REPLY

Paul R. Bierman, Alan R. Gillespie, *Department of Geological Sciences, University of Washington, Seattle, Washington 98195*

In our paper (Bierman and Gillespie, 1991), we found that UCD PIXE analyses of varnish standards were inaccurate primarily because undetected Ba increased the apparent concentration of Ti. Cahill's Comment confirms our finding by stating that between 1987 and 1990, UCD PIXE had no algorithm to detect Ba or separate it from Ti.

Our paper is directly relevant to Dorn's work because Dorn used PIXE varnish analyses made between 1987 and 1990, the period during which UCD PIXE could not detect Ba. Many of Dorn's varnish dates from at least Australia, Nevada, Hawaii, Texas, California, and Colorado are based on these inaccurate PIXE analyses. As our paper shows, pre-1987 PIXE varnish analyses may also be flawed (Bierman and Gillespie, 1991, Fig. 4), but this inference is difficult to test.

Our finding and Cahill's confirmation that PIXE UCD could not detect Ba are significant because they suggest that rock-varnish dates now cited by workers in such diverse fields as archeology, geomorphology, and paleoclimatology are based on inaccurate analyses and thus may be in error.

Many of Cahill's comments were addressed specifically in our original paper. Nevertheless, we respond to each again below.

First, Cahill implies that our samples were run on a different system from the one Dorn used. Our samples were accepted by UCD, under contract, with a cover letter requesting they be run using Dorn's analytical routines. According to memos we received from UCD, our PIXE analyses were performed on the same system Dorn used for his varnish analyses between 1987 and 1990.

Second, Cahill states that protocols used for our samples were different from those used by Dorn. According to a UCD memo, our samples were prepared by UCD personnel using standard techniques for geologic samples and were subject to the same standardization and matrix correction protocols as Dorn's. Because the PIXE system could not detect Ba, any sample-preparation protocol would have generated inaccurate analyses.

Third, Cahill states that PIXE data in our paper did not come from his lab and were published without permission. Data and detection limits in our Table 1 are taken directly from UCD outputs and were used only after Bierman traveled to UCD, reviewed the PIXE analyses with Cahill, and was given permission for publication.

Cahill claims that UCD provided correct analyses before they knew the composition of our samples. Preliminary UCD outputs (May) included no Ba. At our request, UCD reanalyzed our PIXE spectra (July) specifically looking for Ba. None was found. In August we provided Cahill the "correct analyses." Three weeks later Cahill sent the data in his Figure 1 (Comment above), stating, "Upon receipt of your article . . . Ba was easily found in your samples." As stated in our paper (Bierman and Gillespie, 1991, p. 199), Cahill provided the results shown in his Figure 1 only after he knew the composition of our samples.

Cahill claims that many interlaboratory comparisons verify PIXE analyses. The two references cited by Cahill do not verify the accuracy of UCD PIXE analyses; rather, both summarize the same paper (Camp et al., 1975). This paper cannot be used to evaluate UCD PIXE because results for the single geologic standard vary by more than 50% and are not identified by laboratory.

Cahill claims that standards were not run with our samples. Standards were run with our samples (Bierman and Gillespie, 1991, p. 198), but Cahill has not given us permission to release these analyses. We did not correct our data to these standards because the observed and nominal values for elements such as Ca differed by more than 70% and because according to a UCD memo, "the vast majority of rock varnish analyses by [PIXE at UCD] were not corrected to standards."

Varnish dating might be more certain and less controversial had either Cahill or Dorn published their data and methods fully. Specifically, Cahill and Dorn have not published the chemical analyses used to generate individual cation-ratio dates, have not documented or alluded to an "extensive" procedure for the analysis of varnish samples, and have not used standards of varnish-like composition to correct their analyses. The thesis in which cation-ratio dating was developed (Dorn, 1982) includes neither a detailed methodology nor a table of chemical analyses.

The omission of detailed methodologies complicates verification of Cahill's analyses and replication of Dorn's observations. By not publishing chemical analyses, Dorn and Cahill preclude other workers from evaluating the chemical data on which cation-ratio dates are based. These data are of critical importance, especially if sampling criteria appear to change post facto (e.g., Ba concentration; see Dorn's Comment below) or if contradictory descriptions are published. For example, Cahill's present characterization of the 1987–1990 UCD PIXE system ("no Ba subroutine, much poorer sensitivity in the Ti(K)/Ba(L) region") directly contradicts the description he offered in Dorn et al. (1990): "In 1987 the [PIXE] system was changed . . . the improved sensitivity allowed better separation of Ba from Ti."

As long as cation-ratio dates are published without supporting chemical analyses, reference to standards, and detailed methodologies, uncertainty and controversy are probably inevitable. Cahill's admission that UCD PIXE could not detect Ba between 1987 and 1990 confirms our conclusion that many UCD varnish analyses were inaccurate; it follows that the cation-ratio dates, derived from these flawed analyses, are suspect.

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COMMENT 689

R. I. Dorn, *Department of Geography, Arizona State University, Tempe, Arizona 85287*

Bierman and Gillespie's (1991) critique of cation ratio dating is inconsistent with available evidence. First, blind tests have validated CR ages assigned to rock varnishes. Selected examples follow.

In a study comparing different methods for dating glacial landforms on Mauna Kea, Hawaii (Dorn et al., 1991), cation-ratio ages are consistent

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Note: Additional material for this Comment is Supplementary Data 9216, available on request from the GSA Documents Secretary (see footnote 1).

with results of radiocarbon, ^{36}Cl, and in situ ^{14}C ages that were determined months to years after the cation-ratio analyses by PIXE (proton-induced X-ray emission) were conducted at Crocker Nuclear Lab (CNL) at the University of California, Davis.

Cation-ratio ages assigned to Tioga moraines at Pine Creek, eastern Sierra Nevada, based on CNL PIXE measurements (Dorn et al., 1990) closely match new ^{26}Al and ^{10}Be exposure ages (D. Lal, 1990, personal commun.) and a new ^{14}C age of 19.5 ka on charcoal from Tioga till matrix (Bach et al., 1991).

Cation-ratio ages on rock varnish formed on 46 petroglyphs in Colorado are consistent with prior radiocarbon ages that were not made available to me or to CNL. In one case, the test was double blind; Loendorf (1991, p. 253–254) wrote: "a carbon sample from the lowest levels [of a circular pit] was determined at . . . 2340±140 BP, within the statistical overlap of the cation ratios [ages], which were measured before the radiocarbon age of the charcoal was determined." I welcome and actively seek other blind tests of varnish methods.

Second, there is no reason to reject prior PIXE measurements of rock varnish by CNL. CNL has a long record of successful interlaboratory comparisons (Cahill, Comment above), contrasting with Bierman and Gillespie's single claim of bad analysis on three samples.

My experience with CNL supports Cahill's (Comment above) explanation of why Bierman and Gillespie's presentation of CNL data has no bearing on varnish research. When I started using PIXE at CNL, I submitted only a few samples, just as Bierman and Gillespie did. I was also told by CNL that these first results were qualitative, not publishable, and only useful in assessing if dedicated analyses were warranted. As a consequence of the initial qualitative results, I developed a series of detailed sample-preparation protocols and checks for runs dedicated to varnish analyses (Dorn et al., 1990), methods that were not used by Bierman and Gillespie. Hence, I am not surprised that analyses of Bierman and Gillespie's samples differ from my runs.

In reanalyses of the same varnish samples previously measured by CNL, only a few cation ratios determined by CNL were substantially different from those determined by ICP and wavelength dispersive electron microprobe. These independent tests of CNL data were conducted and published before *any* part of this controversy arose (Dorn, 1989, p. 576; Dorn et al., 1990).

I offered to let Bierman and Gillespie reanalyze the exact same varnish material that was previously measured by CNL. It is unfortunate, but they declined (Bierman and Gillespie, October 1990, written commun.). A key assumption of their paper is that my samples were analyzed by CNL in a fashion analogous to the way their material was analyzed. It is unreasonable to reject thousands of prior analyses on the basis of assumptions that they refused to test.

I continue to use CNL analyses because of that lab's enthusiastic support of experimental research, world-wide respect for CNL, and CNL's ability to analyze a wide range of elements in small samples in a nondestructive way. My current work on cation-ratio dating uses ICP and wavelength-dispersive electron microprobe, in addition to PIXE, because when used in combination these methods provide high-quality and low-cost analytical data on rock varnish.

Third, methods work when samples are not susceptible to the Ba-Ti overlap problem. Bierman and Gillespie are correct that rock varnish can contain enough barium to pose a serious problem if energy-dispersive analyses are not deconvoluted properly (Dorn, 1989, p. 575). In fact, high barium concentrations are characteristic of certain types of varnishes (see supplementary material[1]).

The types of varnishes sampled for cation-ratio dating, however, do not contain high Ba concentrations (see selection criteria in Dorn, 1989; Dorn et al., 1990; Krinsley et al., 1990). The lack of Ba in varnish used for cation-ratio dating is exemplified for samples from the Coso Range (Fig. 4 in Bierman and Gillespie, 1991). In "bulk measurements" on cubic millimetres of varnishes from the Coso Range, titanium to barium ratios are ~5, regardless of the method of chemical analysis (PIXE, 5.2 ±1.1; wavelength-dispersive electron microprobe, 4.9 ±0.9; ICP, 4.7 ±1.0; neutron activation, 6.0 ±0.3). Similarly, electron microprobe (wavelength-dispersive) analyses that correspond to prior SEM-EDS analyses reveal Ba at levels $\leqslant$0.1% (see supplementary material; footnote 1).

Low Ba values ($\leqslant$0.1%) are also found for post-1986 samples collected from environments appropriate for cation-ratio dating. The *same* material first analyzed by PIXE from Colorado, South Australia, and Crater Flat gives similarly low Ba when reanalyzed by wavelength-dispersive electron microprobe and ICP (see supplementary material). The implication of low Ba concentrations is that there is no overlap problem with titanium.

Fourth, five different laboratories around the world (two in the United States, one in South Africa, one in the former Soviet Union, one in China; see review in Dorn, 1989) have all found a time-dependent decrease in the varnish cation ratios with time. The method appears to work.

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REPLY

Paul R. Bierman, Alan R. Gillespie, *Department of Geology, University of Washington, Seattle, Washington 98195*

In our paper (Bierman and Gillespie, 1991), we found that PIXE UCD could not accurately analyze standards of varnish-like composition. Because PIXE varnish analyses were used to generate most published cation-ratio ages, we suggested that these ages and the premise of cation-ratio dating be reevaluated.

Cahill's Comment (this issue) confirms our finding by stating that PIXE analyses used to generate cation-ratio ages between 1987 and 1990 were indeed flawed. Dorn's Comment dismisses our findings by claiming that they are inconsistent with an assortment of evidence. Below, we examine Dorn's evidence critically.

First, Dorn claims that "blind" tests validate cation-ratio dating. Dorn's "selected examples" disregard inconsistent ages, omit pertinent information, and include circular reasoning.

Mauna Kea. Jull et al. (1992) have pointed out that sites 2 and 5 have in situ cosmogenic ^{14}C ages less than 40% the varnish ages; despite this inconsistency, Dorn uses both sites to calibrate cation-ratio ages. A single cation-ratio and ^{36}Cl age do agree (8a), but these ages are not independent. ^{36}Cl production rates were calculated from varnish ages, and Dorn's Mauna Kea varnish chronology was used to select altitude and latitude corrections for the ^{36}Cl measurements (Zreda et al., 1991).

Sierra Nevada. Dorn et al. (1990) did not date Pine Creek Tioga moraines by cation ratio; rather, they used Tioga cation ratios for calibrating ages assigned to older moraines. Dorn does not mention that cation-ratio ages for some of these older moraines disagreed, by a factor of two (150 ka vs. 65 ka), with ^{36}Cl ages (Dorn et al., 1987; Phillips et al., 1990). Nor does Dorn mention that the Pine Creek varnish chronology was later revised significantly, so that cation ratio ages now match the ^{36}Cl chronology (Dorn et al., 1990).

Colorado. Loendorf (1991) did not indicate the relation between petroglyphs dated by Dorn and 2340 yr B.P. charcoal from an adjacent pit; near the pit, on the same panel, are 14 cation-ratio-dated petroglyphs ranging in estimated age from 650 to 4675 yr B.P.

Second, Dorn claims there is no reason to reject UCD PIXE measurements. Cahill, when he admits that UCD PIXE could not detect Ba

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[1] Additional material, GSA Supplementary Data 9216, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301.

between 1987 and 1990, provides ample reason to reject at least some PIXE analyses. The "long record of interlaboratory comparisons" cited by Dorn is actually two analyses of a single geologic sample (Camp et al., 1975). Because our study was designed primarily to quantify SEM accuracy, we did not participate in Dorn's proposed tests of PIXE; instead, we offered him our varnish standards.

Third, Dorn asserts that PIXE inaccuracies are unimportant because the varnish he samples for dating contains <0.1% Ba. This assertion directly contradicts Dorn's own publications and numerous analyses published by other workers which show that most rock varnish contains roughly equal amounts of Ba and Ti, 0.5%–2.0%.

For example, in Krinsley et al. (1990, p. 103), Dorn stated that Ba is common in arid-region varnishes and that the concentration of Ba is commonly considerably greater than that of Ti. Dorn and Dickinson (1989, p. 1030) presented typical varnish analyses (1.5%, 1.4%, 0.9% Ba; 2.1%, 1.6%, 1.5% Ti), Dragovich (1988) reported 0.4%–1.4% BaO in 99 varnish analyses from southeast Australia, and Harrington et al. (1991, Fig. 6) reported an average of 1.1% BaO in 271 Nevada (Crater Flat) varnishes. Most notably, Dorn (1989, p. 575) stated that Ba and Ti are present in varnish in equal amounts, about 1.0%, and Dorn et al. (1990, Fig. 4c) showed that 700 of 721 Coso varnish samples contain about equal amounts of Ba and Ti, 0.3% to 2.0%.

We cannot reconcile Dorn's prior publications, which document the abundance of Ba in varnish, with Dorn's present claim that Coso varnish, and other varnish he used for dating, contains <0.1% Ba and the Ti/Ba ratio = 5. If Dorn used only samples having <0.1% Ba for dating, why has he never before alluded to this apparently important sampling criterion, and why has he, until now, repeatedly stressed the ubiquity of Ba in varnish?

Because Dorn has not published specific chemical analyses along with varnish ages, the influence of Ba on the accuracy of any particular varnish analysis or cation-ratio age cannot be convincingly assessed or dismissed.

Fourth, Dorn claims that others have replicated his findings. Dorn is not being sufficiently critical when he states that five labs have measured time-dependent changes in varnish cation ratios. One U.S. lab is his own; the other is Los Alamos, where ratio changes may be best explained by substrate inclusion (Reneau and Raymond, 1991). The African lab used PIXE on in situ varnish, a technique prone to substrate inclusion and Ba interference. The Soviets used SEM/EDS to analyze varnish from two undated moraines, and the Chinese paper does not describe analytical methods. Time-dependent change in varnish chemistry, in samples free from substrate contamination, remains to be demonstrated conclusively.

We made and tested varnish-like standards because none existed and because the accuracy of both SEM and PIXE had been questioned repeatedly (Dorn, 1989; Dorn et al., 1990; Harrington et al., 1991; Krinsley et al., 1990). Our findings and those of Reneau and Raymond (1991) show much greater complexity in varnish analyses and composition than was originally appreciated. There is now compelling evidence that cation-ratio variations are greatly influenced by sampling strategies and measurement techniques.

Although the cation-ratio method appears to work for Dorn, we and others have been unable to reproduce his results or verify the accuracy of analyses on which his ages are based. Because the existing literature is contradictory and because Dorn's results have yet to be explained or replicated by other workers, we urge others to review critically the data and assumptions on which these ages and the cation-ratio method are based.

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Comment and Reply on "Arc rifting of the Carolina terrane in northwestern South Carolina"

COMMENT

Steven K. Mittwede, *McCracken and Associates, P.K. 207,*
06443 Yenişehir, Ankara, Turkey

The paper by Dennis and Shervais (1991) is a valuable contribution to the understanding of the geologic framework and history of the central Piedmont of the southern Appalachians, particularly the western part of the Carolina terrane. Indeed, the evidence is compelling that the zoned intrusive complexes of the Kings Mountain belt formed in an arc setting and were related to an episode of intra-arc rifting. It is unfortunate, however, that Dennis and Shervais included the Hammett Grove metaigneous suite in their analysis and interpretation.

The Hammett Grove suite may be a critical element in understanding the nature and regional tectonic significance of the Piedmont terrane–Carolina terrane boundary; the Hammett Grove metaigneous suite and several similar ultramafic-mafic suites along the Piedmont-Carolina terrane boundary may well be remnants of marginal basin or oceanic crustal