

7/29/94

TO: Mark Delligatti, YMP Project Manager du jour, or review coordinator for the Topical Report on Extreme Erosion

FROM: Tom Bjerstedt *and DOE*

RE: FYI for NRC staff; draft response to Bierman and Gillespie (1994) in Quaternary Research (QR)

A recent paper in QR by Bierman and Gillespie (1994), "Evidence Suggesting that Methods of Rock-Varnish Cation-Ration Dating are Neither Comparable nor Consistently Reliable" (attached), disparages the VCR technique, among other criticisms.

A response to the claims in this article has been prepared for QR by Chuck Harrington and John Whitney (attached). This response is being internally reviewed by USGS and LANL, and a routine DOE publication review will follow shortly thereafter. We have no way of knowing how much of this response will be published by QR so I am providing a draft of the response intended for submission.

It responds to some of the same issues that have been expressed by CNWRA and NRC staff about DOE's Topical Report on Extreme Erosion. DOE has yet to receive NRC comments on the Topical.

The authors and I thought it important for NRC staff to know that DOE is aware if this article, believe it to be technically unsound, and that a detailed response is to be made.

I'm sending this to you because I'm sure you will direct it to the right person. Harold LeFevre was the review coordinator, but with NRC's reorganization I don't know if this is still the case.

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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) collected and analyzed rock varnish from late Holocene chert artifacts and surface clasts, and from chert bedrock at a prehistoric quarry site believed to be "older". Both published techniques of varnish cation-ratio dating were used and the analytical results failed to produce lower cation ratios for samples believed by the authors to be older, although no independent age verification of any samples at this archeological site was available. Based primarily on 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" and "the results are not inconsistent with".

Nearly all published studies that use varnish cation ratios as a dating tool have demonstrated that cation ratios do decrease with increasing age of the exposed surfaces before attempting to date features of unknown age. This relationship is established by

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constructing varnish cation-ratio curves that are tied to samples dated by other chronometric techniques. Bierman and Gillespie (1994) did their study "blind" by assuming that the varnish accumulation behaves in the same manner on very young 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.

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: the suitability of evaluating only a 3-element cation-ratio curve, the role of barium in cation ratio dating, the accuracy of different SEM analytical procedures in *in situ* varnish analyses, the inclusion of substrate in *in situ* varnish analyses, and the suitability of different rock types for varnish cation-ratio dating. Below we address each point.

I) BIERMAN AND GILLESPIE ASSUME CHERT IS A REPRESENTATIVE AND ACCEPTABLE SUBSTRATE ON WHICH TO STUDY VARNISH DEVELOPMENT AND PRESERVATION. THEY ALSO ASSUME THAT ALL CLASTS FROM A GEOMORPHIC SURFACE (EVEN THOSE OF A SINGLE LITHOLOGY), RECORD THE SAME

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EXPOSURE HISTORY AND THAT ANY SUBSET OF THESE CLASTS WILL YIELD CONSISTENT CATION RATIO DATA.

Dethier and others (1988) demonstrated that piedmont and alluvial fan surfaces possess a varied exposure history, and rock varnish sampled across these surfaces is likewise variable in its age and degree of development. Because surfaces are exposed to multiple surficial processes over time, surface clasts can present a highly variable varnish history. An appreciation of the evolution of alluvial surfaces led to the development of a sampling protocol, based on the assumption that the clasts most closely representing the exposure age of a surface are those with the 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 quality of each varnish coat (Whitney and Harrington, 1993). This sample selection procedure reduced the analytic variability in varnish cation ratios for an individual deposit. A failure to follow a sampling strategy that leads to the collection of only the oldest varnished clasts on a geomorphic surface will result in incorporating the variation in rock varnish age of the collected clasts into the variation in rock varnish chemistry inherent in any group of varnished clasts analyzed. Such analyses will overstate the inconsistency in varnish chemistry and rock varnish age for the surface being analyzed and may not detect trends in cation ratios over various varnish ages.

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No study on rock varnish has stated that all rock types varnish equally and 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 conducted tests, on alluvial surfaces along Las Vegas Wash and in the North Las Vegas Valley to determine which lithologies are the better rock substrates on which varnish develops and which rock surfaces are the most stable on which to accrete varnish over long time periods. Chert clasts were common on these surfaces, but proved to be inappropriate substrates for maximum varnish development. Although the chert clasts possessed significant surface irregularities, commonly exhibiting vertical edged steps on the rock face, they lacked the surface microdepressions that are inherent on fine-grained sandstones or volcanic rocks. An example of varied varnish development on an alluvial surface is observed in Figure 1, where varnish development on different clasts ranges from non-existent, to fair, to well developed. If we were to attempt to date the age of this surface, we would only select the clasts with well-developed varnish, not the poorly varnished chert clasts on this surface.

That sampling considerations are critical to cation ratio dating of rock varnish is not unique among geochronologic techniques. Detailed sampling strategies are an equally important component in the application of nearly all dating methods. An analogy can be made to K-Ar or Ar-Ar dating, wherein rocks are avoided if they are vesicular, or weathered, or possess carbonate deposits in vesicles

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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.

II) 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 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 semi-quantitative) that measured relative peak intensities (by integrating the area under the peak) to determine elemental concentrations. Cation ratios were calculated as the ratio of elemental peak intensities. We chose to use this analytic program to avoid the inherent problem of *in situ* varnish analyses on surfaces that possessed an appreciable micro roughness (surface irregularity). Such irregularities on the analyzed surface produces scattering of the electron beam resulting in either a greater or lesser beam return than that produced when analyzing a polished surface. If the analytic program compares the beam return effected 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

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the sample, depending on whether the scattering focuses more electrons at the detector or disperses them so that fewer reach the detector. If one uses such data to calculate a cation ratio, the resulting ratio commonly differs from the true ratio by a greater amount than do the individual elemental concentrations

The SSQ program, however, uses elemental peak intensities (by integrating the area under the peak) to calculate elemental concentrations and cation ratios are the ratio of these peak intensities. Because the cation ratio is a ratio among elements whose atomic numbers are similar (K=19, Ca=20, Ti=22), the effect of beam scattering is similar for all the ratioed elements. 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.

The elemental abundances published by Bierman and Gillespie (1994), however, may not be accurate because the analytic program that was used compares elemental concentrations to standards. Thus, the calculated cation ratios may also be inaccurate, which may mask any trend in cation ratios that occur within their analyzed varnish.

III) BIERMAN AND GILLESPIE EXAMINED TRENDS IN A THREE-ELEMENT [K+CA\TI] CATION RATIO WITH INCREASING VARNISH AGE AT SITE KER-140, ALTHOUGH AGREEING ALL EARLY CATION-RATIO DATING CURVES WERE CALIBRATED USING VARNISH ANALYSES THAT INCLUDED BARIUM AS A

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COMPONENT.

Harrington and others (1989) noted the presence of Ba in rock varnishes from Nevada and commented on the inclusion of part of this Ba in all earlier analyses of rock varnish that were made using analytical software (such as the SSQ program) that did not perform decomposition of elemental peak overlaps. Harrington and others (1991) further noted that if no peak decomposition was performed during analysis, approximately 1/3 of the Ba concentration 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 others (1991) also recognized the inclusion of Ba in rock varnish analyses and contended that all earlier calibrated rock varnish curves include Ba as a component in the calculated cation ratios. Harrington and others (1991) and Bierman and others (1991) further suggest that the included Ba may contribute to the observed decrease in cation ratios with increasing rock varnish age. Bierman and others (1991) also cite the work of Bard (1979), who demonstrated that the only element in varnish to exhibit a trend with varnish age was Ba. We find it puzzling, especially in light of the acceptance by Bierman and Gillespie of the inclusion of Ba in earlier calibrated cation ratio curves, that no attempt was made to evaluate the demonstrated role of barium in their present varnish study; yet, they contend that no trend occurs in cation ratios with varnish age.

We believe it is inappropriate to compare three-element cation

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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. The inability of Bierman and Gillespie to obtain a trend in the three-element cation ratio does not preclude the occurrence 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.

IV) THE TREND OF DECREASING CATION RATIOS WITH INCREASING VARNISH AGE IS NOT PRODUCED BY THE INCORPORATION OF ROCK SUBSTRATE IN 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 when analyzing young, thin varnishes and result in higher cation ratios; lower cation ratios would then result when analyzing older, thicker varnishes because lesser amounts of substrate would be incorporated in the analysis. The procedure Harrington and Whitney, 1987, used to collect their analytic data does not support this hypothesis. In this procedure, each *in situ* varnish analysis was run at multiple energies starting at 15 keV and then increasing the energy level in 5 keV increments

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until the appropriate energy level was reached or exceeded. For each analysis a cation ratio was calculated. To identify the cation ratio to be selected for each analytical site, each analysis was compared to the preceding analysis to determine; (1) if the cation ratio was lower, and (2) if the concentration of Mn (which rarely occurs in the rock types used in the curve calibration) was increasing. The cation ratio selected 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, which results 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 the calculated cation ratio in our studies.

CONCLUSIONS

The study of site KER-140 has demonstrated that varnish cation-ratio dating is not a reliable method for dating young, chert artifacts. We believe that most cherts and other quartz rock types that exhibit very smooth surfaces are poor candidates for varnish cation-ratio dating. However, before any rock type is used

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for VCR dating, investigators must first demonstrate, not assume, that cation ratios do change with time on the host rock, especially if that rock type is one that has not been previously used in VCR studies. The variety of rock varnish preserved on Death Valley 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 and testing different rock types on surfaces of different ages before selecting samples for cation ratio analysis.

Varnish cation-ratio dating is a calibrated technique. Without independent age assignments for cation-ratios determined 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 poorly understood at this time and require more explanation. We do believe that the explanation of changing cation ratios due to substrate inclusion is, on the basis of our SEM studies, incorrect. The role of barium, as discussed by Bard (1979), Harrington and others (1991), and Bierman and others (1991), appears to be a key factor in understanding why cation ratios change with varnish age and thickness. The exclusion of barium from cation ratios calculated for the KER-140 site seriously limits the applicability of the results presented by Bierman and Gillespie (1994) and may, in part, explain the lack of cation-ratio trends in their data. We urge a careful evaluation of the possible dominant role of barium in producing the decreasing trend of cation ratios with varnish age documented in a number of

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studies. Further, we hope that these future evaluations will examine varnish on substrates commonly used in the calibration of rock varnish dating curves and cation ratios that include barium as is now known to be the case in previous studies that calibrate a decreasing trend in cation ratios with increasing varnish age.

In light of the preceding comments, we believe that although Bierman and Gillespie may have demonstrated that rock varnish cation-ratio dating is inappropriate for determining the age of late Holocene chert artifacts, the generalization of these results to assert that all cation-ratio dating is unreliable is not warranted by the data presented in this study.

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Figure 1. Clasts of multiple lithologies on an alluvial fan

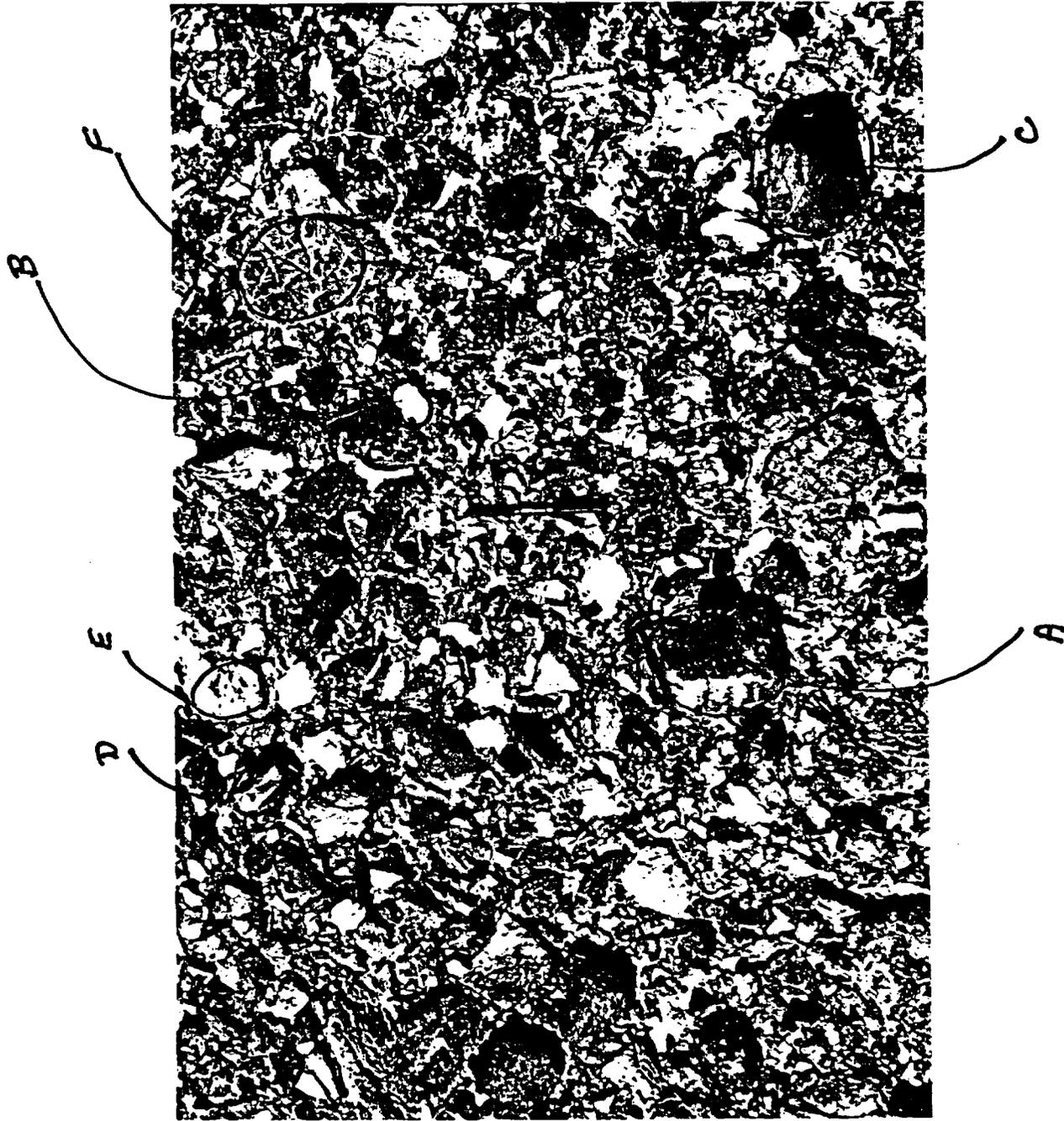
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surface in Death Valley, California. Clasts A and B are metaquartzite clasts with smooth surfaces and poorly developed rock varnish coatings. Clasts C and D are argillites with a surface microroughness and well developed varnish coatings. Clasts E 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.

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