

GSA Data Repository Item # 91-08

Title of article ACCURACY OF ROCK-VARNISH CHEMICAL ANALYSES: IMPLICATIONS
FOR CATION-RATIO DATING

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see Geology v. 19, p. 196 - 199

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Detailed Methodology for
Accuracy of rock-varnish chemical analyses: Implications for
cation-ratio dating

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Preparation of synthetic varnish standards -- Using commercial reagent-grade chemical compounds, we prepared ≈ 10 g each of three different synthetic glasses during January 1990. Reagents were oven dried for at least 24 hours prior to weighing. Oxides were dried at 600°C . Carbonates were dried at 250°C . The reagent mixture was ground in an agate mortar and pestle under ethanol three times. The mixture was then fused twice under air in an iron-seasoned Pt/Au crucible at a temperature of 1420°C for 30 minutes. Between fusions, the glass was again ground under ethanol to a fine powder. The mortar was cleaned between each different mixture with silica. The crucible was cleaned in Na_2CO_3 , HCl , and HF .

Sample distribution -- Several grams of glass from the final fusion were ground to a powder, split into numerous aliquots and analyzed by XRF/WDS, ICP and PIXE UCD. Other glass fragments were mounted in epoxy, polished, and carbon coated for SEM/EDS and SEM/WDS analysis at UW. PIXE microprobe analyses were made on glass fragments at Los Alamos National Laboratory. For each of the 3 synthetic varnishes, approximately 1 g of powder was submitted for XRF analysis, 0.1 g of powder for ICP analysis, 1 g of glass for PIXE microprobe, and five >0.05 g aliquots were submitted for PIXE UCD analysis. Samples were submitted for analysis during January 1990.

ICP analysis -- ICP analyses were performed on May 25, 1990 at the University of Washington on a Baird PS-1, 48 channel spectrometer, under the direction of A. J. Irving. Solutions were prepared using both major and trace element protocols presented in Xue and others (in press). Each solution was analyzed at least twice; each analysis represents the average of three individual spectral measurements. Peak intensities in blanks and 3 different standards were measured before and after intensities were measured in the synthetic varnishes. Major element values of the glasses (Si, Al, Fe, Mn, Mg, Ca, Ti, Ba, Na) were corrected using three-point calibration curves based on

measured peak intensities of U. S. Geological Survey standard rocks BHVO, AGV-1, and GSP-1 and nominal compositions reported in Govindaraju (1989). Minor element analyses (K) were corrected to basalt standard ARHCO-1 (Additon and Seil, 1988; and A. J. Irving, unpublished data). Uncertainties for ICP analyses were calculated from the sample standard deviation (1σ) of the two ICP analyses and include an absolute error due to uncertainty in blank correction. This blank correction error is only significant for K.

XRF/WDS analysis -- XRF/WDS analyses were performed on April 18, 1990 at Los Alamos National Laboratory by G. Ludeman using protocols outlined in Bower (1985). The synthetic varnish glasses were analyzed along with several geologic standards. Uncertainties stated for XRF analyses represent average (1σ) absolute, long-term errors in reference to standards and are not directly comparable to uncertainties listed for other methods.

PIXE UCD analysis -- Five aliquots of each of the three synthetic varnish standards were sent for PIXE analysis at UCD on January 15, 1990. The 15 samples were submitted with a cover letter requesting that the samples be run, "exactly as you would those of Ron Dorn's using the same analytical routines." The samples were analyzed on May 2, 1990.

The methodology used for analysis was supplied by T. Gill, UCD (personal commun. by letter May 10, 1990), "Samples of rock varnish received from the University of Washington were prepared by CNL standard technique for analysis of geological samples by PIXE. The samples received from the University of Washington were received already in a fine silt or clay particle size, so no additional preparation was necessary. Approximately 2 mg of each sample was dispersed evenly on a 2.2 cm² ring of Mylar substrate that had been coated with a microlayer of Apeizon (an organic, non-evaporative, sticky solvent which allows adhesion of the sample to the substrate.) The Mylar rings are mounted on plastic slide frames for insertion into the beamline for analysis. Matrix corrections on these samples were made using our matrix table DRUM1 (assuming a particle size of 8 to 16 microns diameter: standard matrix table for rock varnish)."

Contrary to our request when submitting the samples, output for Ba was not included in the analytical results supplied to us and dated May 2, 1990. At our request, the PIXE spectra were reanalyzed on July 25, 1990. During this reanalysis, Ba was included in the table of elements to be identified. However, neither during the May or July spectral analyses was Ba actually identified by PIXE UCD in any of the synthetic varnish standards.

Uncertainties for PIXE UCD analyses represent the sample standard deviation (1σ) of five blind replicates of each synthetic varnish standard.

PIXE microprobe analysis -- A single piece of each synthetic varnish standard was analyzed by Pam Rogers using the PIXE

microprobe at Los Alamos National Laboratory. Three separate analyses were made on each piece of glass and the results averaged. Concentrations of K, Ti, and Ca were normalized using the observed and nominal concentration of Fe in the synthetic varnish. Uncertainties for PIXE microprobe analyses represent the sample standard deviation (1σ) of three replicate analyses of each synthetic varnish standard. Details of the PIXE microprobe methodology used at Los Alamos may be found in Duffy et al. (1987).

SEM/EDS analysis -- SEM/EDS analyses were performed at the University of Washington on a JOEL 733 superprobe using a 15 keV accelerating voltage. During EDS analysis, the beam was rastered over an area of $\approx 0.8 \text{ mm}^2$. Energy-dispersive X-ray spectra were collected using a Tracor Northern detector and deconvoluted using the Tracor Northern FIT program which utilizes stored reference spectra. Reference spectra were collected so as to include at least 300 eV of interference-free background either side of the peak(s) of interest. In cases such as the Ba/Ti and K/Ca overlap, the regions of interest for each element were widened to include all peaks of the other, overlapping element.

EDS analyses were made in January and in July of 1990 using acquisition times between 1000 s and 4500 s so that Ti abundances could be determined with a precision of better than 3%. The January 1990 analyses were made using a 10 nA beam current, a high pulse-processing rate (time constant $\approx 2 \mu\text{s}$), and a dead time of $\approx 25\%$. Correction factors used in the January analyses were calculated using Tracor Northern software. Reference spectra were collected from the phases shown in Table 1 using the operating conditions stated above and a live acquisition time of 200 s. We analyzed 9 elements: Si, Al, Mg, Ti, Ca, K, Ba, Fe, and Mn.

July 1990 analyses were made using a 15 nA beam current, a high pulse-processing rate (time constant $\approx 2 \mu\text{s}$), and a dead time of $\approx 45\%$. Reference spectra were collected for 500 s and we analyzed 13 elements: Si, Al, Mg, Na, Ti, Ca, K, Cl, Ba, Fe, Mn, S, and P. The reference spectra were collected from the same phases stated in Table 1 except that Si was collected from quartz, Na and Cl were collected from NaCl, P from apatite, and Ba and S from barite. Correction factors used in the July analyses were modified after >15 other geologic standards of various composition were analyzed and the results for each element compared to the nominal values. By altering the correction factors in this fashion we reduced systematic bias for any individual element and have based our analyses on numerous rather than single standards.

All SEM/EDS data were reduced using the Tracor Northern ZAF routine. The uncertainty shown for SEM analyses of each glass represents the sample standard deviation (1σ) of ≥ 8 measurements made on polished glass sections. The uncertainty is usually limited by counting statistics but increases for some elements because the glass is not absolutely homogeneous.

SEM/WDS analysis -- SEM/WDS analyses were performed at the University of Washington on a JOEL 733 superprobe using a 15 keV accelerating voltage and a 10 nA beam current. During WDS analysis, the beam was defocused to a spot $\approx 50 \mu\text{m}$ in diameter. WDS analyses continued until aquisition time for an individual element reached 800 s or 0.5% precision based on counting uncertainty. WDS data were reduced using a Tracor Northern ZAF routine for matrix correction. WDS standards and operating conditions are detailed in Table 2. The uncertainty shown for SEM analyses of each glass represents the sample standard deviation (1σ) of ≥ 8 measurements made on polished glass sections. The uncertainty is usually limited by counting statistics but increases for some elements because the glass is not absolutely homogeneous.

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