

Precision of rock-varnish chemical analyses and cation-ratio ages

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ABSTRACT

New data and statistical analyses indicate that the precision of the mean rock-varnish cation ratio determined for a geomorphic surface and the uncertainty of the age calculated from that ratio are controlled by the area of varnish included in each chemical analysis, the precision with which each cation ratio is determined, and the number of independent chemical analyses. This study has implications for the interpretation of published cation-ratio ages and the future use of cation-ratio dating.

INTRODUCTION

Rock varnish is a <200 μm layer composed primarily of Al, Si, Fe, and Mn oxides. Varnish chemistry may change predictably with time (Bard, 1979). Dorn (1983, 1989) and Harrington and Whitney (1987) have reported that the ratio (K + Ca)/Ti in varnish (the cation ratio) decreases logarithmically with estimated exposure age; they argued that this decrease reflects preferential leaching of K and Ca relative to Ti. Empirical calibration curves have been constructed so that exposure ages may be estimated.

Cation ratios have been determined by three methods. Dorn (1983, 1989) scraped <1 to >50 cm^2 of varnish from numerous rocks and used proton-induced X-ray emission at the University of California, Davis (PIXE UCD), to analyze three to five homogenized samples from each deposit. Harrington and Whitney (1987) used a scanning electron microscope and energy-dispersive spectrometer (SEM-EDS) to analyze varnish in situ at 70 to 90 places (each 10–100 mm^2) on the surface of 8 to 10 samples from each deposit. Dragovich (1988) and Dorn (1989) used a SEM and wavelength-dispersive spectrometer (SEM-WDS = electron microprobe) to determine ratios at points (<2000 μm^2) in varnish cross sections.

The cation-ratio dating method is only calibrated empirically; the processes responsible for the reported change in ratios over time are not understood, and the method lacks an accepted protocol for calculating representative age uncertainties. Prior research has established neither the size nor the number of varnish samples that must be analyzed in order to characterize precisely and accurately the cation ratio that best represents the exposure age of a geomorphic surface.

We present a statistical analysis of cation-ratio precision that is applicable regardless of the method used to measure varnish composition. We do not consider possible problems with the methods employed to determine cation ratios nor with the premise of cation-ratio dating. In

addition, if cation ratios are used to generate numerical rather than relative ages, the precision and accuracy of calibration must also be considered when calculating the uncertainty of a cation-ratio age (cf. Harden et al., 1988).

METHODS

Using a rock drill, we collected varnish from boulders on the rim of Fish Springs cinder cone near Big Pine, California (314 \pm 18 ka; Martel et al., 1987), and from the Bishop Tuff 8 km east-northeast of the town of Rovanna (708 \pm 15 ka; Bailey et al., 1976). Chemical analyses were made of the varnish surface with a Tracor Northern EDS mounted on a JEOL 733 using a 15 keV accelerating voltage and a 10 nA beam current (measured on a Faraday cup). Reference spectra were used in the EDS deconvolution routine (Tracor Northern FIT program). We made quantitative analyses of Si, Al, Fe, Mn, Mg, Ba, Ti, Ca, and K by using the Tracor Northern ZAF procedure for matrix correction.

After examining the varnish surface with

backscattered-electron detectors, which allow identification and avoidance of substrate or microcolonial fungi, we selected 19 6 mm^2 areas for analysis. We analyzed varnish at the 19 locations four times, changing the area over which the electron beam was scanned from 6.0 to 0.99 to 0.062 to 0.002 mm^2 . Duplicate analyses showed no significant machine drift.

Nomenclature is summarized in Appendix 1. Introductory texts, such as Freund (1988), provide detailed explanations of the statistical concepts we use.

MEASUREMENTS AND STATISTICAL ANALYSES RELEVANT TO CATION-RATIO PRECISION

Most geomorphic surfaces are heterogeneous with reference to factors that have been hypothesized by Dorn (1989) to affect cation ratios (e.g., dust flux, precipitation, orientation, vegetation). According to Dorn and Oberlander (1982, p. 321) varnish growth is time transgressive with "many thousands of years required to develop a complete coat." In addition, rock surfaces erode and are revarnished, creating a patchwork of varnish populations at various scales—each of a different age and each, if cation leaching is occurring, having a different true or population mean cation ratio, μ_{CR} .

Because the above-mentioned processes cause varnish on every geomorphic surface to be chemically heterogeneous, understanding the na-

TABLE 1. COMPARISON OF ROCK VARNISH CHEMICAL ANALYSIS TECHNIQUES

Analytical instrument, dwell time (s)	X-ray detector	Approximate analytical uncertainty for rock varnish (%)			Calculated (Ca+K)/Ti uncertainty* (%)	Measured or reported cation ratio uncertainty
		Ti	Ca	K		
PIXE, 100	EDS	8 [*]	6 [*]	6 [*]	9	9–12 [§]
PIXE, 100	EDS	6–11 [#]	5–10 [#]	5–8 [#]	7–12	2–4 [#]
SEM, 200	EDS	10	2.5	1.5	10.3	10.5 ^{**}
SEM, 4000	EDS	1–2	0.5	0.5	\leq 2	No data
SEM, 40	WDS	8–12	2–3	2–3	10–12	No data
SEM, 800	WDS	1–2	0.5	0.5	\leq 2	No data

Note: PIXE is proton induced X-ray emission; SEM is scanning electron microscope; EDS is energy dispersive spectrometer; WDS is wavelength dispersive spectrometer.

* Calculated by using equation 1 (see text).

[#] T. Gill (1989, personal commun.).

[§] Data from Hobbs and Dorn (1988, Table 2).

[#] Range of uncertainty (1 σ , 5 blind replicates of each of 3 synthetic rock varnishes).

** See Figure 1, this paper.

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ture and scale of this variability is prerequisite to collecting meaningful cation-ratio data. The data and statistical analysis that follow begin a rigorous identification of the appropriate scale for cation-ratio sampling and, if the cation-ratio dating is valid, suggest a method to calculate the number and precision of ratio determinations necessary to solve specific geologic problems.

Precision of Each Cation-Ratio Determination

Standard error-propagation theory may be used to calculate the precision of each cation-ratio (CR) determination based on the analytic precision of individual cation analyses:

$$\sigma_{CR} = CR \left[\frac{(\sigma_{Ca}^2 + \sigma_K^2)}{(Ca + K)^2} + \sigma_{Ti}^2 Ti^{-2} \right]^{0.5} \quad (1)$$

Table 1 lists the average precision with which K, Ca, and Ti (at concentrations typically measured in rock varnish) are determined by a single PIXE or SEM analysis. Because the probability of X-ray emission in PIXE or SEM-EDS systems is described by a Poisson distribution (Goldstein et al., 1981), analytic uncertainties ($\sigma_{Ti, Ca, K}$ and σ_{CR}) decrease as a function of the square root of dwell time. Analyses reported in this paper were made by increasing SEM dwell time from the standard 40 s to 4000–6000 s; this change increased measurement precision by a factor greater than three. High-precision analyses are critical for determining the actual variability of varnish chemistry, variability that in the past was masked by less-precise analyses.

Analytic Precision Limits the Certainty of Cation-Ratio Ages

The precision with which each cation ratio is determined limits the certainty of the sample

mean cation ratio, \overline{CR} , and therefore the age calculated for any geomorphic surface according to the standard error of the mean,

$$\sigma_{\mu_{CR}} = n^{-0.5} \overline{\sigma}_{CR} \quad (2)$$

We use equations 1 and 2 to adjust dwell time and/or determine the number of analyses of a single sample necessary to determine the cation ratio for that sample with a specific precision. However, equations 1 and 2 can also be used to calculate the maximum precision with which \overline{CR} can be determined by a given analytic technique and/or number of analyses.

For example, if the analyzed samples are chemically identical (e.g., aliquots of homogenized varnish) and if errors in Ti, Ca, and K are uncorrelated, the sample standard deviation, S_{CR} , of \overline{CR} should approximately equal σ_{CR} as determined by equation 1 (see Fig. 1). However, the actual uncertainty of CR is determined by equation 2, which accounts for the number of analyses used to calculate the mean. Because varnish samples collected from different boulders are not chemically identical, S_{CR} for multiple boulders on a single geomorphic surface should exceed σ_{CR} .

Data reported by Nobbs and Dorn (1988) are inconsistent because the "standard errors" (S_{CR}) for the mean of chemically heterogeneous varnish samples are only 2%–3%, despite cation-ratio uncertainties (σ_{CR}) of 8%–12% (see comment by Harrington and Reneau *in* Nobbs and Dorn, 1988). This inconsistency is even more striking because the reported σ_{CR} reflects only σ_{Ti} without considering σ_K and σ_{Ca} (R. I. Dorn, 1990, personal commun.).

We resolved the inconsistency in data of

Nobbs and Dorn by preparing and analyzing glass analogs of rock varnish. We analyzed 15 samples (5 homogeneous aliquots from each of 3 different synthetic varnishes) by PIXE UCD. Table 1 shows that sample standard deviations for three sets of five independent measurements of Ti, Ca, and K range from 5% to 11%; however, sample standard deviations for cation ratios calculated from these analyses are only 2% to 4%, lower by a factor of two or three than the uncertainty calculated by Nobbs and Dorn or predicted by error propagation (equation 1). Our measurements indicate that uncertainties reported by Nobbs and Dorn (1988) for individual cation-ratio determinations are inaccurate because they did not recognize that errors in Ti, Ca, and K analyses were correlated.

Synthetic varnish analyses suggest that the actual precision (σ_{CR}) of PIXE UCD cation-ratio analyses is 2%–4%. Nobbs and Dorn (1988) and Dorn et al. (1987) reported an average S_{CR} of 2.7% ($n = 24$) and 2.9% ($n = 8$), respectively. Because these values of $S_{CR} \approx \sigma_{CR}$, samples analyzed by Dorn are chemically homogeneous. Harrington and Whitney (1987) reported $S_{CR} \geq \sigma_{CR}$, a finding consistent with chemically heterogeneous varnish.

Representative Method for Expressing the Uncertainty of the Mean Cation Ratio

A varnish sampling program, no matter how well designed, only estimates μ_{CR} of a varnish population. Because most of the varnish population has not been sampled, any \overline{CR} will always have some uncertainty; however, the magnitude of this uncertainty can be reduced by analyzing more samples from the varnish population.

Dorn et al. (1987) and Harrington and Whit-

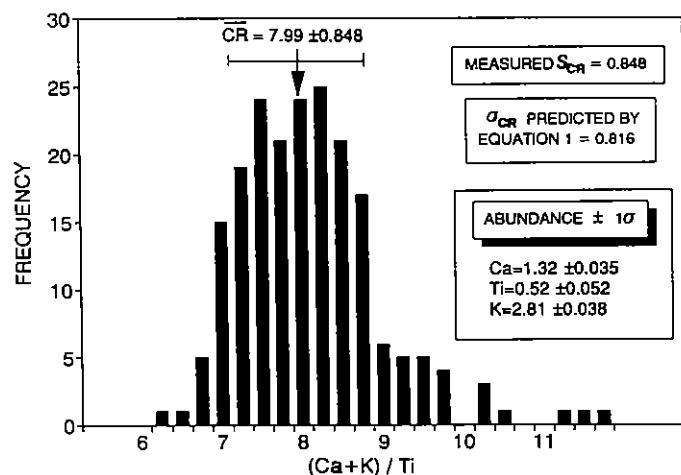


Figure 1. Replicate analyses ($n = 200$; rastered area = 6 mm²; $\sigma_{CR} \sim 10\%$ by equation 1) of same patch of varnish give wide range of cation ratios ($S_{CR} \sim 10.5\%$) as predicted by equation 1 (sample BT-2, Bishop Tuff). Similarity of S_{CR} and σ_{CR} indicates equation 1 correctly predicts uncertainty of a SEM-EDS CR analysis.

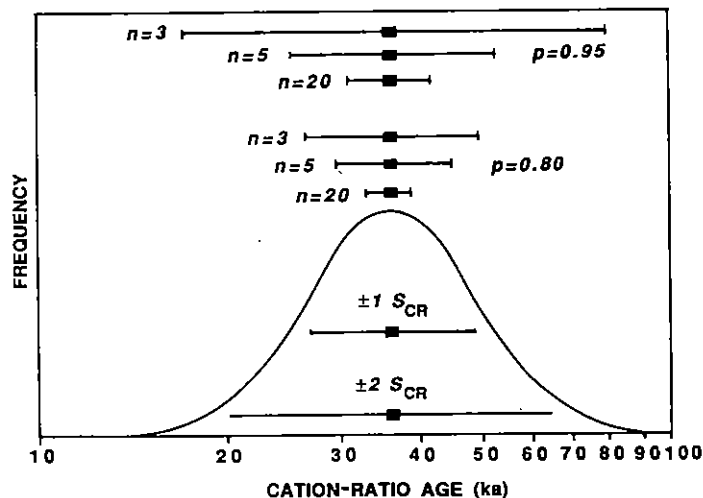


Figure 2. Normally distributed cation-ratio population with $\overline{CR} = 4.5$ and $S_{CR} = 5\%$. Confidence intervals (equation 3) about \overline{CR} are shown for various probabilities p and numbers of samples n . Confidence intervals expressed as ages by using $a = 10^{(13.12 - CR)/1.89}$ (Dorn et al., 1987). One and two standard deviations (S_{CR}) of cation-ratio population are also plotted.

ney (1987) characterized the uncertainty in \overline{CR} and the associated age by reporting only the standard deviation, S_{CR} , of the cation ratios used to estimate \overline{CR} without explicitly stating n . This approach is inappropriate because S_{CR} only describes the population of cation ratios from which samples were taken; alone, S_{CR} does not accurately indicate the uncertainty with which \overline{CR} has been determined. The uncertainty in \overline{CR} can be quantified by using a confidence interval that takes into account the number of analyses used to estimate \overline{CR} :

$$\begin{aligned} (\overline{CR} - [t_{\alpha/2} S_{CR} n^{-0.5}]) < \mu_{CR} \\ < (\overline{CR} + [t_{\alpha/2} S_{CR} n^{-0.5}]), \end{aligned} \quad (3)$$

and

$$\sigma' = 100(t_{\alpha/2} S_{CR} n^{-0.5} \overline{CR}^{-1}). \quad (4)$$

Equation 3 indicates the interval within which there is a $(1 - \alpha)$ probability that the true mean cation ratio μ_{CR} for the sampled population is contained. Equation 4 expresses this interval in terms of σ' , a percentage of \overline{CR} . We refer to σ' as the fractional uncertainty of \overline{CR} .

Because the number of samples used to determine \overline{CR} is usually small ($n < 30$), it is appropriate to calculate confidence intervals with the Student's t probability distribution, $t_{\alpha/2}$ (Freund, 1988). The magnitude of $t_{\alpha/2}$ is inversely proportional to n and is especially large when $n \leq 5$ and $p \geq 0.9$. This relation quantifies the common-sense conclusion that the \overline{CR} for a geomorphic surface will be more reliably determined if a large number of samples from that surface are analyzed. Values of $t_{\alpha/2}$ may be found in Freund (1988).

An example (Fig. 2) illustrates the usefulness of equations 3 and 4. If three cation ratios were averaged to determine a \overline{CR} with $S_{CR} = 5\%$, the

fractional uncertainty σ' of the \overline{CR} at 0.95 probability would be about 12.5%. In this case, reporting the uncertainty as two standard deviations ($2S_{CR}$), approximately equivalent to $p = 0.95$, would underestimate the uncertainty in \overline{CR} (10% vs. 12.5%). However, if 20 rather than 3 cation ratios were averaged to determine \overline{CR} , σ' would be about 2.5%. In this case, reporting the uncertainty as $2S_{CR}$ would overestimate the uncertainty in \overline{CR} by a factor of four (10% vs. 2.5%).

The uncertainty of \overline{CR} is predicted most accurately by equations 3 and 4 if the cation-ratio population from which samples are drawn is normally distributed. Because cation-ratio data do not always satisfy formal criteria for normality, confidence intervals calculated for \overline{CR} for using equations 3 and 4 will be approximate.

Scale of Variance in Rock-Varnish Chemistry

If varnish could be sampled so as to reduce S_{CR} , \overline{CR} would be determined more precisely (equations 3 and 4). Our measurements show that S_{CR} increases as the area of varnish included in a single analysis decreases (Fig. 3), although \overline{CR} changes only slightly. Due to the patchy nature of varnish coatings in Owens Valley, we could not extend these measurements to areas larger than $\sim 6 \text{ mm}^2$. However, S_{CR} will again increase when the sampled area becomes large enough to include multiple populations of cation ratios; e.g., when varnish is inadvertently sampled across the edge of an ancient fire spall.

The scale at which varnish heterogeneity begins to increase has yet to be determined and probably varies with the exposure age and weathering characteristics of the underlying rock. We anticipate that varnish areas of about 10 cm^2 and larger (the average size of fire spalls) may contain multiple cation-ratio populations. If \overline{CR} is determined by analyzing areas of var-

nish small enough to avoid sampling multiple populations, cation-ratio homogeneity can be examined and significantly different chemistry (i.e., different varnish populations) can be recognized (C. Harrington, 1990, personal commun.). Knowing the scale of variability is important because, if leaching assumptions of Dorn (1989) are correct, μ_{CR} will not be a valid indicator of exposure age if multiple cation-ratio populations (i.e., varnish of different ages) are combined in a single chemical analysis.

TWO EXAMPLES OF CATION-RATIO PRECISION

Data from Owens Valley and statistical deductions illustrate the potential temporal resolution of varnish cation ratios. In Figure 4, cation ratios are expressed as age ranges calculated from a calibration determined empirically for Owens Valley cation-ratio dating by Dorn et al. (1987). The calculations show that moraines and alluvial fans from marine oxygen-isotope stages 2, 4, and 6 (ca. 10–200 ka) should be separable by means of cation-ratio data, provided cation ratios change predictably with time and provided \overline{CR} can be determined with $\sigma' \leq 10\%$ (Fig. 4A). By comparison, discrimination of surfaces exposed during Holocene neotectonic events requires that \overline{CR} be determined with a much smaller $\sigma', \leq 3\%$ (Fig. 4B). Obtaining the small σ' values necessary to resolve closely spaced events would require numerous analyses of varnish (large n and small $t_{\alpha/2}$), sampling an area of varnish that minimizes cation-ratio variance (small S_{CR}), and acceptance of a lower probability (small $t_{\alpha/2}$).

Using equation 4, we can estimate the probability with which geologic events might be separated by using cation ratios. For example, the smallest S_{CR} we determined on a 5 cm^2 varnish sample was about 5% of \overline{CR} (Fig. 3). If the \overline{CR}

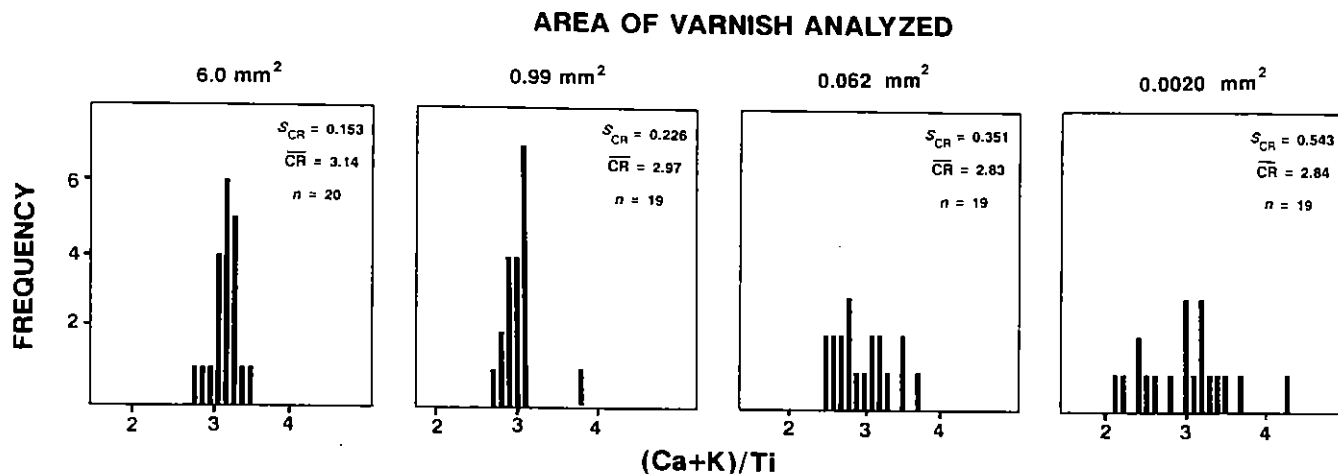
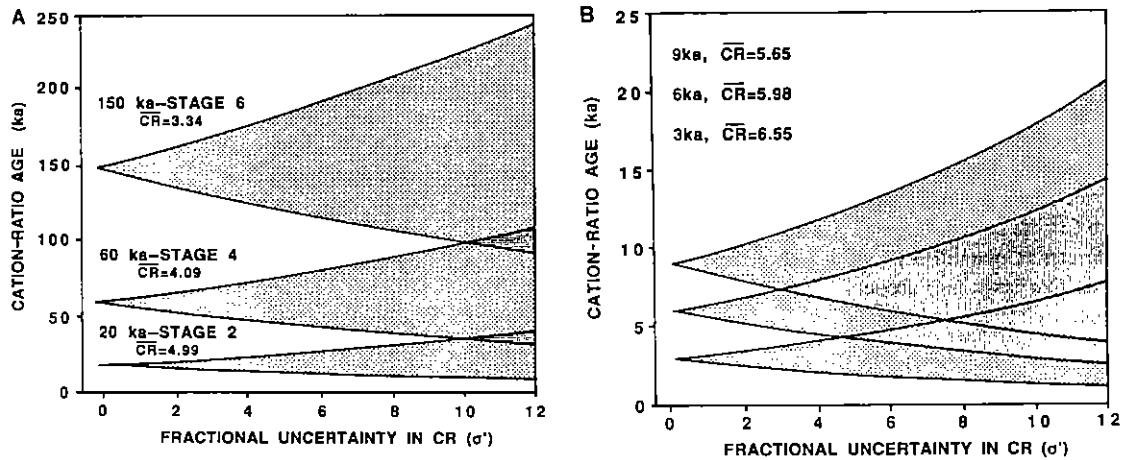


Figure 3. Variance of varnish chemistry and, therefore, S_{CR} increase as area of varnish included in each analysis decreases. Data were collected by using SEM-EDS and acquisition times of 4000–6000 s, sufficient to determine each cation ratio with $\sigma_{CR} < 1\%$. Sample FS-2, Fish Springs cinder cone.

Figure 4. Age ranges calculated by using $a = 10^{(13.12-CR)/1.89}$ (Dorn et al., 1987) after adding and subtracting arbitrary σ' from \overline{CR} . If calculated age ranges overlap (dark stipple), events are not separable at arbitrary value of σ' . Note that actual σ' associated with any reported \overline{CR} can be calculated by using equation 4 and varies with n , $t_{\alpha/2}$ and S_{CR} . A: Late Pleistocene glacial deposits in Sierra Nevada are separable if $\sigma' \leq 10\%$. B: Holocene neotectonic events require $\sigma' \leq 3\%$ to be separable.



and S_{CR} of this single disk are representative of the geomorphic surface from which it was collected and if five or more analyses made on this disk are used to estimate \overline{CR} , then glaciations ($\sigma' \leq 10\%$) will be separable with more than 95% probability and neotectonic events ($\sigma' \leq 3\%$) will be separable with almost 80% probability. This calculation assumes that cation ratios change continuously with time and that each cation-ratio determination is precise ($\sigma_{CR} \leq 2\%$ if $n = 5$). If cation-ratio analyses are less precise, the cation-ratio population more heterogeneous, or a greater level of confidence is required, more samples from the population must be analyzed to achieve a similar σ' .

The temporal separability shown by these calculations suggests that cation ratios may be useful for the relative dating and correlation of landforms. However, if numerical cation-ratio ages are generated using a calibration curve, then the accuracy and precision of cation-ratio calibration must also be considered rigorously before cation-ratio ages can be compared to ages generated by other dating methods.

CONCLUSIONS

The maximum precision with which a mean cation ratio of rock varnish can be determined and the minimum uncertainty in the age calculated from that cation ratio are proportional to the precision of the method used to determine the ratio and inversely proportional to the number of samples analyzed.

The uncertainty of a measured mean cation ratio and of the age calculated from that mean cation ratio depend strongly on the number of samples used to estimate the mean. Therefore, uncertainty in a cation-ratio age should be calculated from the expected variation (equations 3 and 4) of the mean cation ratio rather than the standard deviation of the cation-ratio determinations used to calculate the mean.

The variance of varnish chemistry decreases as larger areas of varnish are sampled, at least up

to a sample area of 6 mm^2 . However, if cation leaching occurs and if too large an area of varnish is included in each analysis, variance will again increase as multiple cation-ratio populations are included in single samples.

APPENDIX 1. NOMENCLATURE

n	Number of independent chemical analyses or cation-ratio determinations
Ca, K, Ti	Analytic abundance (elemental wt%)
CR	Cation ratio, $(K + Ca)/Ti$, of varnish
\overline{CR}	Arithmetic mean of n cation-ratio determinations (sample mean)
$\sigma_{Ti,Ca,K}$	Analytic uncertainty of a single abundance measurement (one standard deviation) (elemental wt%)
σ_{CR}	Analytic uncertainty of a single cation-ratio determination (one standard deviation)
$\sigma_{\mu_{CR}}$	One standard error of the mean cation ratio (n cation-ratio determinations)
$\bar{\sigma}_{CR}$	Average analytic uncertainty of n cation-ratio determinations (one standard deviation)
S_{CR}	Sample standard deviation of n cation ratios used to determine \overline{CR}
σ'	Fractional uncertainty of n cation ratios (%)
μ_{CR}	Population mean cation ratio
p	Probability $(1 - \alpha)$
$t_{\alpha/2}$	Student's t value at $(n - 1)$ degrees of freedom and $(1 - \alpha)$ probability
a	Age (yr)
α	$(1 - p)$ value of probability

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