PRELIMINARY INVESTIGATION OF SELECTED SAMPLES OF VARNISHED ROCK FROM THE BALUCO SURFACE, VICINITY OF PROPOSED LOW-LEVEL WASTE SITE NEAR FT. HANCOCK, TEXAS

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This report summarizes work done from March to June of 1989 in the preliminary investigation of varnished rock samples under consideration for AMS radiocarbon dating (Dorn, in press). The report is in three sections: (1) description of samples, (2) summary of discussions with Dr. Ronald I. Dorn, Arizona State University, and (3) summary of total organic carbon (TOC) determinations. Ultimately, it was concluded that the varnish on these samples is not well enough developed to yield reliable results, and so the work was terminated.

DESCRIPTION OF SAMPLES

The samples examined for this investigation were collected by Jeff Rubin and Eddie Collins from locality No. 82 on the Baluco surface, near the proposed LLW site. There are approximately 30 samples in the collection (see Appendix). Most of the samples are of Cox sandstone, though several pieces of "andesite" were also obtained.

The samples of Cox sandstone typically exhibit medium to dark brown weathering, and are tan colored on fresh surfaces. The rock is made up mostly of medium to fine grains of quartz (range: ~0.016 - 0.20 mm, average: ~0.08 mm), with varying proportions of a matrix containing clays (kaolinite? $\pm$ illite and/or montmorillonite-type clays), calcium carbonate (presumably calcite), iron oxides, and authigenic quartz cement. Some of the samples are moderately porous, whereas others are very tightly cemented by the authigenic quartz.

The "andesite" is medium to dark brownish gray on weathered surfaces and medium to light gray on fresh surfaces. The rock has an aphanitic groundmass, and contains abundant amphibole (hornblende?) phenocrysts. The phenocrysts are more deeply weathered than the groundmass, so that they typically are recessed 1 or 2 mm below the surface of the sample.

On sandstone samples, the actual varnish is the very thin (generally less than 0.01 mm in samples examined), dark brown to black, glossy coating that overlies the surface, and may impregnate the outermost several layers of grains and matrix (as deep as ~0.15 mm below the surface) (see Fig. 1). The surfaces of the sandstone samples are very rough, with the relief typically equal to or greater than several grain diameters (on the order of 0.1 mm). The varnish follows this rough surface topography very closely, and mimicks the relief of the underlying grains. Where the varnish is thickest, it appears to have a lamellar structure. Varnish on andesite samples appears to be somewhat thicker than that on sandstone samples, and is particularly well developed on surfaces of the amphibole phenocrysts. The surface of the andesite is not as rough as that of the sandstone.

The sandstone samples commonly have a weathered rind (as thick as 2 mm, or approximately 25 grain diameters) immediately beneath the varnish (Fig. 1). The rind is not part of the varnish, though in some samples the outermost portion is impregnated by the overlying varnish. The weathered rind of the andesite samples is thinner and less continuous than that of the sandstone.

Five representative samples were examined in the scanning electron microscope (SEM) (labelled 82-SEM1 to 82-SEM5; see Appendix). Samples 82-SEM4 and 82-SEM5 were photographed to provide a visual record of the sample surface and varnish characteristics (see Figs. 2A-D). The photographs show that the very thin varnish just barely coats the surface, and follows the underlying topography (which is very rugged at the scale of SEM examination). No obvious fungal colonies or other organic accumulations of the types described by Dorn and Oberlander (1982) were noted during the SEM examination.

SUMMARY OF DISCUSSIONS WITH DR. RON DORN

The following is a summary of background information and other helpful comments gained from telephone conversations with Dr. Ronald I. Dorn, Arizona State University, on April 7, 14 and 17, 1989:

April 7:

1. Dorn has collected and examined varnish on all types of rocks over a period of about 15 years.
2. His experience is that sandstones are the worst type of rock to work with for the varnish-dating technique.
3. Some of the more usable varnishes are as thick as 0.5 mm.
4. Dorn will commonly sample the lower layers of varnish, and then take a separate sample of the rock which underlies the varnish. This is to determine if the rock itself contains organic matter which may contaminate the varnish sample (the rock could contain organic even still living - this would skew a radiocarbon measurement toward a younger age) (see Dorn, in press, p. 1-3). According to Dorn, endolithic microorganism are common in the Chihuahuan desert.
   Some references on endolithic microorganisms:
      Friedman, in Desert Biology, 1974, v. 2.
      Ron and Friedman, Jour. Geophys. Res.
5. I described the samples from Ft. Hancock to Dorn. He cautioned strongly that the surface of the sandstone samples likely represents a surface of disintegration and spallling. Therefore, a radiocarbon date on such a sample would reflect the cessation of the last period of disintegration and spalling.
6. The general advice is that when attempting to get a radiocarbon age from rock varnish, or weathered rock, or whatever, one must make critical

assumptions about what the sample represents (i.e. when it may have begun to form; is the process ongoing? has it been interrupted periodically? has there been any loss of material due to erosion, either mechanically or perhaps chemically?).

7. I asked Dr. Dorn if it would be reasonable to remove the very thin varnish that is on the Ft. Hancock samples (and cast aside, to get rid of the yougest carbon), and then to sample the underlying (weathered) rock, and to analyze carbon there. His comments were that:
   a) it may be done, but it would actually be a new technique, one that has not been tried or tested;
   b) there may or may not be enough carbon in the underlying rock (this could be determined before sending off the sample, by burning it, and recovering carbon in the form of CO2 gas, which could later be analyzed by AMS);
   c) if there is enough carbon, it could in a large part be from endolithic microorganisms, which may be younger than the varnish layer ... again, the caution: you may get a date, but what does it reflect?

9. Finally, Dorn suggested the possibility of using other dating techniques:
   a) analysis of cosmogenic isotopes (e.g. Cl36, Be10, etc.), which begin to accumulate after the rock is exposed at the surface (or near surface?) ... [References: theory - Lal, 1988, Annual Review of Earth and Planetary Sciences, v. 16, p. 335+; practice - Phillips, 1986, Science, v. 231, p. 41-43] (Fred Phillips, Texas Tech University, can provide this service on a periodic basis, at a cost of possibly $2000 per sample, or group of samples?).
   b) dating of calcium carbonate deposition in soils: D.(B?) L. Allen, Texas Tech University (soil science and agr. dept's).

As a result of the April 7 conversation, I sent a set of seven small pieces of No. 82 rock varnish samples (6 of sandstone, refered to as 82-A to 82-F, and 1 of andesite, refered to as 82-G; see Appendix) to Dr. Dorn for him to examine. I spoke with him on April 14 and 17 and obtained the following comments:

<u>April 14 and 17</u>:

1. Dr. Dorn note that the sandstone samples are not quite as bad as he had imagined (i.e. they are not as friable as some that he has seen, and therefore can potentially yield useful information).
2. Dorn suggested several things:
   a) go after the varnish that coats surfaces <u>within recessed pits</u>, as these most likely containthe earliest formed and preserved, and therefore oldest varnish. This would likelyrequire many more samples, in order to obtain enough volume of material.
   b) next, he recommended retrieving a number of separate scrapings of varnish from the pits, one from each from each individual cobble (he suggests doing this for 10 different cobbles).
   c) then, fuse each sample into a bead, which should be polished, and analyzed on a microprobe (using WDS), to determine cation rations (Ba+Ti, Ca, K) (see Dorn, 1983) for each cobble. The significance of

the results would be: (1) if the cation ratios are all similar, then it would be a reasonable assumption that the surfaces of the cobbles were deposited or exposed at approximately the same time; (2) if the ratios are different, or spread over a range, it indicates that surfaces of different cobbles were exposed at different times, possibly representing weathering and breakup of cobbles that were originially larger (i.e. boulders). If (1) is true, then it would be reasonable to attempt radiocarbon AMS dating, if (2) is true, then any radiocarbon age(s) would represent a mix of possibly widely varying ages of individual surfaces.

d) Dorn's impression, from looking at the samples, is that the varnish is likely to be radio-carbon "alive", meaning that the varnish is probably less than 40,000 yrs. old. The samples with the lowest cation ratios have probably been exposed for the longest times, and therefore would be the most appropriate samples to work with.

e) There are some uncertainties and warnings: (1) what is the cation ratio of the underlying rock? to what degree does it affect the cation ration of the varnish? (2) varnish scraping must be done with a light touch, and with very fine tools (finer than what we have been using so far). As before, the goal is to get at the lower layer of the varnish.

SUMMARY OF TOTAL ORGANIC CARBON (TOC) DETERMINATIONS

Seven representative samples were selected for preliminary checks to determine if there would be enough TOC for ^{14}C analyses. They are refered to as 82-1, 82-2, 82-3, 82-4, 82-5, 82-6, and 82-7b (see Appendix). The samples were rinsed (with light scrubbing) under distilled water, blown dry with an air hose, then scraped, gouged, ground on, chipped, and subjected to various other abuses to remove subsamples (i.e. varnish, weathered rind, and essentially unweathered rock) for analysis. The subsamples (collected and placed in small bottles) were given to Steve Tweedy (Mineral Studies Lab) for analysis. The results are reported in Table 1.

CONCLUSIONS

It was concluded that the varnish on the sandstone samples, which make up the bulk of the sample collection, is not well enough developed to yield reliable results. It was thought that it might be possible to obtain a date from the carbon in the weathered rind, but this idea was abandoned because of the likelihood that the rind represented an open system that was continually being replenished by young and/or recent carbon. Because of these problems, the project was terminated.

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(Good SEM photos)

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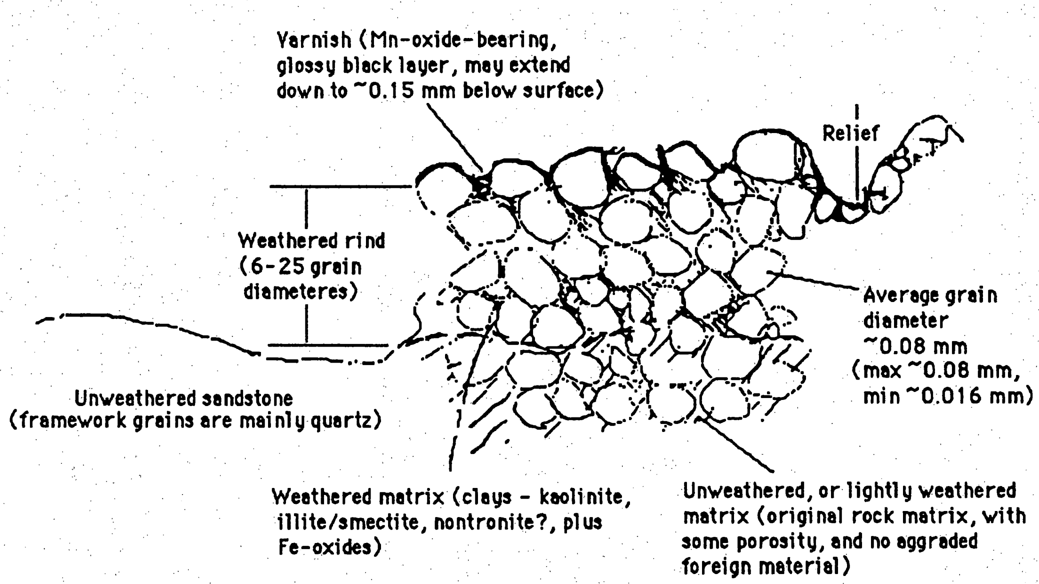

Figure 1. Schematic map of a typical sample of varnished sandstone, showing the varnish layer, weathered rind, and unweathered rock. The varnish layer is discontinuous or not completely developed in some samples; the weathered rind is not present in all samples, and varies considerably in thickness.

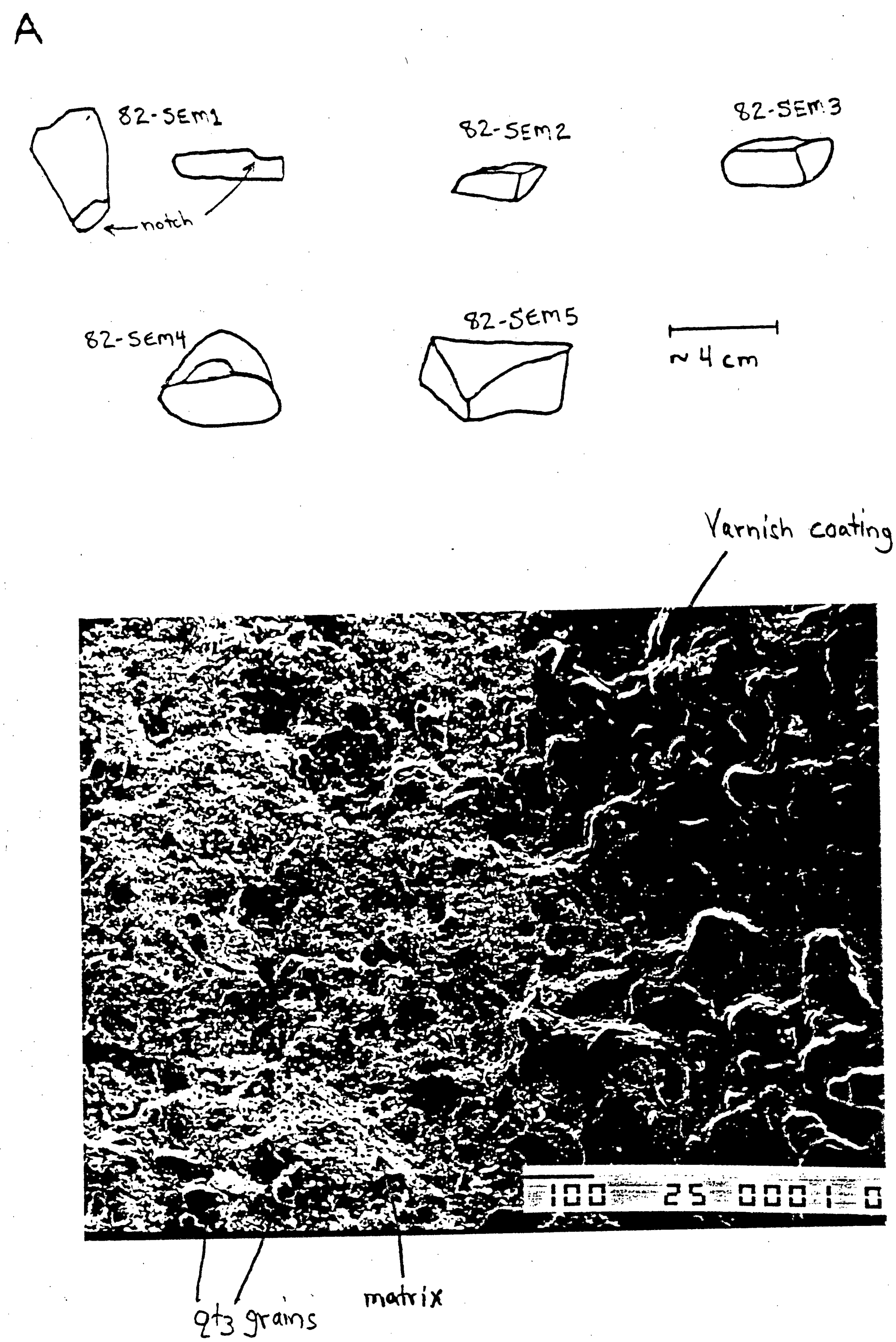

Figure 2. SEM photomicrographs of representative samples of varnished Cox sandstone from locality No. 82 on the Baluco surface. A - Index map showing rough sketches of the five samples (82-SEM1 through 82-SEM5) that were examined in the SEM. B - Photomicrograph of 82-SEM5 showing exposed sandstone on left and varnish coating on right; sandstone consists of grains of quartz (arrows) in a matrix of clays, iron oxides, calcite, and authigenic quartz cement; varnish closely mimicks the topography of the underlying sandstone surface (scale bar is 100 micrometers long; magnification on SEM 100x). (continued on next page)

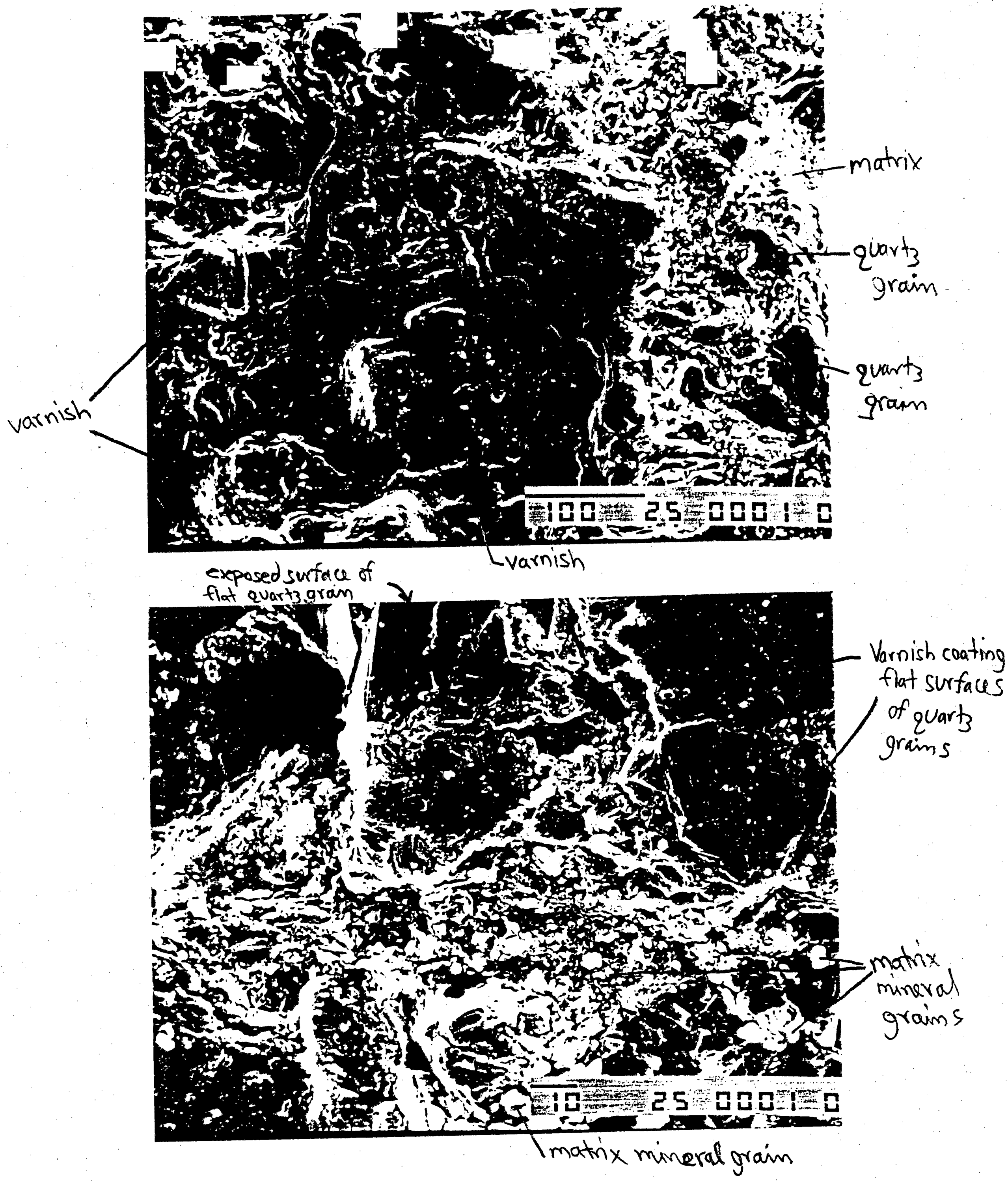

Figure 2 (continued). C - Photomicrograph of 82-SEM4 showing thin (<0.01 mm thick), patchy varnish (arrows) in left two-thirds of view, and exposed sandstone in right one-third (scale bar is 100 micrometers long; magnification on SEM 200x). D - Photomicrograph of 82-SEM4 showing close-up view of several varnish patches (arrows) coating flat surfaces of underlying quartz grains; brighter areas of photomicrograph show abundant minute grains of matrix minerals on framework quartz grains and in voids between grains (scale bar is 10 micrometers long; magnification on SEM 750x).

Table 1. Summary of total organic carbon (TOC) determinations (analyses performed by Steve Tweedy and associates, Mineral Studies Lab of Bureau of Economic Geology).

Bottle No.	Sample wt. = filled wt.-empty wt.	Contents	Total C - Mineral C = TOC
1 (MSL 89-450)	23.67-20.90 = 2.77 g	Outer layer from parts parts of each sample (remaining impurities on sample surface, varnish, and a little bit of weathered rind).	0.39 0.04 0.35 wt. %
2	32.17-21.13 = 11.04 g	Weathered rind from top surface of sample 82-1.	(see no. 4)
3	26.10-21.61 = 5.49 g	Weathered rind from top surfaces of samples 82-2 through 82-7b.	(see no. 4)
4 (MSL 89-451)	22.92-21.03 = 1.89 g	Mixture containing 0.69 g from bottle no. 2 and 1.20 g from bottle no. 3.	0.30 0.15 0.15 wt. %
5	21.93-21.03 = 0.90 g	Unweathered rock from from beneath weathered rind of each sample (note: this sample was obtained by grinding on the rock with a carborundum(?) grinding stone which wore down about 30-50%; the stone turned out to be bonded by a cement which itself contains carbon - see 5a - these samples were thus rescraped, and TOC redetermined - see 6, 7 and 8)	2.22 2.04 0.16 wt. %

(continued on next page)

Table 1. Summary of total organic carbon (TOC) determinations (continued).

Bottle No.	Sample wt. = filled wt.-empty wt.	Contents	Total C - Mineral C = TOC
5a	----	Grinding stone (remaining portion of stone, crushed and analyzed)	1.1 0.0 1.1 wt. %
6	23.45-20.94 = 2.51 g	Outer layer from parts of each sample (includes any remaining surface impurities, varnish, and some of underlying weathered rock; this sample was obtained by light-handed gouging with a steel burr in a dentist's drill).	0.48 (avg. of .47/.49) 0.11 0.37 wt. %
7	22.76-20.49 = 2.27 g	Weathered rind from beneath areas bared during collection of sample in no. 6 (may include a very small amount of remaining varnish, plus some of underlying, unweathered rock; this sample was obtained by light-handed gouging with a steel burr in a dentist's drill).	0.79 (.79/.79) 0.44 (.43/.45) 0.35 wt. %
8	24.08-20.98 = 3.10 g	Unweathered rock from beneath weathered rind bared during collection of sample in no. 7 (this obtained by careful chipping with a pair of pliers and a small hammer (actually, a wrench) - the pieces were crushed to final size in a shatterbox, by Steve Tweedy.	2.98 (2.98/2.98) 2.97 (2.96/2.97) 0.01 wt. %

APPENDIX

Samples examined and scraped:

82-1	(initially scraped by J. Rubin, 3/16/89)
82-2	(82-2 & 82-4 are two pieces of the same sample)
82-3	
82-4	(82-2 & 82-4 are two pieces of the same sample)
82-5	
82-6	
82-7b	(82-7a & 82-7b are two halves of a sample from which two one-inch cores were removed for varnish cation ration (VCR) analysis)

Samples examined: small pieces sent to Dr. Ronald I. Dorn for comments:

82-A	
82-B	
82-C	
82-D	
82-E	(whole sample sent ... we have a nearly identical sample, labelled 82-E')
82-F	
82-G	

Samples examined in SEM:

82-SEM1	
82-SEM2	(same as sample 82-E')
82-SEM3	(scraped initialy by J. Rubin, 3/16/89)
82-SEM4	(scraped initialy by J. Rubin, 3/16/89)
82-SEM5	(scraped initialy by J. Rubin, 3/16/89)

Other samples:

There are about 15 other samples in the locality No. 82 collection which were deemed entirely inappropriate for the varnish dating project (surface is too rough, varnish is too thin or discontinuous, or surface of sample has undergone erosion or disaggregation). These samples have been labelled 82-x1, 82-x2, etc.