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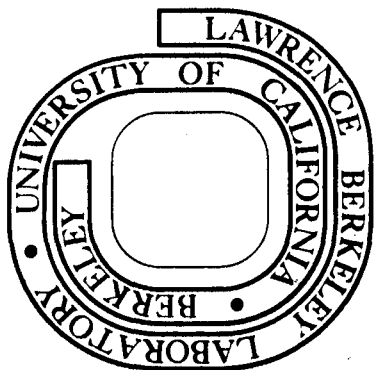
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PERSPECTIVES ON DATING OF GREAT BASIN PETROGLYPHS BY
NEUTRON ACTIVATION ANALYSIS OF THE PATINATED SURFACES*

James C. Bard**

Frank Asaro***

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ABSTRACT

The possible relative dating of petroglyphs by nuclear measurements on desert varnish is explored and a literature review of previous concepts and analytical work is presented. In the present work, the abundances of 28 trace and major elements in desert varnish samples from the Grimes Point Petroglyph Site in western Nevada were measured by precise neutron activation analysis techniques. Samples of both desert varnish and heart-rock from a non-artifactual test boulder of andesite were studied and the elements manganese, uranium, thorium and cerium exhibited the greatest enhancements in the varnish fractions and thus offer the best possibilities for dating purposes by these methods.

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INTRODUCTION

Desert varnish is the term commonly applied to the dark brown and black coatings of iron and manganese oxides which frequently occur on rocks of the desert regions of the southwestern United States and on rock surfaces in environmentally diverse areas in different parts of the world. Early investigations by Blake(1905), Lucas(1905), Linck(1901), Merrill(1898), Turner(1909) and White(1924) are reviewed in some detail by Laudermilk(1931). Archaeologists have long supposed that some way of assigning a time-rate to patination might be discovered, and that if this were achieved, many prehistoric lithic features could thereby be dated. Goodwin(1960) has reviewed the earlier literature on this subject. We may, with present equipment be on the verge of realizing this hope.

Desert varnish is primarily a weathering phenomenon which involves the solutions of Mn, and Fe, their transportation to the varnished surface and deposition there as a fairly stable coating. Most of the varnish substances originate from chemical decomposition of the associated rocks or the surrounding mantle of weathered debris. According to Engel and Sharp(1958:515), Mn and Fe may be transported by migration of solutions or by ionic diffusion through films of moisture supplied, perhaps more by dew than rain. Initial deposition may become more important owing to the catalytic effect of MnO_2 . The high Mn to Fe ratio in varnish may be due to either weathering solutions rich in Mn, deposition of Fe before the solutions reach the site of varnishing, or leaching of Fe subsequent to deposition of the varnish.

General conclusions reached by Engel and Sharp(1958) and earlier investigators are that desert varnish is an 'amorphous' substance whose principal constituents are O, H, Si, Al, Fe, Mn, Ca, Mg, Na, and K; and that Fe_2O_3 and MnO show the greatest enrichment relative to the underlying rock and that Fe and Mn give varnish its distinctive physical characteristics. Hooke, et al.(1969:275) found that varnish appears to be largely amorphous with no recognizable crystalline patterns. The chemical composition of varnish varies from rock to rock and also from point to point on a single rock.

In a study of desert varnish samples from Deep Springs Valley and Death Valley California, Hooke, et al.(1969), using an electron microprobe, determined that FeO and MnO increase outward from the heart rock through the varnish and SiO_2 , Al_2O_3 , and K_2O decrease outward. A boundary can be drawn between the point where MnO and or FeO increase rapidly and the point where SiO_2 and or Al_2O_3 decrease rapidly. The outer or main layer is rich in Fe and Mn, whereas the subordinate layer is rich in Si and Al. Hooke, et al.(1969:284) observed that K_2O and Al_2O_3 variations are similar and this suggests that K may be associated with Al, in some incipient or residual crystal structure. For example, subordinate layers which are rich in these oxides may be altered parts of the rock which have lost their crystalline structure and to which Fe and Mn have been added from external sources. During weathering of rock

surface a rind is formed from which the more mobile elements such as Ca, Mg, and Na have been leached and in which microscopic cracks have presumably developed (Engel and Sharp, 1958:500-501). Such depletion without addition of other elements would produce an apparent increase in concentration of the remaining constituents. Engel and Sharp(1958:501) suggest that Al is almost unchanged in the rind and that there is Fe, Ti, and Mn from external sources being added into the cracks and onto the rock surface such that FeO, TiO₂ and MnO increase outward from the heart rock to the varnish layer. According to Hooke, et al.(1969:285), if the subordinate layer consists partially of altered rock from the rind, elements formerly in this part of the rind will have been contributed to the varnish. Hence, concentrations of most elements in varnish should reflect their concentrations in the rock. Correlations will be poorest for those—elements supplied largely from external sources. There need be no leaching gradient suggesting movement of elements outward from the rock or rind into the varnish.

Hooke, et al.(1969:285-287) discuss the mechanisms of Fe and Mn precipitation and conclude that the process most applicable to desert varnish formation involves precipitation of much of the Fe before the Fe-Mn bearing solutions reach the site of the varnish formation. Because the MnO content of varnish increases outward faster than the FeO content, they suggest that Mn and Fe are further fractionated during precipitation on the varnish. Such fractionation may account for the thicker varnish

found in hollows and cracks. As moisture evaporates from exposed areas, the concentration of dissolved ions should increase. This would result in a concentration gradient towards the areas of deeper water and might cause ionic diffusion of Fe and Mn towards the hollows. Because Mn precipitates last, proportionally less Fe would migrate to the hollows. Varnish in hollows does appear to have a lower Fe/Mn ratio and it is generally dark brown, whereas varnish on exposed surfaces is reddish brown in color (Hooke, et al., 1969:286).

Engel and Sharp(1958) using a combination of classical wet chemical methods along with spectographic analysis, determined the trace element content of some twenty two different varnishes from various locations in the southern California deserts. In order to relative abundance, were found the following trace elements: Ti, Ba, Sr, Cu, Ni, Zr, Pb, V, Co, La, Y, B, Cr, Sc, and Yb. In some but not all varnishes were found Cd, W, Ag, Nd, Sn, Ga, Mo, Be, and Zn. They found that most of the trace elements were enriched in the varnish especially Cu, and Co; also enriched were Ni, Pb, Ba, Cr, Yb, B, Y, Sr, and V. Desert varnish samples from six localities in both northeastern Nevada and Death Valley California were studied by Lakin, et al.(1963) using semi-quantitative spectographic analysis. They were able to detect and measure the following trace elements: Ti, Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Ga, La, Mo, Ni, Pb, Sb, Sc, Sn, Sr, V. W. Y, Zn, and Zr.

In summary, desert varnish has two layers, the subordinate layer

being rich in SiO_2 and Al_2O_3 and the outer layer which is rich in FeO and MnO. The subordinate layer may be altered rock which has lost its crystal structure and to which Fe and Mn have been added. Depending on the heart rock material, FeO, Al_2O_3 and K_2O either increase or decrease in concentration outwards through the varnish from the heart rock-varnish contact. MnO generally increases in concentration outward. Comparisons of these variations with data on the bulk composition of the heart rock suggest that elements which increase outward may be supplied predominately from the underlying heart rock. The ratio of FeO to MnO generally decreases outward through the varnish. Some of the Mn in varnish is dissolved whenever Fe-Mn bearing solutions arrive on the rock and that fractionation occurs during subsequent precipitation such that Mn is precipitated last.

METHOD OF ANALYSIS

In neutron activation analysis (NAA) material is irradiated in a nuclear reactor and minute amounts of the chemical elements which comprise the material are changed into radioactive forms. Some of the resulting radiations (gamma rays), which are emitted have measurable properties (energies) which are characteristic of the component elements. With measuring devices such as solid state detectors coupled to pulse height analyzers one can distinguish between these energies and identify the elements producing them. By comparing the amounts of the characteristic radiations produced by irradiation of samples of interest

and standards of known composition, the amounts of the different chemical elements can be determined. Under carefully controlled conditions with multiple irradiations and measurements, many elements ranging in abundance from percent to less than one part-per-million can be measured simultaneously and with high precision.

The surface of the Grimes Point Test Boulder was cleaned with alcohol in five different locations, each of which averaged some fifty square centimeters in area. Each area [GPPS 1-5] was scraped with a hand-held sapphire scraper until about 100 mg of powder was obtained. The weighed powder was mixed with 50 mg of cellulose and compacted into a pill using a hand operated hydraulic press. The pills were encapsulated in polyethylene foil and packaged in a high density polyethylene capsule for irradiation in the Berkeley Triga reactor (cf. Perlman and Asaro 1969, 1971, for specific details of neutron activation analysis procedures).

Each capsule contains "standard pottery" which serves as a standard by which the elemental abundances of the samples can be compared. The specific content and calibration of "standard pottery" is outlined by Perlman and Asaro(1971) and in Table One, which presents the calibration standards for the elements Nd, Mg, V, Tb, Ta, and Zn.

The recipe for irradiation, cooling and counting was designed to maximize the accuracy in determining the maximum number of useful elements. Each batch of pills is subjected to two irradiations; the first for five minutes at a flux of about 1.7×10^{11} neutrons/cm²-sec,

the second for eight hours at a flux of 2×10^{13} . Following the short irradiation the gamma-ray radioactivity of the pills is measured for one minute after a period of about eight minutes to permit transport of the samples to the measuring area. Al, Ca, Mg, V, and Cl are measured in the short irradiation but the precision is relatively poor, especially for the latter three elements. After an hour to allow these radioactivities to decay, the samples are re-measured for six minutes each. Na, Mn, Dy and K are measured in this analysis. Ga and In are also measured but the sensitivity is poor. The detector for these measurements is a 7cc intrinsic germanium solid-state counter.

About two weeks after the short bombardment the pills are re-wrapped in pure aluminum, repackaged in an aluminum capsule and irradiated again for eight hours at the highest flux of the reactor, about 2×10^{13} neutrons/cm²-sec. They are stored for 11 days (to permit the Na background to diminish) then counted for 20 minutes each with a 1cc Ge-Li detector. This analysis is programmed for radioactive species with half-lives in the range of 1-10 days and gives results for the following elements: Ba, U, Sm, Ti, Lu, La, and As. Mo, W, Ho, Br, and Cd are also measured in this analysis but the precision is poor. The same pills are again set aside for a further cooling period of at least three weeks. This further lowers the background permitting better analysis of the longer lived species. The pills are counted for 150 minutes each with a 5cc Ge-Li detector. As a result of these long counts,

data are obtained for Fe, Sc, Zn, Co, Cs, Sb, Cr, Hf, Th, Ni and Rb. Following this analysis, the samples are analyzed for 80 minutes with the 1cc Ge-Li detector for Ta, Eu, Yb, Ce, Hf, and Nd. A number of elements are measured in several different analyses and these are used to check for measurement errors. Generally nearly all measurements are handled by automatic sample changers and counters with the data transferred to magnetic tapes for subsequent computer analysis.

After the first five scrapes (GPPS 1-5) of the surface varnish were obtained, the same areas were cleaned and scraped again (GPPS 16-20), GPPS-16 was "inoperative," having been lost in the hydraulic press. The test areas were cleaned and a small area in each corner of each test area was abraded down with a power-sander until the heart rock was exposed. Samples (GPPS 6-10) were secured from these areas by drilling with both sapphire and diamond drill bits. Areas of rock were also broken off the bottom of the boulder, and heart rock samples (GPPS 11-15) were obtained from inside these broken pieces.

RESULTS AND DISCUSSION

All elements measured satisfactorily by neutron activation analysis, except Na, are enriched in the varnish samples (GPPS 1-5), 17-20) and the varnish is somewhat homogeneous within all nine of the samples. Because of the uneven test boulder surface, each scrape or sample contains a large amount of heart rock contamination. In order to determine the "pure" varnish fraction of the samples, the abundances

of the oxides of the major and minor elements Mn, Mg, Ca, Fe, and Na in the varnish samples were tabulated [ΣV] and the elemental abundances of these same elements in the heart rock [ΣH] were subtracted. This difference divided by [$1 - \Sigma H$] gives the minimal percentage of pure varnish in the samples. If the abundances of all of the varnish samples and those of the underlying heart rock are treated in this fashion, one calculates a minimum of 11.6 ± 2.8 % for the percentage of varnish in our varnish fractions. Subtracting two standard deviations, we arrive at a figure of 6.1% as the lower limit of pure varnish, and the remainder being the proportion of contaminating heart rock. The differences in elemental abundances in our measurements could just reflect the different amount of heart rock "contamination" in each sample. GPPS-1 probably has less heart rock contamination and thus would account for it apparently being more enriched than GPPS 2-5. Sodium is slightly depleted in the varnish layers, as in Si which is not measured by NAA. The dilution of Na is about 4% which also represents a minimum percentage of pure varnish in our varnish fractions. Table 2 is a presentation of the elemental abundances of some selected elements and rare earths which were considered to be useful. The elemental abundances and group averages of the major elements are presented first, then the elements which are dramatically enriched in the varnish (U, Th, Mn and Ce), then the rare earths, and finally the remaining trace elements in alphabetical order. Table 3 is a

presentation of the abundances, in percent, of major elements in the heart rock expressed as oxides. The rock type corresponding to this chemical composition is andesite. The heart rock data are generally internally consistent from different parts of the boulder, except for the element barium, which is considerably lower in the bottom part.

Hooke, et al. (1969) report that FeO and MnO increase from the heart rock through the varnish. Our NAA data tend to confirm this, however, our Al_2O_3 does not appear to decrease through the varnish as Hooke, et al. (1969) report, but rather appears to be almost unchanged, which is what Engel and Sharp(1958:501) report. Comparisons of SiO_2 and K_2O with other data are not possible, as K is measured poorly by our NAA measurements and Si not at all. We were not able to differentiate between layers because the scraping procedure used in the present work cut through to the heart rock. Any differences between the subordinate layer or rind and the varnish layer would be obscured by the large heart rock component in the varnish samples. Our data does not clearly favor any one particular formation process per se, but are consistent with a combination of weathering and leaching of internal material, and solution and precipitation of material from external sources. Recently, Bauman (1976) suggested broad similarities exist between desert varnish formation and formation of hydrous ferromanganese oxide concretions in marine environments.

DATING OF GREAT BASIN PETROGLYHS

Petroglyph manufacturing involves the removal by pecking the desert varnish coating with a suitable hard material, usually a dense cobble with a pointed end. The lighter colored heart rock contrasts with the dark brown varnish surrounding the pecked out design (cf. Bard and Busby, 1974). At the Grimes site, a great many degrees of patination are present; some petroglyphs (conical "pits") are indistinguishable from the natural rock surfaces in color and degree of weathering, and other petroglyphs sharply contrast with the rock surface as a result of the penetration of the design through the darker surface into the lighter-colored and unaltered interior body of the heart rock. The latter are clearly much more recent than the heavily patinated examples (Heizer and Baumhoff, 1962:284). The presumably oldest style (Pit and Groove) in the Western Great Basin has in almost all instances become re-patinated. The deep pits and grooves have accumulated through the passage of an unknown amount of time, a coating of chocolate brown desert varnish. Heizer and Baumhoff (1962:284) suggest that the youngest petroglyphs at the Grimes site are at least 150-200 years old and appear as fresh as though they were made yesterday. Because the patination appears to have progressed to its ultimate in the conical pits and grooves, Heizer and Baumhoff venture to guess that these pits may be fifteen to twenty times as old as the obviously recent examples.

Results of the analysis of the Grimes Point Test Boulder by neutron activation point to the possible use of NAA in the relative dating of the Western Great Basin petroglyph styles. Because of the relative precision of NAA and the ability it has to provide quantitative elemental abundances for many major elements and trace elements, it may aid in establishing an index of repatination of petroglyphs as a function of time, that is, an age vs. elemental composition index for the relative dating of petroglyphs focusing on rare earth enrichments. Many trace elements are remarkably enhanced in the varnish samples, especially Mn, Ce, Th, and U which range from four to nine times as great in our varnish fraction samples compared to heart rock samples (see Figure 1). Recently executed petroglyphs in the rock surfaces at the Grimes Point locality should show values for the various elements similar to those obtained in this study for heart rock. Old petroglyphs should resemble the varnish samples from this study in terms of elemental and rare earth abundances. Thus, through time, exposed heart rock, such as was exposed when a petroglyph was manufactured, should re-patinate with desert varnish, and progressively older petroglyphs may register larger concentrations of certain elements and rare earths approaching the abundances of unmodified desert varnish.

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TABLE 1
CALIBRATIONS (a)

Abundances of U.S.G.S. BCR Standard Rock
Measured by Same Techniques as Present Work^{1.} Literature Values^{2.}

| | | |
|------|----------------------------|------|
| 2.3 | <u>Mg</u> % ^b | 2.09 |
| 30 | <u>Nd</u> ppm ^c | 29 |
| 490 | <u>V</u> ppm ^c | 399 |
| 0.97 | <u>Tb</u> ppm ^c | 1.0 |
| 0.72 | <u>Ta</u> ppm ^d | 0.91 |
| 150 | <u>Zn</u> ppm ^b | 120 |

1. H.V. Michel, H.R. Bowman, and F. Asaro
1975 Unpublished Data.

2. F.J. Flanagan
1973 1972 Values for International Geochemical
Reference Samples. GEOCHIMICA ET COSMOCHIMIA
ACTA 37:1198-1200.

a Calibrations for all elements not listed were published by Perlman and Asaro (1971) and measurements of these elements in BCR standard rock gave values consistent with the literature (Flanagan, 1973).

b Calibrated with flux monitor.

c Calibration has not been published

d Difference from literature value is much larger than presumed errors of measurement.

TABLE 2

Elemental Abundances ^a of Grimes Point SamplesUPPER VARNISH LAYER FROM TOP OF THE GRIMES POINT TEST BOULDER

| RUN | SAMPLE | Al% | Mg% | Ca% | Fe% | Na% |
|---------|--------------|-------------|-----------|-----------|------------|------------|
| 884 | E GPPS 1 | 9.81 ± .41 | 5.3 ± 1.8 | 7.0 ± 1.3 | 6.59 ± .12 | 2.82 ± .04 |
| | F 2 | 9.93 ± .17 | 3.7 ± 1.3 | 6.8 ± .9 | 6.39 ± .12 | 2.78 ± .04 |
| | G 3 | 9.88 ± .18 | 3.4 ± 1.3 | 6.0 ± .9 | 6.33 ± .12 | 2.73 ± .04 |
| | H 4 | 10.17 ± .22 | 3.5 ± 1.3 | 7.5 ± 1.0 | 6.12 ± .11 | 2.86 ± .04 |
| | J 5 | 10.17 ± .29 | 2.8 ± 1.5 | 7.0 ± 1.1 | 6.25 ± .12 | 2.80 ± .04 |
| AVERAGE | ^b | 9.99 ± .25 | 3.8 ± 1.4 | 6.8 ± 1.0 | 6.34 ± .17 | 2.80 ± .04 |

VARNISH REMOVED FROM SAME AREAS AS PREVIOUS LAYERS EXCLUDING FIRST AREA

| | | | | | | |
|---------|-----------|-------------|-----------|-----------|------------|------------|
| 894 | R GPPS 17 | 9.99 ± .13 | 2.7 ± 1.3 | 3.8 ± .8 | 6.07 ± .08 | 2.75 ± .03 |
| | S 18 | 9.94 ± .14 | < 2.6 | 7.2 ± .9 | 6.18 ± .08 | 2.74 ± .03 |
| | T 19 | 10.09 ± .18 | 2.8 ± 1.3 | 5.4 ± .9 | 5.78 ± .08 | 2.84 ± .04 |
| | U 20 | 10.26 ± .23 | 3.0 ± 1.4 | 6.7 ± 1.1 | 6.04 ± .08 | 2.78 ± .03 |
| AVERAGE | | 10.07 ± .17 | 2.1 ± 1.6 | 5.8 ± 1.5 | 6.02 ± .17 | 2.78 ± .04 |

HEART ROCK FROM SAME AREAS AS VARNISH SAMPLES

| | | | | | | |
|---------|----------|-------------|-----------|----------|------------|------------|
| 884 | K GPPS 6 | 9.34 ± .12 | 3.8 ± 1.1 | 5.1 ± .7 | 5.22 ± .10 | 2.99 ± .03 |
| | M 7 | 9.71 ± .16 | 2.3 ± 1.3 | 5.6 ± .9 | 5.26 ± .10 | 2.90 ± .04 |
| | N 8 | 9.24 ± .15 | 2.9 ± 1.0 | 6.3 ± .8 | 5.24 ± .10 | 2.85 ± .03 |
| | O 9 | 10.13 ± .19 | 1.3 ± 1.0 | 6.0 ± .8 | 5.00 ± .10 | 2.85 ± .03 |
| | P 10 | | 2.4 ± 1.1 | 6.0 ± .9 | 5.06 ± .10 | 2.99 ± .03 |
| AVERAGE | | 9.61 ± .40 | 2.5 ± 1.1 | 5.8 ± .8 | 5.16 ± .12 | 2.92 ± .07 |

HEART ROCK FROM AREAS IN BOTTOM OF THE BOULDER

| | | | | | | |
|---------|-----------|------------|-----------|----------|------------|------------|
| 884 | Q GPPS 11 | 9.30 ± .10 | 1.6 ± 1.2 | 5.4 ± .7 | 4.98 ± .09 | 2.98 ± .03 |
| | R 12 | 9.44 ± .12 | 1.5 ± 1.1 | 5.5 ± .7 | 5.31 ± .10 | 2.98 ± .03 |
| | S 13 | 9.31 ± .13 | .9 ± 1.0 | 6.5 ± .7 | 5.06 ± .09 | 2.95 ± .03 |
| | T 14 | 9.24 ± .15 | 2.0 ± 1.0 | 5.5 ± .8 | 5.34 ± .10 | 2.93 ± .03 |
| | U 15 | 9.48 ± .18 | .7 ± 1.0 | 5.8 ± .8 | 5.17 ± .09 | 2.85 ± .03 |
| AVERAGE | | 9.35 ± .14 | 1.4 ± 1.1 | 5.8 ± .7 | 5.17 ± .16 | 2.94 ± .05 |

UPPER VARNISH LAYER FROM TOP OF THE GRIMES POINT TEST BOULDER

| RUN | SAMPLE | Ti% | U ppm | Th ppm | Mn ppm | La ppm |
|---------|--------|-----------|------------|--------------|-------------|------------|
| 884 E | GPPS 1 | .43 ± .08 | 5.54 ± .11 | 14.84 ± .38 | 8647 ± 85 | 53.1 ± 3.1 |
| | F 2 | .49 ± .06 | 4.62 ± .10 | 11.37 ± .33 | 5854 ± 58 | 40.4 ± 2.8 |
| | G 3 | .51 ± .06 | 4.17 ± .09 | 9.28 ± .31 | 5416 ± 53 | 40.0 ± 2.8 |
| | H 4 | .39 ± .06 | 3.68 ± .09 | 9.56 ± .31 | 5181 ± 50 | 43.0 ± 2.8 |
| | J 5 | .45 ± .07 | 4.86 ± .10 | 8.83 ± .31 | 7063 ± 69 | 45.0 ± 2.9 |
| AVERAGE | | .45 ± .07 | 4.57 ± .70 | 10.78 ± 2.23 | 6432 ± 1434 | 43.2 ± 5.4 |

VARNISH REMOVED FROM SAME AREAS AS PREVIOUS LAYERS EXCLUDING FIRST AREA

| | | | | | | |
|---------|---------|-----------|------------|------------|------------|------------|
| 894 R | GPPS 17 | .57 ± .04 | 4.06 ± .04 | 9.32 ± .26 | 5341 ± 48 | 40.5 ± 1.0 |
| | S 18 | .47 ± .03 | 4.29 ± .04 | 8.81 ± .25 | 5988 ± 54 | 40.8 ± .9 |
| | T 19 | .50 ± .03 | 3.80 ± .04 | 9.03 ± .27 | 5359 ± 49 | 41.4 ± .9 |
| | U 20 | .47 ± .03 | 4.39 ± .04 | 8.14 ± .24 | 6753 ± 61 | 43.9 ± .9 |
| AVERAGE | | .50 ± .05 | 4.14 ± .26 | 8.83 ± .40 | 5860 ± 666 | 41.7 ± 1.7 |

HEART ROCK FROM SAME AREAS AS VARNISH SAMPLES

| | | | | | | |
|---------|--------|-----------|------------|------------|-----------|------------|
| 884 K | GPPS 6 | .52 ± .04 | .71 ± .06 | 1.69 ± .22 | 1240 ± 13 | 15.5 ± 2.2 |
| | M 7 | .42 ± .06 | .67 ± .08 | 1.45 ± .27 | 1214 ± 14 | 11.6 ± 2.2 |
| | N 8 | .41 ± .05 | 1.03 ± .07 | 1.70 ± .22 | 1270 ± 14 | 16.1 ± 2.3 |
| | O 9 | .43 ± .05 | .80 ± .07 | 1.88 ± .23 | 1141 ± 13 | 18.2 ± 2.4 |
| | P 10 | .44 ± .05 | .77 ± .06 | 1.80 ± .20 | 1129 ± 13 | 17.1 ± 2.2 |
| AVERAGE | | .44 ± .05 | .80 ± .14 | 1.70 ± .23 | 1199 ± 62 | 16.2 ± 2.9 |

HEART ROCK FROM AREAS IN BOTTOM OF THE BOULDER

| | | | | | | |
|---------|---------|-----------|-----------|------------|-----------|------------|
| 884 Q | GPPS 11 | .42 ± .04 | .60 ± .06 | 1.66 ± .21 | 1055 ± 10 | 14.0 ± 2.0 |
| | R 12 | .50 ± .04 | .67 ± .06 | 1.42 ± .21 | 1081 ± 10 | 13.4 ± 2.1 |
| | S 13 | .41 ± .02 | .70 ± .06 | 1.51 ± .21 | 1034 ± 10 | 12.8 ± 2.0 |
| | T 14 | .49 ± .05 | .60 ± .06 | 1.40 ± .22 | 1089 ± 10 | 17.9 ± 2.2 |
| | U 15 | .45 ± .05 | .77 ± .06 | 1.62 ± .21 | 1036 ± 10 | 16.6 ± 2.1 |
| AVERAGE | | .45 ± .04 | .65 ± .06 | 1.52 ± .21 | 1059 ± 25 | 15.1 ± 2.1 |

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UPPER VARNISH LAYER FROM TOP OF THE GRIMES POINT TEST BOULDER

| RUN | SAMPLE | Ce ppm | Nd ppm | Sm ppm | Eu ppm | Tb ppm |
|---------|--------|----------------|------------|------------|------------|------------|
| 884 E | GPPS 1 | 182.29 ± 1.80 | 49.5 ± 3.0 | 9.00 ± .05 | 2.42 ± .02 | 1.22 ± .08 |
| | F 2 | 146.34 ± 1.53 | 40.7 ± 2.7 | 7.62 ± .04 | 2.16 ± .02 | .98 ± .07 |
| | G 3 | 125.26 ± 1.38 | 36.8 ± 2.6 | 7.00 ± .04 | 1.99 ± .02 | .97 ± .07 |
| | H 4 | 122.26 ± 1.35 | 42.5 ± 2.7 | 7.21 ± .04 | 2.08 ± .02 | .91 ± .07 |
| | J 5 | 129.24 ± 1.41 | 40.9 ± 2.7 | 7.83 ± .05 | 2.20 ± .02 | .93 ± .07 |
| AVERAGE | | 141.14 ± 24.81 | 42.1 ± 2.7 | 7.73 ± .78 | 2.17 ± .16 | 1.00 ± .13 |

VARNISH REMOVED FROM SAME AREAS AS PREVIOUS LAYERS EXCLUDING FIRST AREA

| | | | | | | |
|---------|---------|---------------|------------|------------|------------|-----------|
| 894 R | GPPS 17 | 124.55 ± 1.21 | 40.6 ± 2.0 | 7.11 ± .02 | 2.02 ± .02 | .95 ± .05 |
| | S 18 | 128.13 ± 1.22 | 41.0 ± 2.0 | 7.39 ± .02 | 2.09 ± .02 | .85 ± .05 |
| | T 19 | 119.81 ± 1.22 | 45.6 ± 2.2 | 7.40 ± .02 | 2.08 ± .02 | .87 ± .05 |
| | U 20 | 114.86 ± 1.14 | 44.9 ± 2.1 | 7.68 ± .02 | 2.17 ± .02 | .91 ± .05 |
| AVERAGE | | 121.84 ± 5.77 | 43.0 ± 2.6 | 7.40 ± .23 | 2.09 ± .06 | .90 ± .05 |

HEART ROCK FROM SAME AREAS AS VARNISH SAMPLES

| | | | | | | |
|---------|--------|-------------|------------|------------|------------|-----------|
| 884 K | GPPS 6 | 36.25 ± .72 | 18.2 ± 1.9 | 4.11 ± .03 | 1.37 ± .01 | .50 ± .05 |
| | M 7 | 37.63 ± .90 | 20.1 ± 2.4 | 4.01 ± .04 | 1.30 ± .02 | .57 ± .06 |
| | N 8 | 36.93 ± .73 | 19.7 ± 2.0 | 3.97 ± .03 | 1.30 ± .01 | .59 ± .06 |
| | O 9 | 36.14 ± .76 | 20.5 ± 2.0 | 3.88 ± .03 | 1.28 ± .01 | .66 ± .06 |
| | P 10 | 36.91 ± .74 | 21.1 ± 2.0 | 3.93 ± .03 | 1.32 ± .01 | .61 ± .06 |
| AVERAGE | | 36.77 ± .77 | 19.9 ± 2.1 | 3.98 ± .09 | 1.31 ± .03 | .59 ± .06 |

HEART ROCK FROM AREAS IN BOTTOM OF THE BOULDER

| | | | | | | |
|---------|---------|-------------|------------|------------|------------|-----------|
| 884 Q | GPPS 11 | 35.38 ± .71 | 22.0 ± 2.0 | 3.78 ± .03 | 1.30 ± .01 | .51 ± .05 |
| | R 12 | 37.26 ± .73 | 22.9 ± 2.1 | 3.98 ± .03 | 1.37 ± .01 | .51 ± .05 |
| | S 13 | 35.64 ± .71 | 16.8 ± 2.0 | 3.85 ± .03 | 1.37 ± .01 | .45 ± .05 |
| | T 14 | 35.71 ± .72 | 22.8 ± 2.1 | 3.91 ± .03 | 1.33 ± .01 | .50 ± .05 |
| | U 15 | 36.50 ± .72 | 20.9 ± 2.0 | 3.82 ± .03 | 1.30 ± .01 | .50 ± .05 |
| AVERAGE | | 36.01 ± .77 | 21.1 ± 2.5 | 3.87 ± .07 | 1.33 ± .03 | .51 ± .05 |

UPPER VARNISH LAYER FROM TOP OF THE GRIMES POINT TEST BOULDER

| RUN | SAMPLE | Dy ppm | Yb ppm | Lu ppm | Ba ppm | Cr ppm |
|---------|--------|------------|------------|-----------|------------|------------|
| 884 E | GPPS 1 | 6.02 ± .80 | 3.42 ± .05 | .49 ± .03 | 1468 ± 31 | 41.1 ± 4.1 |
| | F 2 | 6.38 ± .68 | 2.94 ± .04 | .41 ± .02 | 1063 ± 25 | 38.9 ± 3.9 |
| | G 3 | 5.50 ± .40 | 2.65 ± .04 | .40 ± .02 | 1063 ± 25 | 44.0 ± 3.9 |
| | H 4 | 6.35 ± .40 | 2.86 ± .04 | .40 ± .02 | 1201 ± 26 | 31.2 ± 3.8 |
| | J 5 | 6.50 ± .49 | 3.15 ± .05 | .46 ± .03 | 1300 ± 28 | 33.9 ± 3.9 |
| AVERAGE | | 6.15 ± .55 | 3.00 ± .29 | .43 ± .04 | 1219 ± 171 | 37.8 ± 5.2 |

VARNISH REMOVED FROM SAME AREAS AS PREVIOUS LAYERS EXCLUDING FIRST AREA

| | | | | | | |
|---------|---------|------------|------------|-----------|------------|------------|
| 894 R | GPPS 17 | 4.97 ± .56 | 2.79 ± .04 | .38 ± .02 | 1007 ± 19 | 30.6 ± 2.1 |
| | S 18 | 5.68 ± .59 | 2.89 ± .04 | .38 ± .02 | 1191 ± 24 | 36.6 ± 2.1 |
| | T 19 | 6.95 ± .63 | 2.88 ± .04 | .36 ± .02 | 1275 ± 26 | 26.6 ± 2.2 |
| | U 20 | 6.71 ± .66 | 3.05 ± .04 | .39 ± .02 | 1412 ± 26 | 36.3 ± 2.1 |
| AVERAGE | | 6.08 ± .93 | 2.90 ± .11 | .38 ± .02 | 1221 ± 169 | 32.5 ± 4.8 |

HEART ROCK FROM SAME AREAS AS VARNISH SAMPLES

| | | | | | | |
|---------|--------|------------|------------|-----------|------------|------------|
| 884 K | GPPS 6 | 3.53 ± .21 | 1.74 ± .03 | .25 ± .02 | 1380 ± 28 | 24.8 ± 3.5 |
| | M 7 | 2.78 ± .27 | 1.73 ± .04 | .26 ± .02 | 2286 ± 45 | 26.5 ± 4.3 |
| | N 8 | 3.32 ± .22 | 1.72 ± .03 | .25 ± .02 | 1109 ± 25 | 25.6 ± 3.5 |
| | O 9 | 3.17 ± .22 | 1.72 ± .04 | .23 ± .02 | 1163 ± 26 | 16.3 ± 3.6 |
| | P 10 | 3.04 ± .22 | 1.70 ± .03 | .26 ± .02 | 1076 ± 25 | 22.1 ± 3.6 |
| AVERAGE | | 3.17 ± .28 | 1.72 ± .03 | .25 ± .02 | 1403 ± 508 | 23.1 ± 4.1 |

HEART ROCK FROM AREAS IN BOTTOM OF THE BOULDER

| | | | | | | |
|---------|---------|------------|------------|-----------|----------|------------|
| 884 Q | GPPS 11 | 3.37 ± .19 | 1.59 ± .03 | .24 ± .01 | 591 ± 16 | 34.8 ± 3.7 |
| | R 12 | 3.53 ± .19 | 1.64 ± .03 | .25 ± .01 | 647 ± 18 | 29.1 ± 3.8 |
| | S 13 | 3.18 ± .20 | 1.60 ± .03 | .20 ± .01 | 707 ± 18 | 25.7 ± 3.7 |
| | T 14 | 3.37 ± .20 | 1.66 ± .03 | .24 ± .01 | 626 ± 17 | 33.6 ± 3.9 |
| | U 15 | 3.17 ± .20 | 1.63 ± .03 | .26 ± .01 | 676 ± 18 | 29.8 ± 3.8 |
| AVERAGE | | 3.32 ± .20 | 1.62 ± .03 | .24 ± .02 | 649 ± 44 | 30.6 ± 3.8 |

UPPER VARNISH LAYER FROM TOP OF THE GRIMES POINT TEST BOULDER

| RUN | SAMPLE | Co ppm | Cs ppm | Hf ppm | Sc ppm | Ta ppm |
|---------|--------|--------------|------------|------------|-------------|-----------|
| 884 E | GPPS 1 | 44.30 ± .53 | 1.59 ± .21 | 3.26 ± .10 | 16.23 ± .06 | .35 ± .00 |
| | F 2 | 39.35 ± .48 | 1.57 ± .21 | 3.13 ± .10 | 15.79 ± .06 | .36 ± .00 |
| | G 3 | 37.28 ± .46 | 1.27 ± .20 | 2.96 ± .10 | 15.78 ± .06 | .38 ± .00 |
| | H 4 | 34.42 ± .44 | 1.40 ± .20 | 3.40 ± .10 | 14.88 ± .06 | .34 ± .00 |
| | J 5 | 39.13 ± .48 | 1.43 ± .20 | 2.84 ± .10 | 15.56 ± .06 | .32 ± .00 |
| AVERAGE | | 38.90 ± 3.61 | 1.45 ± .22 | 3.12 ± .22 | 15.65 ± .50 | .32 ± .02 |

VARNISH REMOVED FROM SAME AREAS AS PREVIOUS LAYERS EXCLUDING FIRST AREA

| | | | | | | |
|---------|---------|--------------|------------|------------|-------------|-----------|
| 894 R | GPPS 17 | 35.00 ± .42 | 1.17 ± .21 | 2.87 ± .08 | 15.43 ± .05 | .36 ± .00 |
| | S 18 | 37.88 ± .45 | 1.28 ± .20 | 3.02 ± .08 | 15.71 ± .05 | .34 ± .00 |
| | T 19 | 33.72 ± .42 | 1.55 ± .21 | 3.01 ± .09 | 14.55 ± .05 | .34 ± .00 |
| | U 20 | 35.67 ± .43 | 1.62 ± .20 | 2.63 ± .08 | 15.32 ± .05 | .32 ± .00 |
| AVERAGE | | 35.57 ± 1.74 | 1.40 ± .22 | 2.88 ± .18 | 15.25 ± .50 | .35 ± .01 |

HEART ROCK FROM SAME AREAS AS VARNISH SAMPLES

| | | | | | | |
|---------|--------|-------------|-----------|------------|-------------|-----------|
| 884 K | GPPS 6 | 17.87 ± .27 | .90 ± .18 | 3.01 ± .09 | 13.86 ± .06 | .27 ± .00 |
| | M 7 | 17.29 ± .31 | .64 ± .22 | 2.77 ± .11 | 13.32 ± .07 | .28 ± .00 |
| | N 8 | 18.68 ± .28 | .81 ± .18 | 2.81 ± .09 | 14.22 ± .06 | .25 ± .00 |
| | O 9 | 17.19 ± .27 | .93 ± .18 | 2.89 ± .09 | 12.84 ± .06 | .27 ± .00 |
| | P 10 | 16.73 ± .27 | .99 ± .18 | 3.04 ± .09 | 13.23 ± .06 | .27 ± .00 |
| AVERAGE | | 17.55 ± .75 | .85 ± .19 | 2.90 ± .09 | 13.49 ± .55 | .27 ± .01 |

HEART ROCK FROM AREAS IN BOTTOM OF THE BOULDER

| | | | | | | |
|---------|---------|-------------|-----------|------------|-------------|-----------|
| 884 Q | GPPS 11 | 17.19 ± .25 | .57 ± .17 | 2.92 ± .09 | 13.87 ± .06 | .26 ± .00 |
| | R 12 | 18.10 ± .26 | .97 ± .17 | 3.00 ± .09 | 14.66 ± .06 | .28 ± .00 |
| | S 13 | 17.66 ± .26 | .73 ± .17 | 2.91 ± .09 | 13.87 ± .06 | .28 ± .00 |
| | T 14 | 18.46 ± .27 | .95 ± .17 | 2.93 ± .09 | 14.62 ± .06 | .28 ± .00 |
| | U 15 | 18.50 ± .27 | .84 ± .17 | 2.84 ± .09 | 14.51 ± .06 | .26 ± .00 |
| AVERAGE | | 17.98 ± .56 | .81 ± .17 | 2.92 ± .09 | 14.31 ± .40 | .27 ± .01 |

UPPER VARNISH LAYER FROM TOP OF THE GRIMES POINT TEST BOULDER

| RUN | SAMPLE | V ppm | Zn ppm | As ppm ^c |
|---------|--------|----------|----------|---------------------|
| 884 E | GPPS 1 | 250 ± 69 | 187 ± 7 | |
| | F 2 | 190 ± 31 | 163 ± 7 | |
| | G 3 | 193 ± 34 | 149 ± 7 | |
| | H 4 | 215 ± 39 | 142 ± 7 | |
| | J 5 | 193 ± 50 | 163 ± 7 | |
| AVERAGE | | 208 ± 45 | 161 ± 17 | |

VARNISH REMOVED FROM SAME AREAS AS PREVIOUS LAYERS EXCLUDING FIRST AREA

| | | | | |
|---------|---------|----------|---------|------------|
| 894 R | GPPS 17 | 218 ± 31 | 180 ± 7 | 24.6 ± 2.9 |
| | S 18 | 240 ± 34 | 167 ± 7 | 27.3 ± 1.8 |
| | T 19 | 249 ± 40 | 159 ± 7 | 17.5 ± 1.8 |
| | U 20 | 192 ± 45 | 173 ± 6 | 17.9 ± 1.6 |
| AVERAGE | | 225 ± 38 | 170 ± 9 | 21.8 ± 4.9 |

HEART ROCK FROM SAME AREAS AS VARNISH SAMPLES

| | | | |
|---------|--------|----------|---------|
| 884 K | GPPS 6 | 150 ± 22 | 110 ± 6 |
| | M 7 | 187 ± 29 | 113 ± 7 |
| | N 8 | 135 ± 25 | 114 ± 6 |
| | O 9 | 148 ± 28 | 107 ± 6 |
| | P 10 | 102 ± 31 | 104 ± 5 |
| AVERAGE | | 144 ± 31 | 110 ± 6 |

HEART ROCK FROM AREAS IN BOTTOM OF THE BOULDER

| | | | |
|---------|---------|----------|---------|
| 884 Q | GPPS 11 | 169 ± 22 | 104 ± 5 |
| | R 12 | 160 ± 23 | 112 ± 6 |
| | S 13 | 168 ± 24 | 105 ± 5 |
| | T 14 | 153 ± 25 | 102 ± 6 |
| | U 15 | 151 ± 28 | 96 ± 6 |
| AVERAGE | | 162 ± 24 | 104 ± 6 |

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FOOTNOTES TO TABLE 2

- a. Abundances are given in parts per million or percent as indicated after the chemical symbol. The entries after the \pm signs for the individual samples are the random errors of measurement.
- b. The first entries (6) in the values of $M \pm 6$ are the averages (M) of the individual abundances for a given type of sample and the entries after the \pm signs (6) are the root-mean-square deviations for those samples.
- c. Arsenic was measured accurately for only four of the samples.

TABLE 3ABUNDANCES (%) OF MAJOR ELEMENTS IN HEART ROCK
EXPRESSED AS OXIDES

| | |
|--------------------------------|---------------|
| (SiO ₂)* | 58 |
| Al ₂ O ₃ | 18.2 ± 0.5 |
| (FeO)** | 6.64 ± 0.11 |
| CaO | 8.1 ± 0.5 |
| MgO | 4.2 ± 1.8 |
| Na ₂ O | 3.94 ± 0.06 |
| K ₂ O | less than 1.0 |
| TiO ₂ | 0.73 ± 0.04 |
| MnO | 0.15 ± 0.003 |
| BaO | 0.16 ± 0.05 |

* SiO₂ abundance obtained by difference between 100% and total of the other oxide abundances. Any water, carbonate or potassium would have to be subtracted from this value to obtain a true SiO₂ abundance.

** Total elemental iron is expressed as FeO.

FIGURE CAPTIONS

Figure 1 Top Row. Abundances (in parts per million) of those trace elements showing the greatest enrichment in the varnish fractions. First Bar (V, GPPS 1-5) is the first varnish scraping; second bar (V_1 , GPPS 17-20) is the second varnish scraping; third bar (H, GPPS 6-10) is the heart rock fraction directly below varnish scrapings; fourth bar (H_1 , GPPS 11-15) is heart rock fractions from underneath the test boulder. Hatched areas show root-mean-square-deviation in the abundances. Lower Row. Similarly presented data for the best measured major elements.

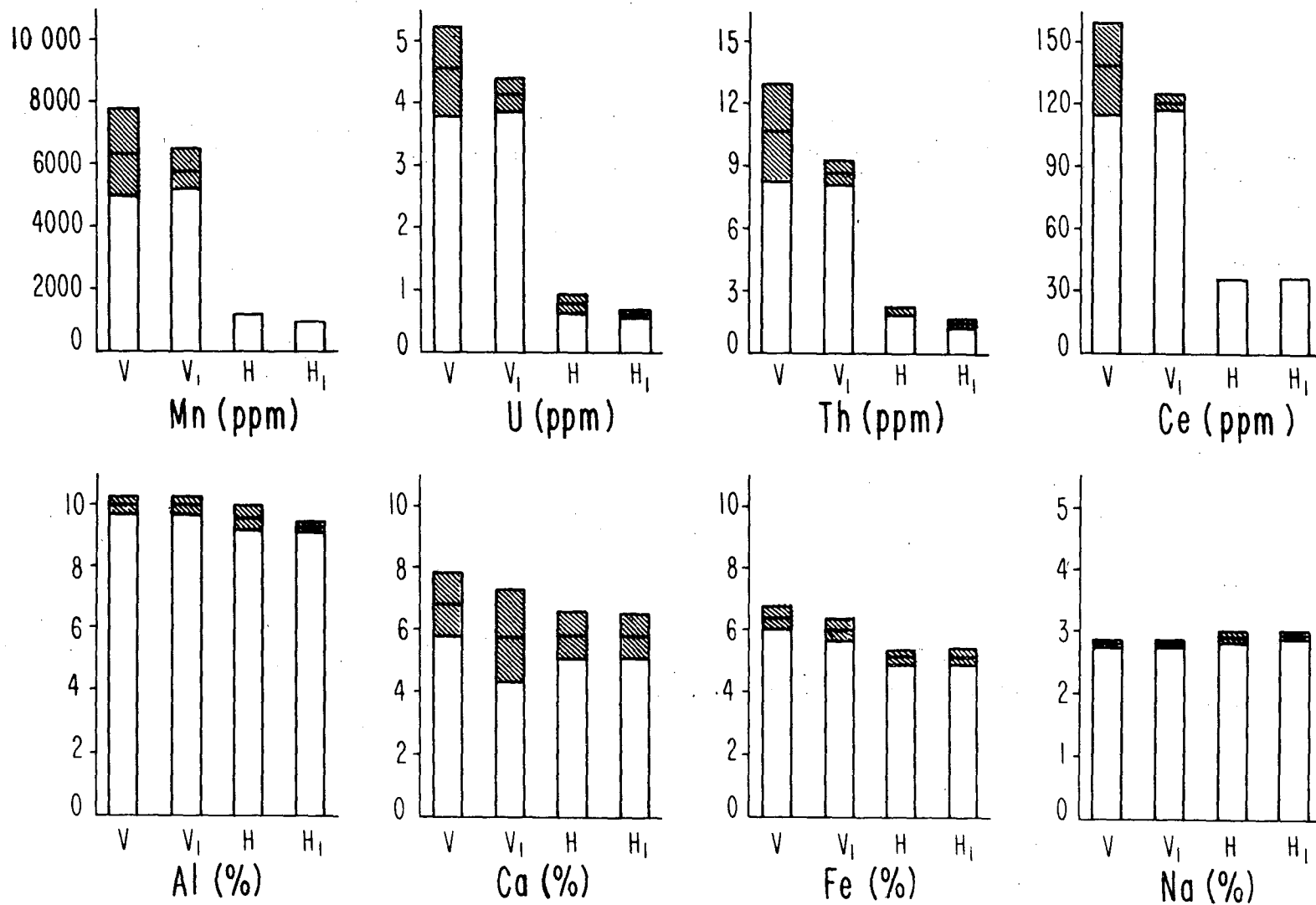


Fig. 1

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