QUATERNARY RESEARCH 43, 274–276 (1995)

LETTER TO THE EDITOR

Reply to Comments by R. Dorn and by C. Harrington and J. Whitney

Our recent paper (Bierman and Gillespie, 1994) reported the data we gathered using two different published methods of rock varnish chemical analysis (Dorn, 1983; Harrington and Whitney, 1987) to determine the composition of varnish found on chert substrates in the Mojave desert. Our data showed no correlation between the cation ratio, (Ca + K)/Ti, of rock varnish and the relative age of the chert substrates underlying the varnish. Moreover, we found that the two methods gave different apparent elemental abundances and cation ratios. These data led us to assert in the title of our paper that ". . . methods of rock-varnish cation ratio dating are neither comparable nor consistently reliable." Dorn (1995) and Harrington and Whitney (1995) have taken issue with some of our findings and data-collection techniques; we address their major comments below. We find nothing in their comments, however, which leads us to change our conclusions regarding the KER 140 data, specifically, and rock-varnish cation-ratio dating, in general. We stand by the final sentence of our paper, which states that, "Considered along with other recent findings, KER-140 data suggest that rock-varnish cation ratios, whether determined *in situ*, by scraping, or in cross-section do not provide a well understood basis for dating."

Both Dorn (1995) and Harrington and Whitney (1995) raise the issue that there is "no numerical" or "independent" verification of the age for any of the samples at KER-140. We agree that there is no numerical chronology; however, we chose the site for study because (1) there is no possibility of substrate contamination of the varnish cation ratios, and (2) there is a well established relative age sequence, as we stated explicitly in our paper (p. 82–83), that is sufficient for the purpose of the test we conducted. This age sequence is based on two reasonable observations and assumptions: (1) varnish on a flake scar is younger than varnish on the cortex, and (2) the extremely well developed varnish (up to 500 μm thick) on bedrock surfaces is much older than the weakly developed varnish on flaked surfaces. Many of the "tests" used to demonstrate the veracity of cation-ratio dating were based on similar relative dating criteria (Dorn, 1983).

Dorn (1985) and Harrington and Whitney (1995) suggest for contradictory reasons that varnish from KER-140 is inappropriate for cation-ratio dating. Dorn dismisses our study with the *ad hoc* explanation that "all" varnishes at KER-140 were formed in joints before subaerial exposure; yet he uses no objective criteria, presents no chemical analyses, and cites no field evidence to support this conclusion. Furthermore, his claim to have examined "every" bedrock face is untenable because of the size and complexity of the outcrops. Harrington and Whitney suggest (their comment 1) that chert is unsuitable for varnish development because it lacks critical "micro depressions" and so remains poorly varnished. The continuity and thickness (>500 μm) of varnish on bedrock outcrops and some cortical surfaces indicates that varnish can accrete quite successfully on the KER-140 chert. We do, however, agree with Harrington and Whitney that, in light of the KER-140 data, chert is an unsatisfactory rock type for cation-ratio dating.

Dorn misquotes our work and continues to disregard the statistical significance of cation ratio data (cf. Lanteigne, 1989; Lanteigne, 1991; Reneau and Harrington, 1988). He claims, by citing a sentence on p. 87 of our paper, that our data show ". . . the scraping technique yields a valid age sequence." Dorn neglects to include our following sentence which states that the thin varnish on a cultural surface had a lower cation ratio than the extremely well developed varnish on a bedrock surface. If Dorn's comment were correct, the bedrock varnish would be younger than that on the flaked surface, a conclusion we consider extremely unlikely because of the thickness and continuity of bedrock varnish. Dorn also misrepresents our data by omitting important qualifiers and ignoring statistical considerations. Specifically, in his comment Dorn suggests that the grand mean cation ratios we determined for different varnish subpopulations ". . . certainly appear to support CR [cation ratio] dating. . . ." We disagree, and pointed out in our paper (p. 87) that the cation ratio differences, which Dorn claims support cation ratio dating, are statistically insignificant.

Dorn continues to cite the work of others selectively and uncritically in order to bolster his own arguments. For example, Glazovsky's data (1985) do not show that cation ratios decrease with time. Glazovsky made SEM analyses of varnish collected from Soviet moraines of unknown age, applied Dorn's Mojave calibration curve,

0033-5894/95 $6.00

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and concluded that the resulting dates were "false" (i.e., geologically unreasonable). Bull (1991) considers rock varnish primarily by reviewing Dorn's findings and provides scant new data, specifically one graph described in a single paragraph (Bull, 1991, Fig. 2.27, p. 94). The validity of the data cited by Bull cannot be judged rigorously because the number of analyses is not provided, substrates are unstated, no sampling strategy is presented, and the accuracy of EDS measurements and the specific protocol by which they were made have not been published. Ironically, Dorn now cites such SEM/EDS studies to support cation-ratio dating when only several years ago he concluded that there were ". . . very serious uncertainties about the SEM method" and that it had "severe problems" (Dorn, 1988, p. 1). Moreover, Dorn himself stated that ". . . the long-term future of CR [cation ratio] dating is limited" and that other "surface exposure methods will prove to be far more precise than CR dating, more accurate and of a cost comparable to CR dating. . . ." (Dorn, 1988, p. 50).

We agree with Harrington and Whitney that varnish present on clasts exposed on a geomorphic surface will have a variety of exposure histories; the scatter in our data likely reflects these varied histories (their comment 2). We followed much the same protocol as Harrington and Whitney by selecting the most heavily varnished clasts on which to make our analyses. However, we are aware of no published data supporting the "common sense" assumption that the best-developed varnish is the oldest varnish and therefore that the most heavily varnished clasts best reflect the age of the geomorphic surface. All varnish sampling, including ours, and much relative dating of geomorphic surfaces is based either on such apparently reasonable but untested assumptions or on statistically insignificant data (e.g., Dorn, 1989). Until the geochemistry of varnish diagenesis is well understood, sample selection will remain arbitrary and dependent on the individual investigator's particular biases.

Harrington and Whitney (comment 3) imply that our standard-based EDS analyses and cation ratios are less accurate than their standardless SSQ-based cation ratios. Their claims are not consistent with their own data, which demonstrate Ba-induced inaccuracies in SSQ analyses (Harrington *et al.*, 1991), nor with data we have published showing that normalized elemental abundances and cation ratios obtained using our analytical system are similar for roughened and polished standard surfaces (Bierman and Kuehner, 1992, Fig. 6, Table 3). Furthermore, it is our understanding that both our data-reduction program and that of Harrington and Whitney (SSQ) integrate peak areas, make fluorescence and matrix corrections, and are similarly affected by surface scattering. The programs differ because ours relies on the collection of reference spectra from primarily silicate minerals whereas SSQ relies on calculated spectra. The program we used reliably deconvolves Ba and Ti, both common constituents of varnish (Bierman and Kuehner, 1992). As stated in their comment, the program used by Harrington and Whitney does not perform this deconvolution. Thus, their published three-element cation ratios are inaccurate because undetected Ba masquerades as Ti (Bierman and Gillespie, 1991; Bierman and Gillespie, 1992; Bierman and Kuehner, 1992; Harrington *et al.*, 1991). The effect on either analytic method of varnish surface roughness and varnish porosity is uncertain and difficult to test rigorously.

Harrington and Whitney (comment 4) note that we examined only three-element cation ratios and suggest that it is inappropriate to compare our accurate three-element data with presumably inaccurate four-element data inadvertently gathered by other investigators whose analytic techniques failed to deconvolve Ba. At their suggestion, we have recast our cation ratios in terms of (Ca+K)/(Ti+Ba/3). Contrary to their speculation, Ba appears to have no influence on our conclusions regarding the lack of time dependence of varnish cation ratios at KER-140 (Fig. 1) and thus does not, as Harrington and Whitney suggest, limit the applicability of our study.

Harrington and Whitney (comment 5) reject the role of inadvertent substrate contamination as a factor in reported time-dependent trends of varnish chemistry. As we stated in our paper (p. 88), the lack of time-dependent cation-ratio changes on a noncontaminating substrate (chert) and the lack of Ca and K loss in relatively older samples suggested to us that substrate contamination of varnish analyses on other rock types might be a more important factor than cation leaching in lowering apparent (four-element) cation-ratios over time. Although Ba may have been an important factor in observed four-element cation-ratio decreases elsewhere (Bierman and

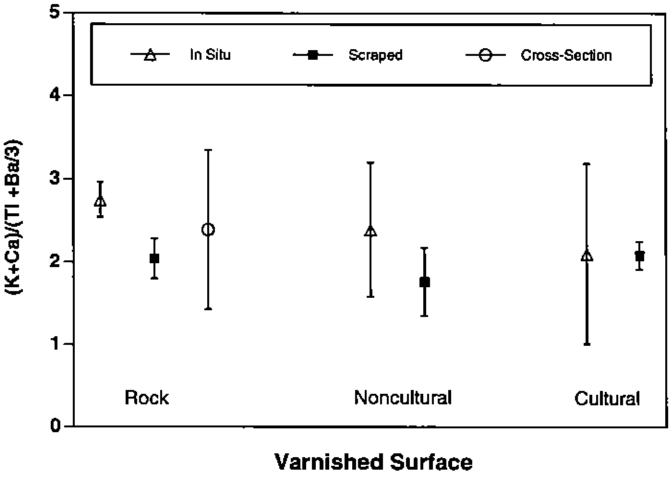

FIG. 1. Four-element cation ratio (Ca+K)/(Ti+Ba/3) means and 90% confidence intervals of KER-140 rock varnish for samples analyzed by scraping, in cross section, and *in situ* show no temporal trend. Data from Table 1 of Bierman and Gillespie (1994).

Gillespie, 1991; Harrington *et al.*, 1991), inclusion of Ba with KER-140 data does not generate cation-ratio trends reflecting relative substrate age (Fig. 1). We stand by our conclusion (p. 88) that ". . . substrate contamination may be a more important factor than cation leaching in causing previously reported cation-ratio variations. . . ."

Making accurate analyses on a noncontaminating (silica) substrate, we found no consistent time-dependent trend in the chemical composition of rock varnish. Making inaccurate analyses on a variety of other, potentially contaminating substrates, other investigators have reported such trends (Dorn, 1989; Harrington and Whitney, 1987). The cause of these trends is uncertain and widely and acrimoniously debated (Dorn, 1989; Dorn and Krinsley, 1991; Harrington and Whitney, 1987; Reneau and Raymond, 1991). We find the existence of apparent trends in varnish composition over time frames of >100,000 yr perplexing, given rates of rock erosion determined independently by other techniques such as measuring the buildup of cosmogenic nuclides. Isotopic data show that many seemingly stable and heavily varnished bedrock surfaces are eroding at finite rates, most of which are >2 μm/yr (Bierman, 1994). It is difficult to reconcile the cosmogenic data with continued maintenance of submillimeter varnish coatings over 0.1- to 1.-myr time scales as suggested by Dorn (1987) and Dorn *et al.* (1987). With the widening application of cosmogenic isotopes, there is now the opportunity to test this assertion of exceptional varnish and substrate stability directly.

It remains our opinion that until the cause of apparent time-dependent changes in varnish chemistry is understood and reliably demonstrated in meaningful, reproducible and statistically significant experiments, the meaning of any cation-ratio date will remain uncertain. We strongly suggest, given the apparent time trends found by several other investigators, that fundamental research continue into the formation and nature of rock varnish and the biases and uncertainties inherent in measuring its composition. Perhaps, after rock varnish and the techniques used to analyze it are better understood, existing data may be reconcilable. Until that time, we continue to urge caution in the acceptance and application of rock-varnish chronologies.

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APPENDIX

Intrinsic to the sample processing technique we have developed is the assumption that ^{36}Cl analyzed has been produced only by the reaction ^{35}Cl (n, γ)^{36}Cl. The following calculations support this assumption.

There are two possible pathways by which spallation-produced ^{36}Cl could be removed by the water-leaching procedure—K- and Ca-rich minerals could dissolve or water soluble phases containing K and Ca could be present.

Soluble Calcium and Potassium phases

It is likely that most of the Cl extracted was originally present in fluid inclusions. Analyses of the minerals and elements present in fluid inclusions show that Ca and K are indeed present in water-soluble phases such as KCl or $CaCl_2$. One can make the "worst-case" assumption that either Ca and K are present in equimolar quantities with Cl.

Assume that the sample is 4 cm thick and exposed at the surface using the production and stopping rates of Zreda et al., 1991; one mole of K generates 3560 atoms ^{36}Cl per year. One mole of Ca generates 2740 atoms ^{36}Cl per year. One mole of Cl has 6.023×10^{23} atoms; assuming a thermal neutron capture cross-section of 43.7 b and an effective flux of 1.87×10^{-3} n s^{-1} cm^{-2}, one mole of Cl will generate 1.20×10^{6} atoms ^{36}Cl per year.

At equimolar concentrations of $^{-}$Cl and either K or Ca, spallation of Ca will produce about 0.2% of the ^{36}Cl and spallation of K will produce about 0.3% of the ^{36}Cl produced by neutron activation of Cl. At depths greater than 40 g cm^{-2}, the effect of Ca and K spallation will be reduced by a factor of ≥ 2 as the thermal-neutron flux increases relative to the spallation-producing, fast nucleon component.

Dissolution of spallation ^{36}Cl produced from Potassium and Calcium Feldspars

Assume that a sea level rock is saturated in ^{36}Cl and that a feldspar contains 15 oxide wt % CaO or K_2O. ^{36}Cl produced by spallation should be located randomly within the crystal lattice. The saturation abundance for Ca-feldspar will be $(488*15)/2.31*10^{-6} = 3.16 \times 10^{9}$ atoms g^{-1} ^{36}Cl. The saturation abundance for K-feldspar will be $(755*15)/2.31*10^{-6} = 4.90 \times 10^{9}$ atoms g^{-1} ^{36}Cl. According to Fabryka-Martin (1988), each g of granite has 0.048 moles of atoms or 2.9×10^{22} atoms g^{-1}.

Assume that the rock is ground into pieces 1 μm on a side. In 1 g (0.37 cm^{3} or 3.7×10^{11} μm^{3}) of rock, there will be 3.7×10^{11} of these μm-sized pieces. Considering the abundance of spallogenic ^{36}Cl calculated above, only 1 in 50 of the μm-scale pieces will contain a spallogenic ^{36}Cl atom. The chance of this atom being near the surface where it could enter solution is even less because each μm-size piece contains 7.8×10^{10} atoms. This calculation strongly suggests that ^{36}Cl produced by spallation in feldspars will not be released by water extraction.