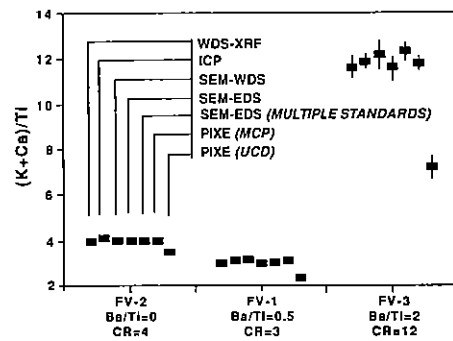


TABLE 1. COMPOSITION OF SYNTHETIC VARNISH STANDARDS

TECHNIQUE: LAB:	MIXTURE	XRF/WDS LANL	ICP UW	SEM/WDS UW	SEM/EDS ⁺ UW	SEM/EDS [*] UW	PIXE/MCP LANL	PIXE UCD
Glass FV-1 (Ba/Ti = 0.5)								
Number of analyses:		1	6	12	8	11	3	5
SiO ₂	49.54	48.36 +/- 0.44	48.64 +/- 0.13	48.39 +/- 0.21	48.12 +/- 0.33	49.24 +/- 0.24	NA	25.05 +/- 1.61
Al ₂ O ₃	22.92	23.11 +/- 0.13	22.54 +/- 0.03	22.90 +/- 0.11	22.67 +/- 0.19	23.52 +/- 0.12	NA	14.12 +/- 1.06
Fe ₂ O ₃	11.83	11.96 +/- 0.28	11.71 +/- 0.05	11.46 +/- 0.11	12.07 +/- 0.15	11.65 +/- 0.1	NA	10.68 +/- 2.09
MnO	7.12	7.76 +/- 0.01	7.62 +/- 0.05	7.61 +/- 0.05	8.39 +/- 0.05	7.51 +/- 0.04	NA	7.62 +/- 1.19
MgO	1.83	1.89 +/- 0.69	1.87 +/- <.01	1.89 +/- 0.01	1.70 +/- 0.03	1.94 +/- 0.05	NA	<0.06
TiO ₂	1.84	1.85 +/- 0.03	1.75 +/- 0.01	1.74 +/- 0.04	1.95 +/- 0.03	1.81 +/- 0.02	2.13 +/- 0.02	1.91 +/- 0.11
BaO	0.62	0.54 +/- 0.01	0.54 +/- <.01	0.58 +/- 0.02	0.54 +/- 0.03	0.63 +/- 0.02	0.59 +/- 0.02	<0.02
K ₂ O	1.99	1.95 +/- 0.02	1.89 +/- 0.04	1.96 +/- 0.01	2.10 +/- 0.03	1.98 +/- 0.02	2.46 +/- 0.05	1.60 +/- 0.08
CaO	2.31	2.38 +/- 0.06	2.40 +/- <.01	2.35 +/- 0.01	2.45 +/- 0.01	2.32 +/- 0.02	2.72 +/- 0.05	1.87 +/- 0.09
Na ₂ O	0.00	0.10 +/- 0.20	0.18 +/- <.01	NA	NA	0.21 +/- 0.03	NA	<0.25
TOTAL	100.00	99.90	99.14	98.88	100.00	100.60		62.85
(K+Ca)/Ti &	3.00	3.00 +/- 0.07	3.13 +/- 0.03	3.17 +/- 0.07	3.00 +/- 0.05	3.05 +/- 0.04	3.12 +/- 0.05	2.33 +/- 0.16
(K+Ca)/Ti #		(n = 1)	**	3.18 +/- 0.09	3.00 +/- 0.03	3.05 +/- 0.04	3.11 +/- 0.07	2.32 +/- 0.05
Glass FV-2 (Ba/Ti = 0)								
Number of analyses:		1	6	12	8	10	3	5
SiO ₂	50.96	49.84 +/- 0.44	49.58 +/- 0.02	49.27 +/- 0.75	48.98 +/- 1.32	50.27 +/- 0.88	NA	27.82 +/- 2.78
Al ₂ O ₃	22.76	23.20 +/- 0.13	22.60 +/- 0.03	23.14 +/- 0.22	22.98 +/- 0.78	23.93 +/- 0.54	NA	15.29 +/- 1.78
Fe ₂ O ₃	11.74	12.03 +/- 0.28	11.65 +/- 0.06	11.49 +/- 0.15	12.00 +/- 0.28	11.73 +/- 0.21	NA	13.31 +/- 2.95
MnO	7.07	7.74 +/- 0.01	7.57 +/- 0.07	7.67 +/- 0.03	8.38 +/- 0.11	7.58 +/- 0.12	NA	7.45 +/- 1.65
MgO	1.82	1.98 +/- 0.69	1.85 +/- <.01	1.90 +/- 0.02	1.75 +/- 0.14	1.98 +/- 0.06	NA	<0.06
TiO ₂	1.37	1.38 +/- 0.03	1.32 +/- 0.01	1.36 +/- 0.04	1.44 +/- 0.03	1.36 +/- 0.02	1.56 +/- 0.02	1.31 +/- 0.14
BaO	0.00	<0.01	<0.02	<0.02	<0.02	<0.03	<0.006	<0.02
K ₂ O	1.98	1.90 +/- 0.02	1.86 +/- 0.05	1.93 +/- 0.03	2.04 +/- 0.09	1.92 +/- 0.07	2.22 +/- 0.03	1.62 +/- 0.13
CaO	2.30	2.37 +/- 0.06	2.41 +/- 0.02	2.35 +/- 0.02	2.44 +/- 0.03	2.32 +/- 0.03	2.65 +/- 0.09	1.97 +/- 0.19
Na ₂ O	0.00	0.04 +/- 0.20	0.27 +/- 0.20	NA	NA	0.19 +/- 0.03	NA	<0.25
TOTAL	100.00	100.28	99.11	99.11	100.01	101.07		68.77
(K+Ca)/Ti &	4.00	3.96 +/- 0.10	4.13 +/- 0.06	4.03 +/- 0.12	3.99 +/- 0.12	4.01 +/- 0.09	4.00 +/- 0.09	3.51 +/- 0.44
(K+Ca)/Ti #		(n = 1)	**	4.02 +/- 0.09	3.98 +/- 0.08	4.01 +/- 0.09	3.99 +/- 0.07	3.51 +/- 0.14
Glass FV-3 (Ba/Ti = 2)								
Number of analyses:		1	6	12	10	8	3	5
SiO ₂	51.11	49.83 +/- 0.44	50.09 +/- 0.26	49.21 +/- 0.61	49.81 +/- 0.37	50.95 +/- 0.24	NA	28.73 +/- 1.98
Al ₂ O ₃	22.83	23.20 +/- 0.13	22.57 +/- 0.33	22.78 +/- 0.11	22.60 +/- 0.15	23.56 +/- 0.08	NA	15.84 +/- 1.15
Fe ₂ O ₃	11.78	11.95 +/- 0.28	11.73 +/- 0.04	11.47 +/- 0.11	12.05 +/- 0.18	11.73 +/- 0.1	NA	14.98 +/- 1.47
MnO	7.09	7.74 +/- 0.01	7.58 +/- 0.05	7.57 +/- 0.04	8.35 +/- 0.05	7.52 +/- 0.03	NA	8.36 +/- 0.78
MgO	1.82	1.79 +/- 0.69	1.78 +/- <.01	1.82 +/- 0.01	1.62 +/- 0.05	1.87 +/- 0.08	NA	<0.06
TiO ₂	0.46	0.47 +/- 0.03	0.46 +/- 0.01	0.45 +/- 0.04	0.50 +/- 0.03	0.44 +/- 0.02	0.57 +/- 0.01	0.63 +/- 0.05
BaO	0.61	0.55 +/- 0.01	0.54 +/- <.01	0.57 +/- 0.02	0.57 +/- 0.02	0.64 +/- 0.05	0.68 +/- 0.01	<0.02
K ₂ O	1.98	1.92 +/- 0.02	1.88 +/- 0.04	1.94 +/- 0.02	2.09 +/- 0.03	1.96 +/- 0.01	2.49 +/- 0.04	1.64 +/- 0.14
CaO	2.31	2.35 +/- 0.06	2.39 +/- 0.01	2.34 +/- 0.01	2.42 +/- 0.01	2.28 +/- 0.01	2.74 +/- 0.06	1.90 +/- 0.17
Na ₂ O	0.00	0.08 +/- 0.20	0.26 +/- 0.20	NA	NA	0.22 +/- 0.04	NA	<0.25
TOTAL	100.00	99.88	99.28	98.15	100.01 ++	100.95		72.08
(K+Ca)/Ti &	12.00	11.63 +/- 0.76	11.86 +/- 0.28	12.18 +/- 1.08	11.57 +/- 0.70	12.30 +/- 0.53	11.79 +/- 0.26	7.21 +/- 0.73
(K+Ca)/Ti #		(n = 1)	**	12.40 +/- 1.11	11.64 +/- 0.35	12.34 +/- 0.55	11.76 +/- 0.06	7.22 +/- 0.17

Note: Uncertainties are one sample standard deviation except for XRF/WDS for which long-term average uncertainties are stated. NA = not analyzed.

& Cation ratio determined from average values for Ti, Ca, and K; uncertainty from standard error propagation (Bierman et al., 1991).

Cation ratio is average of multiple determinations; uncertainty is one sample standard deviation.

** Data reduction does not provide results for individual analyses.

* Multiple standards used for calibration.

+ Results normalized to 100%.

error in PIXE UCD Ti measurements is proportional to the amount of Ba in the synthetic varnish. For synthetic varnish FV-2, which contains no Ba, the measured concentration of Ti is 5% lower than the known value; it is 4% higher if Ba/Ti = 0.5 (FV-1) and 37% higher if Ba/Ti = 2 (FV-3). The undetected Ba in FV-1 and FV-3 lowers the cation ratio by raising the apparent concentration of Ti. For FV-2 (no Ba), cation ratios determined by PIXE UCD are 12% lower than the known value. PIXE UCD cation ratios are 23% lower for Ba/Ti = 0.5 (FV-1) and 40% lower for Ba/Ti = 2 (FV-3).

A shift in apparent Ti peak position, proportional to the amount of Ba in the synthetic varnish, indicates that PIXE UCD cation ratios are inaccurate primarily because Ba L_{α} and L_{β} X-ray counts are assigned to the Ti K_{α} and K_{β} X-ray peaks (Fig. 3). T. Cahill (1990, personal commun.) has suggested that by assuming the observed shift is a linear function of concentration and by incorporating a factor for the efficiency of X-ray generation, Ba/Ti can be estimated. Using this method, we calculated Ba/Ti ratios of 0.63 for FV-1 (Ba/Ti = 0.50) and 3.15 for FV-3 (Ba/Ti = 2.00). There is no indication that peak shift has ever been used to deconvolve PIXE spectra of rock varnish.

Although we attempted to duplicate the protocol used to generate previous PIXE UCD varnish analyses by contacting Dorn and by working with UCD, there may be minor and apparently inconsequential differences between our protocol and that used for previous varnish analyses: (1) Samples of synthetic varnish were mounted by UCD personnel, using a different substrate (Mylar) and adhesive (Apeizon) than that used by Dorn (Kapton and unspecified adhesive). (2) Synthetic varnish grains (5–20 μm) may be larger than those used by Dorn, although the magnitude of this discrepancy cannot be determined because the particle size used for previous PIXE varnish analyses has not been stated explicitly. (3) Our analyses were matrix corrected with the RACE program (Cahill,

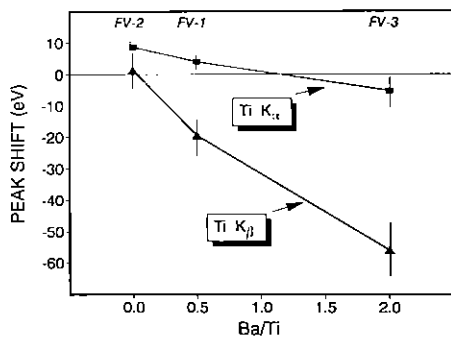


Figure 3. Center of apparent Ti K_{α} and L_{β} peaks undetected by PIXE UCD (see Fig. 1). Mean and sample standard deviation, five replicate analyses for each synthetic varnish.

1975) assuming a particle size of 8–16 μm , and it has not been specified whether matrix corrections were used for previous PIXE varnish analyses. (4) Although standards were run with our PIXE analyses, we present uncorrected PIXE data because there is no indication that previous PIXE rock-varnish analyses were corrected to standards.

T. Cahill, director of the Crocker Nuclear Lab (UCD), suggested (1990, personal commun.) how these differences might affect our analyses: (1) Substrate and adhesive are unimportant because PIXE spectra are blank corrected. (2) Grain size and matrix correction will preferentially affect concentrations reported for light elements such as Na, Mg, Si, and Al; values reported for heavier elements, such as Ti, Fe, Mn, and Ba, are less sensitive to grain size and matrix correction; the effects on (Ca + K) are moderate but must be $\leq 16\%$, the difference between PIXE UCD and the mixture values for the glasses. (3) Because Ba was not detected by PIXE UCD analyses, its concentration cannot be modified by matrix or standard correction.

Any errors in PIXE UCD analyses of synthetic varnish related to the above-mentioned factors are subordinate to those caused by inadequate Ba-Ti deconvolution because (1) the inaccuracy of Ti and cation-ratio measurements is proportional to the Ba/Ti ratio (Fig. 2) and (2) the Ba-dependent inaccuracy of Ti equals or exceeds the Ba-independent inaccuracy of (Ca + K) at Ba concentrations typical of rock varnish. It is important to consider that RACE software used at UCD was designed and tested not for analysis of compositionally complex geologic materials but for the analysis of $< 1\text{-}\mu\text{m}$ atmospheric particles of simple composition (T. Cahill, 1990, personal commun.).

IMPLICATIONS

Analysis of rock-varnish standards shows that quantitative SEM-EDS can accurately determine the abundance of Ba and Ti at concentrations typical of rock varnish if reference spectra are used for deconvolution. This finding supports Harrington et al. (1990) and contradicts Dorn (1989a, 1989b) and Dorn et al. (1990). Dorn has not specified the software, equipment, or operating conditions he used to make SEM-EDAX (EDS) measurements; however, his SEM-EDAX protocol must differ from that used in this study and in Harrington et al. (1990) because of its stated inability to deconvolve Ba-Ti X-rays.

Our analyses of synthetic rock varnish support assertions of Harrington et al. (1990) and suggest that most published cation ratios are inaccurate, because PIXE UCD was incapable of measuring accurately the concentration of Ti in the presence of Ba. This inaccuracy is specific to the UCD RACE program, rather than the PIXE method, because PIXE microprobe software

used by Los Alamos National Laboratory (LANL, Table 1) can accurately deconvolve Ba and Ti X-rays.

Published data support our finding that PIXE UCD analyses are flawed. Dorn et al. (1990, Fig. 4b) reported that of > 100 rock-varnish samples collected from the Coso Range and analyzed by ICP, most contain Ba (median concentration Ba ≈ 0.5 wt%). However, Dorn (1989a) also demonstrated that cation ratios of varnish samples collected from 16 calibration sites in the Coso Range and analyzed by both PIXE and SEM-EDAX were well correlated (Fig. 4). Because Dorn has not been able to separate Ba and Ti with SEM-EDAX deconvolution programs (Dorn et al., 1990, p. 4), the correlation between PIXE and SEM-EDAX suggests that both methods included Ba X-rays in the Ti peak, raising the apparent concentration of Ti and lowering the calculated cation ratio.

The problem of correctly deconvolving Ba and Ti X-rays is not limited to PIXE UCD or to the SEM-EDAX software used by Dorn; most, if not all, previously published cation-ratio calibration curves appear to be similarly flawed. Ba and Ti were not deconvolved in either Harrington and Whitney (1987) or Dethier et al. (1988) (see Harrington et al., 1990). Data of Pineda et al. (1988) show the apparent Ti peak shift we observed, and Liu and Zhang (1990) did not mention deconvolution of Ba and Ti.

Only a few published analyses of rock varnish are unaffected by problems in measurement of Ti and Ba. Bard (1979) scraped varnish from petroglyphs of well-documented typological age and measured the abundance of 32 elements using NAA (not susceptible to Ba-Ti overlap); only Ba showed a simple trend with typological age (Fig. 5). Although Dorn (1983, p. 50) suggested that the ratio of Ca/Ti should decrease with age, Bard's data show no such trend.

Concentrations of Ba and Ti are not strongly

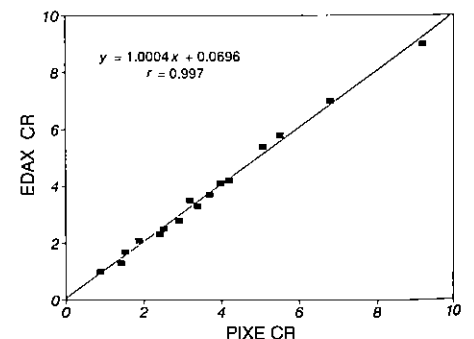
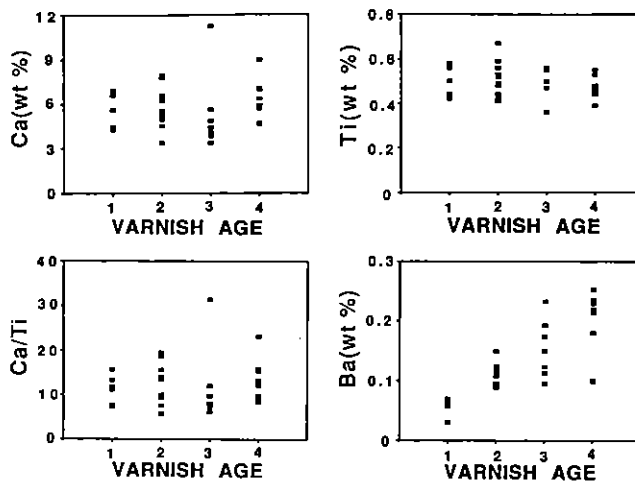


Figure 4. PIXE UCD and SEM-EDAX cation ratios (CR) from 16 sites in Coso Range (Dorn, 1989a, Table 3). Because Coso varnishes contain Ba (Dorn et al., 1990) and because SEM-EDAX used by Dorn (1989a, 1989b) cannot deconvolve Ba and Ti X-rays, this correlation suggests that PIXE UCD is also incapable of accurately measuring Ti in presence of Ba.

Figure 5. NAA data from Bard (1979, Table 19). Relative varnish age (1 = youngest, 4 = oldest) based on typological analysis of petroglyphs from which it was scraped. No change with assumed age is shown for Ca, Ti, or Ca/Ti, a ratio that should decrease with age (Dorn, 1983). Ba increases with age.



correlated in rock varnish (S. Reneau, 1990, personal commun.), so it is not possible to correct published cation ratios retrospectively for previously undetected Ba. Nor is it possible to replicate previously published, Ba-contaminated, three-element curves by using an accurately determined four-element ratio $(Ca + K)/(Ti + Ba)$ (S. Reneau, 1990, personal commun.). However, Raymond et al. (1990) have shown a strong spatial correlation between the concentration of Ba and Mn in rock varnish; this suggests that changes in Mn concentration could affect cation ratios. We and workers at Los Alamos are testing the temporal significance of Raymond et al.'s observations.

The effect of inaccurate chemical analyses on the accuracy of published cation-ratio dates is not clear. Previous workers have found a systematic change with time in what were previously assumed to be three-element cation ratios, despite or because of the inclusion of an undetermined amount of Ba. However, the apparent inaccuracy of previous analyses, the lack of standards of varnishlike composition, and the ubiquitous presence of Ba in rock varnish cast doubt on the empirically determined central premise of cation-ratio dating, the systematic change in a three-element cation ratio. It is possible that Ba, either alone or coupled with changes in Mn, Ca, K, and Ti, could account for the apparent temporal trends in cation ratios. Because of these uncertainties and because there is no theoretical or experimental verification that the ratio of $(Ca + K)/Ti$ changes with time in varnish, we suggest that the basic assumptions underlying the use of the cation-ratio method as a dating tool be reexamined. We urge caution in the acceptance and use of existing cation-ratio ages.

NOTE ADDED AFTER REVIEW

Concurrent with submission of this paper for review, we made available to participating laboratories the results of all analyses. Subsequently, T. Cahill (director, Crocker Nuclear

Lab, UCD) notified us that a change had been made to the RACE program (September 1990) that allowed Ba to be identified in at least two of our 15 samples. He suggested that the ability to discriminate Ba was diminished when the UCD PIXE system was reconfigured in late 1986. The efficiency of Ba-Ti deconvolution by RACE prior to 1986 cannot be determined rigorously because the system and the computer code used to analyze spectra have been dismantled; however, the close correlation between Dorn's SEM-EDAX and PIXE data for the Coso Range (Fig. 4) strongly suggests that Ba and Ti were not accurately deconvolved by PIXE UCD even before the 1986 reconfiguration.

REFERENCES CITED

- Bard, J.C., 1979, The development of a patination dating technique for Great Basin petroglyphs using neutron activation and X-ray fluorescence analysis [Ph.D. thesis]: Berkeley, University of California, 409 p.
- Bierman, P.R., Gillespie, A.R., and Kuehner, S.M., 1991, Precision of rock-varnish cation-ratio ages: *Geology* (in press).
- Cahill, T.A., 1975, Ion excited X-ray analysis of environmental samples, in Ziegler, J.F., ed., *New uses of ion accelerators*: New York, Plenum, p. 1-67.
- Dethier, D.P., Harrington, C.D., and Aldrich, M.J., 1988, Late Cenozoic rates of erosion in the western Espanola Basin, New Mexico: Evidence from geologic dating of erosion surfaces: *Geological Society of America Bulletin*, v. 100, p. 928-937.
- Dorn, R.I., 1980, Characteristics and origin of rock varnish [B.S. thesis]: Berkeley, University of California, 409 p.
- 1983, Cation-ratio dating: A new rock varnish age-determination technique: *Quaternary Research*, v. 20, p. 49-73.
- 1989a, A critical evaluation of cation-ratio dating of rock varnish, and evaluation of its application to the Yucca Mountain repository by the Department of Energy and its subcontractors, in Nevada nuclear waste site investigation, Evaluation of the geologic relationships and seismotectonic stability of the Yucca Mountain area: Reno, Nevada, Mackay School of Mines, Appendix A.
- 1989b, Cation-ratio dating of rock varnish: A geographic assessment: *Physical Geography*, v. 13, p. 559-596.

- Dorn, R.I., and Oberlander, T.M., 1981, Rock varnish origin, characteristics and usage: *Zeitschrift für Geomorphologie*, v. 25, p. 420-436.
- Dorn, R.I., and 11 others, 1986, Cation-ratio and accelerator radiocarbon dating of rock varnish on Mojave artifacts and landform surfaces: *Science*, v. 231, p. 830-833.
- Dorn, R.I., Turrin, B.D., Jull, A.J., Linick, T.W., and Donahue, D.J., 1987, Radiocarbon and cation-ratio ages for rock varnish on Tioga and Tahoe morainal boulders of Pine Creek, eastern Sierra Nevada, California, and their paleoclimatic implications: *Quaternary Research*, v. 28, p. 38-49.
- Dorn, R.I., Cahill, T.A., Eldred, R.A., Gill, T.E., Kushko, B.H., Bach, A.J., and Elliot-Fisk, D.L., 1990, Dating rock varnish by the cation ratio method with PIXE ICP, and the electron microprobe: *International Journal of PIXE*, v. 1.
- Dragovich, D., 1988, A preliminary electron probe study of microchemical variations in desert varnish in western New South Wales, Australia: *Earth Surface Processes and Landforms*, v. 13, p. 259-270.
- Engle, C.G., and Sharp, R.P., 1958, Chemical data on desert varnish: *Geological Society of America Bulletin*, v. 69, p. 487-518.
- Harrington, C.D., and Whitney, J.W., 1987, Scanning-electron microscope method for rock varnish dating: *Geology*, v. 15, p. 967-970.
- Harrington, C.D., Reneau, S.L., Raymond, R., and Krier, D.J., 1990, Barium concentrations in rock varnish: Implications for calibrated rock-varnish dating curves: *Scanning Microscopy International*.
- Liu, T., and Zhang, Y., 1990, Establishment of a cation-leaching curve of varnish for the Dunhuang region, western China (in Chinese, translation supplied by R. I. Dorn, 1989): *Seismology and Geology*.
- Nobbs, M., and Dorn, R.I., 1988, Age-determinations for rock varnish formation with petroglyphs: Cation-ratio dating of 24 motifs from the Olary region of arid south Australia: *Rock Art Research*, v. 5, p. 108-146.
- Pineda, C.A., Peisach, M., and Jacobson, L., 1988, Ion beam analysis for the determination of cation-ratios as a means of dating southern African rock art: *Nuclear Instruments and Methods in Physics Research*, v. B35, p. 463-466.
- Raymond, R., Reneau, S.L., and Harrington, C.D., 1990, Elemental relationships as seen with SEM/EDX elemental line profiling: *Scanning Microscopy International*.

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