LETTER TO THE EDITOR

Comment on "Evidence Suggesting That Methods of Rock-Varnish Cation-Ratio Dating Are neither Comparable nor Consistently Reliable," by P. R. Bierman and A. R. Gillespie

In their recent paper on cation-ratio dating of rock varnish, Bierman and Gillespie (1994) describe how they collected and analyzed rock varnish from late Holocene chert artifacts, surface clasts, and from chert bedrock at a prehistoric quarry site they believed to be "older." No independent age verification was available, however, for any of the samples at this archeological site. They used both of the published techniques of varnish cation-ratio dating (Dorn, 1983; Harrington and Whitney, 1987) and the analytical results failed to produce lower cation ratios for samples believed by the authors to be older. Primarily on the basis of these results the authors seek to discredit cation-ratio dating as a useful chronometer. We believe that this is an example of "throwing the baby (cation-ratio dating) out with the bath water (a poorly conceived and executed study)." Additionally, we believe they have inappropriately generalized their results far beyond their specific study area by use of justifications such as "the varnish is chemically similar to other varnishes in the Southwest"; they have also drawn conclusions from weak inferences (e.g., "the results are not inconsistent with" their interpretations).

Several misconceptions and inappropriate conclusions about cation-ratio dating and specifically about *in situ* varnish analyses are presented in this study. We believe the investigators are incorrect in their assumptions or interpretations of the following points: (1) the suitability of chert as a varnish substrate; (2) the suitability for varnish cation-ratio dating of all clasts from a geomorphic surface; (3) the accuracy of SEM analytical procedures in *in situ* varnish analyses; (4) the suitability of evaluating only a three-element cation-ratio curve that does not include barium; and (5) the role of substrate inclusion in *in situ* varnish analyses. We address each point below.

1. Bierman and Gillespie assume chert is a representative and acceptable substrate on which to study varnish development and preservation.

No study on rock varnish has stated that all rock types varnish equally; neither has any study maintained that any rock type can be used for cation-ratio dating. Bierman and Gillespie (1994) took the approach that *every rock is a good rock* for surface dating, and nothing could be farther from the truth. We tested clasts on alluvial surfaces along Las Vegas Wash and in the North Las Vegas Valley to determine which rock types are better receptors for varnish development and which rock surfaces are the most stable, accreting varnish over long time periods. Chert clasts were common on these alluvial surfaces but proved to be inappropriate substrates for maximum varnish development. Although chert clasts possessed significant surface irregularities, commonly vertical-edged steps on the rock face, they lacked the surface microdepressions that are inherent on fine-grained sandstones or volcanic rocks. The varied development of rock varnish on surface clasts of an alluvial surface is shown in Figure 1, where varnish on different rock types ranges from nonexistent to well developed. If we were to attempt to determine the age of this surface, we would select only the clasts with well-developed varnish (which here are volcanic rocks and sandstones), not the poorly varnished (here the metaquartzites and chert) clasts.

Bierman and Gillespie (1994) assumed that varnish accumulates in the same manner on very young chert artifacts and on bedrock exposures composed of chert as it does on proven substrates such as fine-grained welded tuffs, basalts, and well-cemented fine-grained quartz sandstones. Indeed, this study confirms our own testing of the suitability of different rock types as hosts for varnish development: chert is an unsuitable rock type for cation ratio dating.

2. The authors assume that all clasts from a geomorphic surface record the same exposure history, and thus any subset of these clasts will yield consistent cation-ratio data.

Dethier and others (1988) demonstrated that piedmont and alluvial fan surfaces possess varied exposure histories, and rock varnish sampled across these surfaces is likewise variable in its age and degree of development. Because surfaces contain both young and fully mature subareas or clast populations, surface clasts, even on a surface of a single age, can present highly variable varnish histories. An appreciation of the evolution of alluvial surfaces led to the development of our sampling protocol, based on the assumption that the clasts most closely representing the exposure age of a surface are those with the
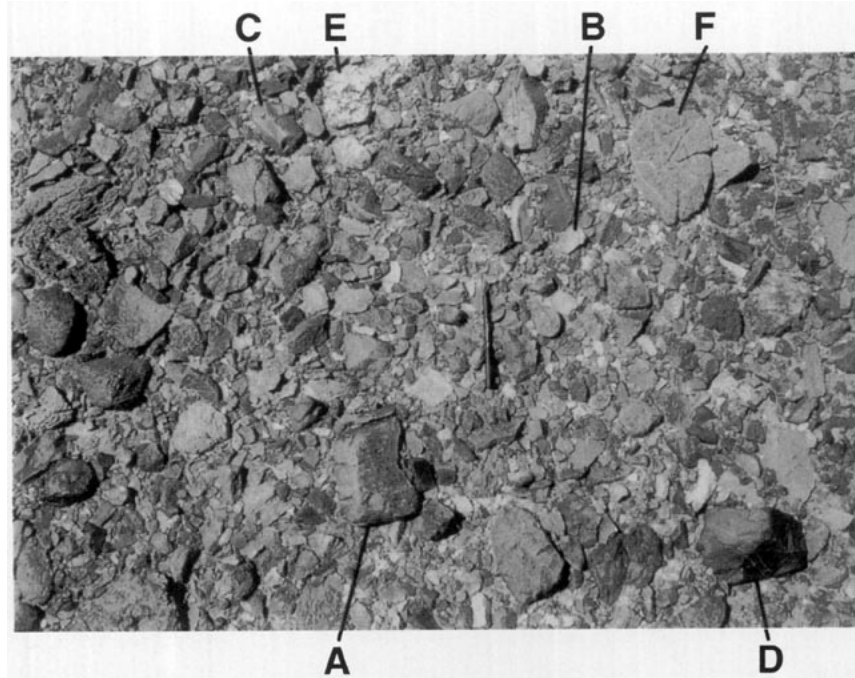
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FIG. 1.   Clasts of multiple rock types on an alluvial fan surface in Death Valley, California. Clasts A and B are metaquartzite or chert clasts with smooth surfaces and poorly developed rock varnish coatings. Clasts C and D are argillites with surface micro-roughness and well developed varnish coatings. Clasts E and F are clasts that are being actively weathered and possess unstable surfaces for varnish development. Other rock types on this surface record intermediate levels of varnish patination.

most developed (oldest) varnish (Harrington and Whitney, 1987; Whitney and Harrington, 1993). To maximize the probability of selecting the oldest clasts on a surface we originally collected ~20 clasts from a deposit or surface and then culled them to the best 8 to 10 clasts, based on the macroscopic quality of each varnish coat (Whitney and Harrington, 1993). This sample selection procedure reduces the analytic variability in varnish cation ratios for an individual deposit. Failure to follow a sampling strategy that assembles only the oldest varnished clasts on a geomorphic surface will combine the variation in varnish age of the collected clasts and the variation in rock varnish chemistry inherent in any group of varnished clasts. Analyses will then overstate the inconsistency in varnish chemistry and rock varnish age for the surface being analyzed.

Sampling considerations are critical in cation ratio dating of rock varnish. Detailed sampling strategies are an equally important component in the application of nearly all dating methods. K–Ar and Ar–Ar dating protocols, for example, exclude rocks that are vesicular, or weathered, or possess carbonate deposits in vesicles or along fractures, in addition to other imperfections. Collecting appropriate samples demands careful evaluation of many more candidates than those few ultimately selected for the dating application.

3. Bierman and Gillespie contend that *in situ* varnish measurements in which elemental concentrations are derived by comparison to standards produce results of high analytical accuracy.

The elemental abundances published by Bierman and Gillespie (1994) may not be accurate because the analytic program that was used compares data from rough, porous varnish surfaces to elemental concentrations for dense polished standards. Such analyses will commonly be inaccurate, and thus, the cation ratios calculated from these data will also be inaccurate, which may mask any trend in cation ratios that occurs within their analyzed varnish.

In situ varnish analyses on surfaces that possess appreciable micro-roughness (surface irregularity) are problematic in that irregularities on the analyzed surface produce scattering of the electron beam, resulting in either a greater or a lesser beam return than that produced when analyzing a polished surface. Additionally, (1) variable X-ray path lengths owing to topography of the rough samples will lead to different absorption-fluorescence interaction volumes in the unknown and standard; and (2) porosity and microstratigraphy in the *in situ* samples but not in the standards leads to complex X-ray scattering, different effective mass absorption coefficients, and an asymmetric volume of excitation in the unknowns. If the analytic program compares the X-ray beam return affected by surface scattering to the beam return from a polished standard, the resulting concentrations will be inaccurate—sometimes more and sometimes less than the real concentration in the sample, depending on whether the beam scattering and the variable X-ray paths focus more X-rays at the detector or disperse them so that fewer reach the detector. If one uses such data to

calculate a cation ratio, the resulting ratio will also be inaccurate, commonly differing from the true ratio by a greater degree than the inaccuracies in individual elemental concentrations.

In contrast, the scanning electron microscope (SEM) varnish analyses of Harrington and Whitney (1987), as well as those in Whitney and Harrington (1993), used a software program called SSQ (standardless semiquantitative) that uses elemental peak intensities (by integrating the area under the peak) to calculate elemental concentrations. The cation ratios they calculate are the ratios of these peak intensities. Because the cation ratio is a ratio determined from fluorescent emissions in a narrow energy range ($KK\alpha = 3.31$ keV; $CaK\alpha = 3.69$ keV; $TiK\alpha = 4.51$ keV; $BaL\alpha = 4.47$ keV), the effect of X-ray beam scattering and variable X-ray path lengths is similar for all the ratioed elements. Most importantly, as noted in our methodology paper (Harrington and Whitney, 1987), the concentration of individual elements may not be very accurate; however, the ratio among elements is accurate.

4. Bierman and Gillespie examined trends only in a three-element [$(K + Ca)/Ti$] cation ratio, although all earlier cation-ratio dating curves were calibrated using four-element ratios that included barium.

We believe it is inappropriate to compare three-element cation ratios derived with software programs that deconvolute peak overlaps and do not include Ba with earlier data generated by programs that do not deconvolute peak overlaps and therefore do incorporate Ba into the cation ratio calculated. We find it puzzling, especially in light of the acceptance by Bierman and Gillespie (1991) of the inclusion of Ba in earlier calibrated cation ratio curves, that they made no attempt to evaluate the role of barium in their present varnish study.

Harrington and others (1989) noted the presence of Ba in rock varnishes from Nevada and commented on the mismeasurement of part of this Ba as Ti in all earlier analyses of rock varnish that were made using analytical software (such as the SSQ program) that did not perform deconvolution of elemental peak overlaps. Harrington and others (1991) further noted that if elemental peaks were not deconvoluted, about a third of the Ba would be included as Ti. Thus, the cation ratio used to calibrate the cation ratio curves of Harrington and Whitney (1987), and Dethier and others (1988) is $(Ca + K)/Ti + \sim 1/3Ba)$ instead of $(Ca + K)/Ti$ as originally published.

Bierman and Gillespie (1991) also recognized that all earlier calibrated rock varnish curves include Ba as a component in the calculated cation ratios, and they cite the work of Bard (1979), who suggested that the only element in varnish to exhibit a trend with varnish age was Ba. Harrington and others (1991) and Bierman and Gillespie (1991) further suggest that the included Ba may contribute to the observed decrease in cation ratios with increasing rock varnish age.

The inability of Bierman and Gillespie to obtain a trend in the three-element cation ratio does not preclude the possibility of a trend in the cation ratio if Ba is included. In fact, their study suggests that Ba may be a significant, if not major, contributor to the decrease in cation ratios with varnish age.

5. Bierman and Gillespie contend that the trend of decreasing cation ratios with increasing varnish age is produced by the reduced incorporation of rock substrate into the varnish analyses.

Bierman and Gillespie (1994) and Reneau and Raymond (1991) suggest that the trend of decreasing cation ratios with increasing varnish age may be an artifact of incorporation of rock substrate in the varnish analysis. According to Reneau and Raymond, greater amounts of substrate are incorporated into analysis of young, thin varnishes and result in higher cation ratios; lower cation ratios then result from analyses of older, thicker varnishes which incorporate lesser amounts of substrate.

The analytic procedure of Harrington and Whitney (1987) does not support this hypothesis. In this procedure, an in situ varnish analysis was run at 15 keV and then at greater energy in 5 keV increments, which deepen the beam penetration in association with the larger volume analyzed, until the maximum Mn concentration was reached (Mn is only a trace or minor constituent in the rock substrates commonly used in varnish studies). The calculated cation ratio selected as representative of a particular analytic site was the lowest that occurred at or before the peak Mn concentration was reached.

If incorporation of substrate into the volume of material being analyzed played a role in producing a decreasing trend in cation ratios from older varnishes, then each increase in the energy level (e.g., from 15 to 20 keV) during analysis, resulting in greater depth penetration of the electron beam, should also result in a greater volume of substrate being included in the analysis, with an attendant decrease in Mn concentration. By using the maximum Mn concentration as the cutoff point for cation ratio selection, we preclude the inclusion of greater quantities of substrate as energy levels are increased. Therefore, substrate inclusion is not a major determinant of calculated cation ratios.

DISCUSSION

We believe that most cherts and other siliceous rock types that exhibit very smooth surfaces are poor candidates for varnish cation-ratio dating. The variety of rock varnish preserved on Death Valley alluvial fans clearly shows that cation-ratio analyses on different rock types would yield radically different results. We do not discard the technique because some rock types are poor hosts for, or do not preserve, rock varnish. Indeed, we urge extreme caution in sampling. Several different rock types

on geomorphic surfaces of different ages should be tested before selecting samples for cation ratio analysis.

Varnish cation-ratio dating is a calibrated technique. Nearly all published studies that report varnish cation ratios used as a dating tool have first demonstrated that cation ratios do decrease with increasing age of the exposed surface. These reported cation-ratio dates depend on varnish cation-ratio curves that are tied to samples dated by other chronometric techniques. Before any rock type is used for varnish cation-ratio dating, investigators must first demonstrate, not assume, that varnish cation ratios change with time on the host rock, especially if that rock type is one that has not previously been used in varnish cation ratio studies. Without independent age assignments for cation ratios determined on clasts from an exposed surface, the usefulness of the technique for a particular region and specific rock type is severely limited.

The systematics of varnish chemistry are still poorly understood. On the basis of our SEM studies, we believe that the explanation of changing cation ratios owing to substrate inclusion is incorrect. The presence of barium, as discussed by Bard (1979), Harrington et al. (1991), and Bierman and Gillespie (1991), appears to influence the decrease of cation ratios with varnish age and thickness. The exclusion of barium from cation ratios calculated by Bierman and Gillespie (1994) for the KER-140 site seriously limits the applicability of their results and may, in part, explain the lack of cation-ratio trends in their data.

We urge a careful evaluation of the role of barium in producing the decreasing trend of cation ratios with varnish age that is documented in a number of studies (Harrington and Whitney, 1987, and Dethier et al., 1988). Further, we hope that these evaluations will examine varnish on substrates commonly used in the calibration of rock varnish dating curves. Additionally, we hope that the cation ratios used will include barium, as in previous studies that found a decreasing trend in cation ratios with increasing varnish age.

CONCLUSIONS

The study of site KER-140 has demonstrated that varnish cation-ratio dating is not a reliable method for dating young chert artifacts. Although Bierman and Gillespie may have demonstrated that rock varnish cation-ratio dating is inappropriate for determining the age of late Holocene chert artifacts, we believe the generalization of these results to assert that all cation-ratio dating is unreliable is not warranted by the data presented in their study.

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