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A Statistical Evalution of Some Columbia River Basalt Chemical Analyses

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MASTER

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A STATISTICAL EVALUATION OF SOME
COLUMBIA RIVER BASALT CHEMICAL ANALYSES

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A B S T R A C T

This study had a threefold purpose: (1) to examine the atomic absorption gamma spectroscopy, emission spectroscopy, and neutron activation data accumulated by Atlantic Richfield Hanford Company through 1976 (predecessor company to Rockwell Hanford Operations), and evaluate the precision of the data and their calibration reliability; (2) to determine from these chemical data those elements that were best for characterizing basalt flows for correlation purposes; and, (3) to use these chemical data to establish statistical correlations among type locality reference groups and the basalt flows penetrated by deep core holes in the Pasco Basin or exposed on the surface at certain field section locations.

Evaluation of the atomic absorption data indicates that most K_2O , Na_2O , SiO_2 , TiO_2 , FeO , Al_2O_3 , and CaO were measured with a precision of better than 4 percent, but MgO measurements were less precise (~6 percent). Calibration differences for these oxides were usually within 3 percent of those obtained by other laboratories. Evaluation of neutron activation analysis data indicates that Cr, Co, Sc, La, and Sm were all measured with a precision better than 6 percent. Calibration differences for these elements were commonly about 10 percent. Long-term variations in precision occurred for some atomic absorption analyses and some neutron activation analyses.

Samples from Core Holes DDH-1, DH-2, DDH-3, DH-4, and DH-5 were compared with the type locality reference groups to determine if correlations could be established statistically using the data. Overall, 90 percent of the basalt core samples in DDH-3, DH-4, and DH-5 down to the level of the Priest Rapids IV could be statistically correlated, and for many the correlations were nearly unambiguous. Statistical correlation of basalts below the Priest Rapids IV level were more ambiguous because of the overall greater chemical similarity of these basalts. A satisfactory correlation of these units by chemical measurements alone could very likely be achieved from accurate and precise measurements on the elements considered in this study and the incorporation of additional trace elements (such data are currently being obtained). In practice correlations of basalt units below the Priest Rapids IV have been obtained using a combination of petrography, wireline geophysics, paleomagnetism, and chemical variations of selected elements.

CONCLUSIONS

OVERALL QUALITY OF THE CHEMICAL DATA

Most of the atomic absorption data examined as part of this study were measured for K_2O , Na_2O , SiO_2 , TiO_2 , FeO , Al_2O_3 , and CaO with a precision of better than 4 percent. This value includes flow inhomogeneities, as well as measurement uncertainties. Long-term variations caused by changes in analytical procedures or techniques were generally less than 3 percent (1 sigma value), but CaO (5 percent), TiO_2 (8 percent), and, possibly, K_2O (6 percent) were exceptions. The overall calibration for these oxide values was good and usually gave values within 3 percent of those obtained by other laboratories. MgO , however, was measured with less precision than the other oxides and its overall calibration was about 11 percent different than that obtained by other laboratories. Ba , as measured by atomic absorption, gave values which were about 180 parts per million too high. The precision of the Ba measurement is unknown, because of possible flow inhomogeneities. The above comments for all of the elements apply to the general body of data, but there were a number of examples of apparently bad values for most of the atomic absorption measurements.

The quality of the neutron activation analysis data depended strongly on the element being measured. Na was done as well by neutron activation analysis as by atomic absorption, while Fe was not. Cr , a very important element for characterization, Co , Sc , La , and Sm were all measured with a precision of better than 6 percent. Eu was measured somewhat less precisely. Long-term variations were generally better than 4 percent for all of the elements just discussed, although that for Cr could not be determined. Notable exceptions were Sm and La , which had very large apparent changes in calibration from one sample group to another. Therefore, these elements were not used in the characterization despite their high precision of measurement.

Differences of 10 percent between the overall calibration of the trace element analyses in this report and those from other laboratories were common.

CHEMICAL CHARACTERIZATIONS OF INDIVIDUAL BASALT UNITS

The most important elements for basalt characterization, as shown by these analyses, were: Cr, a trace element measured by neutron activation analysis; and, secondly, Fe, a major element as measured by atomic absorption (as mentioned below, this was unexpected for Fe). The next most important elements were: Sc; Eu; K; Mg; and, Ti, followed closely by Ba, Ca, Co, Al, and Na. The least useful was Si.

The gamma spectroscopy data and emission spectroscopy data were generally not useful for characterization purposes because of low precision and erroneous values.

CHEMICAL CORRELATIONS OF INDIVIDUAL BASALT UNITS

Statistical comparisons of analyses from the type locality groups of analyses with basalt core samples are adequate to assign correlations for about 90 percent of the basalt core samples from Core Holes DDH-3, DH-4, and DH-5 down to the level of Priest Rapids IV. These units include Ice Harbor I, Ice Harbor II, Ward Gap, Elephant Mountain, Pomona, Gable Mountain (Esquatzel), Huntzinger, and Priest Rapids IV. The correlations are very prominent and the flow assignments are nearly unambiguous when trace and minor, as well as major, element abundances are available. The prominence of the correlations also indicates that the general character of the core hole chemical data for Core Holes DDH-3, DH-4, and DH-5 down to the Priest Rapids IV level is comparable to that of the type locality data. The correlations of these units in Core Holes DDH-1 and DH-2 were more ambiguous because useful trace element data were not available. Correlations of basalt units stratigraphically

between the Priest Rapids IV and the Vantage Sandstone are considerably more ambiguous. The High Mg, Grande Ronde Basalt in Core Holes DH-4 and DH-5 occurring immediately below the Vantage Sandstone correlates well with the Museum and Rocky Coulee type locality groups. Generally, the other Grande Ronde Basalt units do not correlate with any of the type locality groups, but this is to be expected, inasmuch as type locality data for units stratigraphically below the Rocky Coulee flow were not included in this study.

Correlations in this study were established using statistical procedures alone applied to a set of geochemical analyses. These correlations agree with other previously derived correlations based on visual and graphical comparisons of the same analyses. Correlations having an even higher reliability can be established using statistical procedures such as those given in this report in conjunction with known stratigraphic relationships and with geophysical, petrographic, and paleomagnetic data.

The nearly unambiguous chemical correlations (down to the level of Priest Rapids IV) among the core holes, field sections, and type locality reference groups, when considered in terms of the relative stratigraphic sequence of the units, is evidence for their overall lateral continuity and lateral chemical homogeneity and limited post-emplacement chemical change, even over areas of hundreds of square miles.

STRATIGRAPHIC LIMITATIONS OF RESULTS

Because of the data limitations at the initiation of this study, the results contained in this report are aimed toward emphasizing geochemical relationships within the upper few flows of the total basalt stratigraphy section in the Pasco Basin, primarily the upper Yakima basalt. Additional data have recently been obtained for the middle and lower Yakima basalt,

particularly the lower Yakima basalt in Core Holes DDH-3, DH-4, and DH-5. These additional data consist of major element compositions measured by X-ray fluorescence analysis, a more accurate and precise method than the atomic absorption techniques evaluated in this work. The type of study described in this report should be repeated with the inclusion of the new data.

INTRODUCTION

PURPOSE

In the development of nuclear energy, an area of great importance concerns the safe final storage of nuclear wastes. The feasibility of storing such wastes in mined caverns in the basalt layers of the Columbia River Basalt Group has been the subject of an extensive on-going study.⁽¹⁾ To guarantee the integrity of the stored material over periods of time long enough to allow its radioactivity to decay to acceptable levels, it is necessary to evaluate water migration through interflow zones and the extent of isolation afforded by the flow interiors. An important facet in such studies is the identification, correlation, and mapping of the basalts, both in the vertical and horizontal directions. To this end, a considerable corpus of geophysical, petrographic, and chemical data was accumulated by the Atlantic Richfield Hanford Company and its successor, Rockwell Hanford Operations, from core holes and from many surface outcrops. The present study was undertaken for the purpose of statistically evaluating the basalt chemical data accumulated by Rockwell Hanford Operations and determining their usefulness for identifying and correlating basalt units.

GENERAL GEOLOGY

The Columbia River Basalt is a layered mass of more than 200,000 cubic kilometers of tholeiitic lavas covering an area of more than 150,000 square kilometers in parts of Washington,

Oregon, and Idaho (Figure 1). This mass of basalt represents the accumulation of repeated eruptions from middle Miocene (approximately 16 million years before present) through late Miocene (approximately 8 million years before present) that filled a slowly subsiding basin shaped planoconvex downward in cross section. An estimated 80 percent of the volume of the Columbia River Basalt was emplaced during a 3-million-year volcanic pulse between 16 million years before present and 13 million years before present.

In the Pasco Basin, near the center of the area covered by the Columbia River Basalt, the total thickness of the Columbia River Basalt is a minimum of approximately 1,500 meters.

Between 1968 and 1972, 4 core holes were drilled in the Pasco Basin. These core holes are roughly located at the corners and center of a 500-square-mile square in the Pasco Basin (Figure 1). The basalt flows penetrated by these core holes were correlated using geochemical, petrographic, and geophysical data collected from core samples of individual flows, and using known stratigraphic relationships from within the Pasco Basin and from the region. These correlations form the basis for the current model of the basalt stratigraphy in the Pasco Basin.⁽¹⁾

BASALT STRATIGRAPHY

The approximate ages, stratigraphic positions, and descriptions of the rocks within the Pasco Basin are summarized in Figure 2. The stratigraphic chart is under revision, but, for purposes of this discussion, it is used in its present form. The Columbia River Basalt Group is subdivided into five formations. The upper three formations (the Saddle Mountains - upper Yakima, the Wanapum - middle Yakima, and Grande Ronde - lower Yakima) collectively constitute the Yakima Basalt Subgroup. These formations are, in turn, subdivided into various members and flows. The lower two formations, the Imnaha and Picture Gorge, are not currently known in the Pasco Basin.

TYPE LOCALITIES (T.L.) AND FIELD SECTIONS (F.S.)

- 1 ICE HARBOR T.L.
- 2 WARD GAP T.L.
- 3 ELEPHANT MOUNTAIN T.L.
- 4 POMONA T.L.
- 5 GABLE MOUNTAIN
- 6 HUNTZINGER T.L.
- 7 PRIEST RAPIDS T.L.
- 8 ROZA T.L.
- 9 SENTINEL GAP T.L.
- 10 SAND HOLLOW T.L.
- 11 GINKGO T.L.
- 12 MUSEUM T.L.
- 13 ROCKY COULEE T.L.
- 14 SILLUSI BUTTE F.S.
- 15 SPUKSHOWKI CANYON F.S.
- 16 SELAH BUTTE F.S.
- 17 BLAIR POINT F.S.
- 18 RUSH CANYON F.S.
- 19 YELLEPIT POND F.S.

TYPE LOCALITY NAMES ARE INFORMAL, CURRENTLY UNDER REVISION

V7607-13.27

FIGURE 1

INDEX MAP

FIGURE 2

STRATIGRAPHY OF THE PASCO BASIN

The Wanapum and Saddle Mountains basalts occur stratigraphically above the Vantage Sandstone and are divided into nine members. Each member consists of one or more individual basalt flows. The Grande Ronde Basalt flows occur stratigraphically below the Vantage Sandstone and can be divided into at least two stratigraphic units on the basis of marked differences in chemistry. The lowermost unit, the Low Mg-High K Chemical Type, consists of at least 20 flows identified in Core Holes DH-4 and DH-5. The uppermost unit, the High Mg Chemical Type, consists of 7 to 13 flows, also identified in DH-4 and DH-5.

The Saddle Mountains and Wanapum basalts contain some laterally extensive units covering hundreds of square kilometers wherein chemical variations are related to stratigraphic position. In the Grande Ronde Basalt, much less is known concerning the nature of intra- and inter-flow chemical variations and the lateral extent or shape of individual flows.

SOURCE OF DATA

The Rockwell Hanford Operations' data supplied for use in this study were from the following sources:

Type Locality Data

Volume I, Page 43, ARH-ST-137;⁽¹⁾

Field Section Data

Volume II, Pages B-1 to B-42, ARH-ST-137;⁽¹⁾

Core Hole Data

Volume II, Pages C-1 to C-103, ARH-ST-137;⁽¹⁾

and

ARH-2610.⁽²⁾

In addition, non-Rockwell Hanford Operations' data were also used.^(3,4,5)

EVALUATION OF CHEMICAL DATA

The chemical data evaluated here are principally from type locality and field section samples because more data were available from these for cross-checking different analytical techniques. The different analytical techniques used were: atomic absorption; neutron activation analysis; gamma ray spectrometry; and, emission spectroscopy.

Atomic absorption was used for the major elements with the results expressed as abundances of SiO_2 , Al_2O_3 , FeO , MgO , Na_2O , CaO , K_2O , and TiO_2 . Barium and other minor elements were sometimes measured, but those measurements were not evaluated.

Neutron activation analysis was used on many samples. Abundances of Na, La, Sm, Fe, Co, Sc, Cr, Eu, Th and Hf were measured for most samples, and abundances of Tb and Ta on a lesser number.

Gamma ray spectrometry was used on many samples to determine abundances of ^{40}K , ^{228}Th , and ^{226}Ra that can be used to calculate the abundance of K, Th, and U.

Emission spectroscopy was used for a number of samples; Ba, Cr, Ni, Rb, Sc, Sn, V, Zr, and, sometimes, Zn were measured.

ANALYTICAL TECHNIQUES AND STATISTICAL PROCEDURES

(In this work, precision refers to the root-mean-square deviations of a group of measurements of the same material, presumably made in the same laboratory over a short period of time. Generally, only measurements of different rocks were available and these, therefore, gave an upper limit of the precision. Also, a concordance between groups of samples and the laboratories which analyzed them was not available. It is, therefore, assumed that measurements of samples with sample numbers close to each other were made in the same laboratory at about the same time. Some apparent exceptions to the assumption are noted.)

All calculations used in this work were made using Lawrence Berkeley Laboratory computer facilities.

1. One of the most effective methods of data evaluation was a comparison of the abundances of a given element as measured on the same samples by different techniques; e.g., Na as measured by atomic absorption and by neutron activation analysis. The ratio of these values (expressed as either the elemental or oxide abundances) should be equal to one within the experimental uncertainties. If one or both of the techniques are improperly calibrated, but the calibrations are consistent throughout a group of data, then the ratio will be consistently different from one. Variations in the ratio reflect short-term or long-term errors in measurement. A comparison of the apparent precisions of measurement for two different techniques and the precision in their individual ratios can determine, in favorable cases, source variations as well as the actual measurement for each technique.
2. The root-mean-square deviation of the averages of measurements of groups of samples is one method of determining a calibration variation which presumably takes place over a relatively long period of time. If the average of ratios of measurements by different techniques for different sites are themselves averaged, and the root-mean-square deviation determined, this latter value should be appreciably better than its overall root-mean-square deviation. If not, then it is an indication of calibration variations.
3. Where measurements of the same element of the same samples by different techniques are not available, comparisons were sometimes made between different elements which are chemically similar. For example,

if the precision of measurement were much better for Hf than for Zr, there was assumed to be a problem in the Zr measurement.

- 4.. Another type of comparison was made with measurements from other laboratories; i.e., the U. S. Geological Survey and the Lawrence Berkeley Laboratory. Data used from the U. S. Geological Survey came from two publications. One was an open file report⁽³⁾ which was used because it includes a large number of individual analyses which permitted calculation of root-mean-square deviations. The other was a journal publication that contained average values for major element compositions.⁽⁴⁾ These latter values may be more accurate as they conform to the U. S. Geological Survey standards. The Lawrence Berkeley Laboratory data are unpublished, but appear in the form of graphs in a Lawrence Berkeley Laboratory report.⁽⁵⁾ Comparisons with other laboratories determine upper limits for calibration errors for specific units. If both U. S. Geological Survey and Lawrence Berkeley Laboratory agree, and Rockwell Hanford Operations' does not, the Rockwell Hanford Operations' measurements are assumed to have a calibration error. The variation in this error over a number of units is a long-term calibration variation.
5. When samples from different areas appear to belong to the same unit from geophysical and stratigraphic arguments and from most of their chemical abundances, large deviations from the overall mean of the abundances of a specific element at a given site are regarded as suspicious. When the site behaves the same way for two or more units, there is assumed to be a calibration error in the measurements for that site.

RESULTS

Precisions of measurements (or limits) and calibration variations (or limits) for the various elements and oxides are summarized in Table I. The relative value for characterization purposes of the elements and oxides found to be useful is shown in Table II in terms of a Figure of Merit. Omitted from Table II are Na and Fe determined by neutron activation analysis because oxide percentages of the elements determined by atomic absorption are of higher precision for Fe and comparable precision for Na. In addition, Sm and La were determined to have unacceptable calibration variations and Th values were unreliable; therefore, they are also omitted from this table.

The Figure of Merit in Table II was calculated using the following procedure. For each element (except Ba), the limits of precision and the calibration variation shown in Table I were combined by taking the square root of the sum of the squares, which gave an overall percentage uncertainty. This was multiplied by the average abundance of the element in the range considered which gave an uncertainty in the Rockwell Hanford Operations' data in percent or parts per million. The range of variation for each element shown in Volume I, Page 43, ARH-ST-137⁽¹⁾ from the flows with the second highest to the second lowest abundances was divided by this uncertainty and resulted in the Figure of Merit shown in Table II. The Ba uncertainty was calculated by combining the 42 parts per million calibration variation with 11 percent of the average abundance in the range considered.

As can be seen in Table II, Cr is found to be the most useful element. Fe is the second most useful, although better measurements of Eu, Mg, Ti, and K and, possibly, Sc and Ba might make them comparable. Si is the least useful element in the existing data, but more reliable values might improve its usefulness considerably.

TABLE I

SUMMARY OF EVALUATION OF ROCKWELL
HANFORD OPERATIONS CHEMICAL DATA

	<u>Precision of Measure- ment^a</u>	<u>Calibration Variation^b</u>	<u>Rockwell Hanford Operations and Others</u>
<u>Atomic Absorption</u>			
K ₂ O	≤4%	≤6%	1.02
Na ₂ O	<3%	≤2.2%	1.01
SiO ₂	≤2.2%	2.7%	1.03
TiO ₂	≤3.8% or ≤0.081 ^d	8%	0.97
FeO	≤2%	<2%	1.00
Al ₂ O ₃	<3%	<2.2%	0.96
CaO	<3.3%	4.7%	0.97
MgO	5.6%	<2.7%	1.11
Ba	<11%	~42 ppm	< 180 ppm ^c
<u>Neutron Activation Analysis</u>			
Na	<3%	≤2.2%	.98
Fe	~4%	<2%	.96
Sc	<3.7%	<1.4%	.88
Co	<4.9%	<1.2%	.92
Eu	<8.4% or <.19 ppm ^e	<3.6%	.90
Cr	<5.4% or <3.4 ppm ^e	----	~1.06
La	<4.1%	10%	1.15 → .95
Sm	<2.8%	7.1%	.91 → 1.05
Th	-----Very Poor-----		

^aStandard deviation expressed as percent of the mean, except for TiO₂ which is also expressed in absolute percent.

^bStandard deviation expressed as percent of the mean, except for Ba which is expressed in absolute amounts (parts per million).

^cRockwell Hanford Operations minus others = 180 parts per million.

^dFor small TiO₂ abundances the precision is <0.081 absolute percent.

^ePrecision of measurement is the larger of the two values.

TABLE II

USEFULNESS OF VARIOUS ELEMENTS
AS MEASURED BY ROCKWELL HANFORD OPERATIONS
FOR BASALT CHARACTERIZATION

<u>Oxide or Element Measured by Rockwell Hanford Operations</u>	<u>Method</u>	<u>Figure of Merit For Characterization</u>
SiO ₂	AA	2.7
Na ₂ O	AA	3.9
Al ₂ O ₃	AA	4.4
Co	NAA	5.2
CaO	AA	5.6
Ba	AA	6.5
TiO ₂	AA	7.7
MgO	AA	8.4
K ₂ O	AA	8.9
Eu	NAA	10.1
Sc	NAA	10.5
FeO	AA	12.8 ^a
Cr	NAA	34

^a This is an unexpectedly high Figure of Merit, FeO analyses of basalts in the Wanapum and Grande Ronde basalts have such high within-flow variations that they appear to be of limited usefulness for basalt characterization.

Details of the results of the evaluation of the Rockwell Hanford Operations' atomic absorption, neutron activation, gamma spectroscopy, and emission spectroscopy data are available upon request from the Waste Isolation Program Library.

TYPE LOCALITY CHARACTERIZATION

STATISTICAL PROCEDURES

The mean abundances and root-mean-square deviations of the 13 elements determined to be most useful for basalt characterization (Table II) are shown in Table III. This includes 19 type locality groups⁽¹⁾ and a group composed of samples from Spukshowki Canyon, Blair Point, Yellepit Pond, and Selah Butte. The Umatilla type locality group also includes samples from Spukshowki Canyon, Blair Point, Yellepit Pond, and Mound Pond. The groups are in the same order as shown in ARH-ST-137,⁽¹⁾ except for the Umatilla and Wahluke groups. Table IV shows the concordance of groups and Rockwell Hanford Operations' samples.

For nearly all groups, the root-mean-square deviations were calculated with the equation:

$$(\text{RMSD})_{ik} = \sqrt{\frac{\sum_{j=1}^n (x_{ij} - \bar{x}_{ik})^2}{n-1}} \quad (1)$$

where x_{ij} is the abundance of element i in rock j , $\bar{x}$ is the mean value of the abundance of element i for the group k , and n is the number of group members. In each calculation, the resulting $(\text{RMSD})_{ik}$ were compared with minimum values deduced from the preceding section, and the larger was tabulated. The minimum root-mean-square deviation values used for Table III were the following: SiO_2 - 3.5 percent; Al_2O_3 - 3.6 percent; FeO - 2.8 percent; MgO - 7.2 percent; CaO - 5.4 percent; Na_2O - 3.9 percent;

TABLE III

TYPE LOCALITY GROUP

	ICE HARBOR II	ICE HARBOR I	WARD GAP	ELEPHANT MOUNTAIN
Major Elements (In Percent)				
SiO ₂ ^{+a}	49.1 ± 1.7	48.4 ± 1.7	51.1 ± 1.8	50.0 ± 1.8
Al ₂ O ₃	11.3 ± .4	12.7 ± .5	12.8 ± .5	12.5 ± .4
FeO	16.3 ± .5	13.6 ± .4	14.6 ± .6	13.8 ± .4
MgO	4.6 ± .3	6.9 ± .5	4.6 ± .3	4.3 ± .3
CaO	9.0 ± .5	10.5 ± .6	8.2 ± .4	9.5 ± 1.4
Na ₂ O	2.53 ± .15	2.30 ± .14	2.50 ± .10	2.54 ± .22
K ₂ O	1.12 ± .09	.75 ± .07	1.13 ± .09	1.26 ± .10
TiO ₂	3.4 ± .3	3.1 ± .3	2.80 ± .25	3.6 ± .3
Trace and Minor Elements (Parts Per Million)				
Sc	39.0 ± 1.6	42.0 ± 1.7	30.0 ± 1.7	33.0 ± 1.3
Eu	5.4 ± .5	3.3 ± .3	2.83 ± .26	2.90 ± .26
Co	39.0 ± 2.0	45.0 ± 2.2	41.7 ± 2.1	48.0 ± 2.4
Ba	2145 ± 112	837 ± 75	614 ± 55	771 ± 69
Cr	40 ± 4	62 ± 6	23.0 ± 2.3	27.0 ± 2.7
Ave. 13 Elements	6.4%	6.5%	6.4%	7.2%
RMSD Best 12 Elements	6.0%	6.2%	6.1%	6.6%

^aSiO₂⁺ = SiO₂ + MnO + P₂O₅ + SrO + BaO + Trace Elements (see text).

TABLE III (continued)

	<u>POMONA</u>	<u>ROZA</u>	<u>SENTINEL GAP</u>	<u>SAND HOLLOW</u>
Major Elements (In Percent)				
SiO ₂ ^{+a}	50.7 ± 1.8	51.8 ± 1.8	52.9 ± 1.9	52.8 ± 1.8
Al ₂ O ₃	14.4 ± .5	13.1 ± .5	12.8 ± .5	12.6 ± .5
FeO	10.8 ± .3	14.3 ± .4	14.4 ± .4	13.7 ± .4
MgO	7.8 ± .6	4.9 ± .4	4.5 ± .3	4.8 ± .3
CaO	10.0 ± .5	8.0 ± .4	7.5 ± .4	8.0 ± .4
Na ₂ O	2.42 ± .09	2.77 ± .11	2.78 ± .11	2.85 ± .11
K ₂ O	.68 ± .11	1.20 ± .10	1.26 ± .10	.97 ± .08
TiO ₂	1.58 ± .14	2.53 ± .23	2.62 ± .23	2.57 ± .23
Trace and Minor Elements (Parts Per Million)				
Sc	33.0 ± 1.3	34.3 ± 1.4	34.8 ± 1.4	36.0 ± 1.4
Eu	1.54 ± .22	2.40 ± .22	2.18 ± .20	2.18 ± .20
Co	41.6 ± 2.1	37.7 ± 2.3	38.6 ± 1.9	39.3 ± 2.0
Ba	489 ± 101	678 ± 61	727 ± 65	688 ± 110
Cr	103 ± 10	43 ± 15	25.2 ± 4.3	50 ± 6
Ave. 13 Elements	8.1%	8.2%	6.7%	6.9%
RMSD Best 12 Elements	7.0%	6.0%	5.9%	6.2%

TABLE III (continued)

	<u>GINKGO</u>	<u>MUSEUM</u>	<u>ROCKY COULEE</u>	<u>GABLE MOUNTAIN</u>
Major Elements (In Percent)				
SiO ₂ ^{+a}	51.1 ± 1.8	54.0 ± 1.9	53.5 ± 1.9	52.6 ± 1.8
Al ₂ O ₃	12.9 ± .5	13.9 ± 1.5	13.4 ± .5	13.0 ± .5
FeO	14.7 ± .4	10.8 ± .8	10.8 ± .3	13.9 ± .8
MgO	4.4 ± .3	5.0 ± .5	4.9 ± .4	4.1 ± .3
CaO	7.6 ± .4	8.0 ± .4	8.0 ± .4	7.7 ± .5
Na ₂ O	2.74 ± .09	2.80 ± .11	2.82 ± .15	2.67 ± .10
K ₂ O	1.10 ± .16	.95 ± .08	.96 ± .09	1.68 ± .19
TiO ₂	2.62 ± .23	1.65 ± .15	1.70 ± .15	2.58 ± .23
Trace and Minor Elements (Parts Per Million)				
Sc	34.4 ± 1.4	34.0 ± 1.4	33.0 ± 1.3	28.7 ± 2.1
Eu	2.26 ± .21	2.6 ± .15	1.54 ± .14	2.37 ± .22
Co	37.4 ± 1.9	39.0 ± 2.0	34.6 ± 1.7	43.0 ± 2.2
Ba	712 ± 79	686 ± 62	671 ± 60	695 ± 63
Cr	25 ± 7	56 ± 22	48 ± 14	7.5 ± 2.1
Ave. 13 Elements	8.5%	9.0%	7.8%	8.5%
RMSD Best 12 Elements	6.5%	6.5%	6.1%	6.8%

TABLE III (continued)

	PRIEST RAPIDS			
	<u>HUNTZINGER</u>	<u>IV</u>	<u>III</u>	<u>II</u>
Major Elements (In Percent)				
SiO ₂ ^{+a}	52.0 ± 1.8	58.9 ± 2.2	50.3 ± 1.8	50.3 ± 1.8
Al ₂ O ₃	15.2 ± .5	12.7 ± .5	12.3 ± .4	12.2 ± .4
FeO	10.6 ± .3	14.4 ± .8	15.3 ± .8	14.2 ± .4
MgO	6.9 ± .5	6.1 ± .4	4.5 ± .4	4.8 ± .3
CaO	8.9 ± .5	8.2 ± .4	7.6 ± .5	8.3 ± 1.0
Na ₂ O	2.44 ± .10	2.40 ± .09	2.52 ± .19	2.53 ± .10
K ₂ O	1.00 ± .08	.85 ± .07	.94 ± .15	.97 ± .08
TiO ₂	1.62 ± .14	2.72 ± .24	2.92 ± .26	2.97 ± .26
Trace and Minor Elements (Parts Per Million)				
Sc	27.6 ± 1.1	27.0 ± .15	38.0 ± 1.6	36.7 ± 1.5
Eu	1.76 ± .21	2.70 ± .25	2.82 ± .26	2.80 ± .27
Co	41.4 ± 2.1	40.0 ± 2.0	39.4 ± 2.0	38.0 ± 1.9
Ba	557 ± 50	688 ± 179	612 ± 55	611 ± 55
Cr	175 ± 17	86 ± 9	14 ± 4	16 ± 2
Ave. 13 Elements	6.4%	7.8%	8.9%	6.9%
RMSD Best 12 Elements	6.0%	6.3%	7.3%	6.4%

TABLE III (continued)

	PRIEST RAPIDS I	UMATILLA	SPUKSHOWKI CANYON BLAIR POINT YELLEPIT POND GROUP	WAHLUKE
Major Elements (In Percent)				
SiO ₂ ^a	51.4 ± 1.8	55.3 ± 1.9	51.0 ± 1.8	53.2 ± 1.9
Al ₂ O ₃	12.2 ± .8	13.3 ± .5	13.1 ± .5	13.6 ± .5
FeO	15.0 ± .6	12.4 ± .7	14.3 ± .4	12.2 ± .3
MgO	4.6 ± .4	2.9 ± .4	4.5 ± .3	5.3 ± .4
CaO	7.7 ± .4	5.8 ± .3	7.8 ± .4	8.1 ± .4
Na ₂ O	2.57 ± .10	3.22 ± .18	2.76 ± .18	2.80 ± .11
K ₂ O	1.00 ± .17	2.67 ± .22	1.42 ± .21	1.90 ± .15
TiO ₂	2.93 ± .26	2.41 ± .21	2.67 ± .24	1.80 ± .16
Trace and Minor Elements (Parts Per Million)				
Sc	38.0 ± 1.5	25.1 ± 1.6	34.0 ± 1.4	25.5 ± 1.0
Eu	2.75 ± .25	4.2 ± .4	2.19 ± .20	2.05 ± .19
Co	39.5 ± 2.0	25.9 ± 2.1	37.5 ± 2.1	37.5 ± 1.9
Ba	650 ± 58	3544 ± 319	690 ± 98	1115 ± 100
Cr	13.5 ± 1.4	8 ± 4	24 ± 4	36 ± 7
Ave. 13 Elements	7.3%	9.9%	7.8%	6.9%
RMSD Best 12 Elements	6.5%	7.2%	6.1%	5.9%

TABLE IV

ROCKWELL HANFORD OPERATIONS' BASALT SAMPLES
COMPRISING GROUPS IN TABLE III AND FIGURE 3

1. Ice Harbor II	A-1424 No Sc, Eu, Co or Cr A-1426, A-1427
2. Ice Harbor I	A-1425 No Sc, Eu, Co or Cr A-1423
3. Ward Cap	A-1276, A-1277, A-1278
4. Elephant Mountain	A-1393 No Sc, Eu, Co or Cr A-1394, A-1395, A-1396, A-1397
5. Pomona	A-1266, A-1267, A-1268, A-1269, A-1270
6. Gable Mountain	A-2017, A-2018, A-2019 No Sc, Eu, Co or Cr A-1037, A-1038, A-1039
7. Huntzinger	A-1301, A-1302, A-1303, A-1304, A-1305
8. Priest Rapids IV	PR-01, PR-02, PR-21, PR-22
9. Priest Rapids III	PR-04, PR-05, PR-08, PR-23, PR-24
10. Priest Rapids II	PR-09, PR-10, PR-11
11. Priest Rapids I	PR-12, PR-13, PR-27A
12. Roza	A-1279, A-1280, A-1281
13. Sentinel Gap	K-5032, K-5033, K-5034, K-5035, K-5036
14. Sand Hollow	K-5001, K-5002, K-5003, K-5005, K-5007, K-5009
15. Ginkgo	K-5012, K-5014, K-5015, K-5017, ^a K-5020
16. Museum	K-5010, K-5011
17. Rocky Coulee	K-5025, K-5026, K-5027, K-5028, K-5029
18. Umatilla (Includes samples from Sillusi Butte, Rush Canyon, Yellepit-Mound Pond, and Blair Point)	A-1237, A-1238, A-1239, A-1283, A-1254, A-1255, A-1256, A-1175, A-1236, A-1235, A-1261, A-1262, A-1263, A-1264, A-1265 No Sc, Eu, Co or Cr A-1214, A-1215, A-1216, A-1217, A-1221, A-1220, A-1219, A-1348, A-1236
19. Group Formed Principally From Spukshowki Canyon Rocks (But some from Blair Point, Yellepit Pond, and Selah Butte)	A-1177, A-1178, A-1179, A-1180, A-1181, A-1183, A-1253, A-1252, A-1251, A-1250, A-1249, A-1248, A-1204, A-1203, A-1202, A-1234 No Sc, Eu, Co or Cr A-1210, A-1209, A-1208, A-1207, A-1206, A-1205, A-1298, A-1297, A-1296
20. Wahluke	A-4016, A-4017

^aNeutron activation analysis data were used for the Na₂O value
for K-5017

K_2O - 8.1 percent; TiO_2 - 8.9 percent; Sc - 4.0 percent; Eu - 9.1 percent; Co - 3.0 percent; Ba - 9 percent; Cr - 10 percent. The Ba and Cr values are estimates determined from the data evaluation discussed in the preceding section.

The SiO_2^+ values are the abundances of $SiO_2 + MnO + P_2O_5 + SrO + BaO +$ trace elements. These values were found in the data evaluation to be somewhat more reliable than the SiO_2 data and could be determined from the other major element and volatility measurements.

As seen in Table III, the average (by squares) of the root-mean-square deviations of all 13 elements ranges between 6.4 percent and 9.9 percent. If the worst element were discarded, then the average root-mean-square deviation ranges from 5.9 percent to 7.2 percent. As these values include measurement errors, the flows in the localities sampled may be even more homogeneous. Thus, each flow has a definite chemical composition pattern with a small variation for a certain group of elements.

The next step was to determine if these groups are sufficiently different from each other to make unambiguous assignments of flow origin. One sample was selected from each group and it was usually the first sample in the chart in Volume I, Page 43, ARH-ST-137⁽¹⁾ which had measurements of trace elements. The elemental abundances of samples were compared with each group and a root-mean-square index of the agreement was determined with the following equation:

$$IRMSD_{j,k} = \sqrt{\frac{\sum_{i=1}^m \left(\frac{V_{ij} - \bar{V}_{ik}}{RMSD_{ik}} \right)^2}{m - 1}} \quad (2)$$

where V_{ij} is the abundance of element i in the sample j , $\bar{V}_{ik}$ is the average abundance of element i in the group k , RMSD_{ik} is the root-mean-square deviation of element i in group k , and m is the number of elements used in the calculation. This calculation was made for each value of j and each value of k . Before discussing the values which were obtained, a brief discussion of their significance is worthwhile. If sample j is a member of group k , if group k is large enough that RMSD_{ik} has small errors, and if m is very large, then $\text{IRMSD}_{j,k}$ should equal 1. If j is not a member of group k , then $\text{IRMSD}_{j,k}$ should be larger than 1.

In a practical situation, the number of rocks used in forming a type locality group may be quite small and the uncertainty in the $\text{RMSD}_{i,k}$ would be significant:

$$\sigma (\text{RMSD}_{i,k}) \sim \text{RMSD}_{i,k} / \sqrt{2(n-1)} \quad (3)$$

where n is the number of rocks comprising group k . Erroneously small values of $\text{RMSD}_{i,k}$ (because of the small number of samples) could then inflate $\text{IRMSD}_{i,k}$ considerably. The use of minimum $\text{RMSD}_{i,k}$ to reduce this effect tends to depress the values of $\text{IRMSD}_{j,k}$ considerably even below 1. As an example, if the minimum root-mean-square deviation were chosen correctly, in a group comprising 26 rocks, the root-mean-square index for group members would be .87 and would be rather insensitive to the number of rocks in the group. The error in root-mean-square index, however, is very sensitive to the number of elements in sample j used in the calculation, and this uncertainty is: $\sqrt{m/2} (\text{IRMSD} * (m - 1))$.

This factor is pertinent to the number of elements used in the comparison between a sample and a group. In the example given above for 13 elements, the uncertainty in root-mean-square index would be 0.24. As a test, the abundances of 24 samples of the Umatilla group were compared with their group elemental averages and root-mean-square deviations in the fashion

described above. The average of the 24 values of the root-mean-square was 0.85 and the root-mean-square deviation in the values was .29 which is consistent with theoretical expectations. A cut-off of 1.5 on the value of root-mean-square indexes will be used in the next section in the comparisons between borehole rocks and reference groups. Only ~1 percent of the group members would be expected to have a root-mean-square index as large as 1.5.

RESULTS

The comparisons (root-mean-square index values) between the individual type locality samples and the various type locality groups are shown in Figure 3. A dashed line is placed in each drawing to indicate the root-mean-square index of 0.7. For Groups 1 and 2 in Figure 3, only one trace element analysis was available. Thus, there is zero deviation for each of the trace elements and only the major elements contribute to the root-mean-square index. These root-mean-square indexes then are anomalously low for the group members. In general, for the small number of samples comprising most groups, the root-mean-square indexes are smaller than the 0.85 mentioned earlier. This arises as the minimum root-mean-square deviation (for each element) used in the calculation contains not only uncertainties due to rock inhomogeneity and instrumental precision errors which would appear in the small groups, but also calibration variations which generally would not appear in such groups. It was necessary to include these in the calculations because measurements of borehole samples discussed in the next section were made at a different time and possibly in different laboratories. There are no ambiguities in assignment of the first 8 samples (A-1424 to PR-01) in Figure 3, as in each case the rock agrees well with one group; i.e., root-mean-square index <1 , and all other groups have root-mean-square index >1.5 . It should be pointed out that this is an analysis of groups as measured by Rockwell Hanford Operations and not of flows. In the following section, the significance of these groups with respect to flows will be discussed.

Rock Designation	Source	Rock Designation	Source	Group No.	Group
A-1424	Ice Harbor II	K-5032	Sentinel Gap	1	Ice Harbor II
A-1425	Ice Harbor I	K-5001	Sand Hollow	2	Ice Harbor I
A-1276	Ward Gap	K-5012	Ginkgo	3	Ward Gap
A-1393	Elephant Mountain	K-5010	Museum	4	Elephant Mountain
A-1266	Pomona	K-5025	Rocky Coulee	5	Pomona
A-2017	Gable Mountain	A-1241	Sillusi Butte	6	Gable Mountain
A-1301	Huntzinger	A-1237	Sillusi Butte	7	Huntzinger
PR-01	Priest Rapids IV	A-1253	Spokshowki Canyon	8	Priest Rapids IV
PR-04	Priest Rapids III	A-1295	Selah Butte (Only Major Elements)	9	Priest Rapids III
PR-09	Priest Rapids II	A-1184	Blair Point	10	Priest Rapids II
PR-12	Priest Rapids I	A-4016	DH-4	11	Priest Rapids I
A-1279	Roza			12	Roza
				13	Sentinel Gap
				14	Sand Hollow
				15	Ginkgo
				16	Museum
				17	Rock Coulee
				18	Unatilla
				19	Spokshowki Canyon

FIGURE 3

TYPE LOCALITY SAMPLE VERSUS
TYPE LOCALITY GROUP COMPARISONS

Figure 3 shows rocks whose correlation is uncertain from the chemical data. PR-04 could belong to Group 9 (Priest Rapids I), PR-09 could belong to Groups 9 or 10 (Priest Rapids III or II), and PR-12 could belong to Groups 9, 10, or 11 (Priest Rapids III, II, or I). Rock A-1279 agrees with the Roza, even though it may have an erroneous Cr measurement. This possible Cr error may be contributing an unnecessarily large root-mean-square deviation to the Cr value for the Roza group and allow some rocks to agree in composition with Roza which otherwise would be eliminated.

In Figure 3, Rock K-5032 agrees with Roza (Group 12), Sentinel Gap (Group 13), and Ginkgo (Group 15). It also agrees with Group 19, a group made up of rocks (from Spukshowki Canyon and other sites) which were found directly under the Umatilla. Rock K-5001 agrees with both Sand Hollow and Roza. Better and more extensive Cr measurements of the Roza group should remove this ambiguity. Rock K-5012 agrees with Roza, Sentinel Gap, Ginkgo, and Group 19. This is a reiteration of the effects mentioned for Rock K-5032. Rocks K-5010 and K-5025 agree with the Museum or Rocky Coulee. More data are needed for the Museum, especially Cr values. Rock A-1241 from Sillusi Butte agrees with the Pomona. Rock A-1241 is representative of a group of rocks from Sillusi Butte, Rush Canyon, Spukshowki Canyon, and, possibly, Selah Butte.

In Figure 3, Rock A-1237 obviously belongs to the Umatilla. Rock A-1253 agrees with Group 19 and the same comments apply as for Rock K-5032. Rock A-1295 is from Selah Butte. It agrees with the Rocky Coulee and Museum groups, although only the major elements are measured. Rock A-1184 is representative of a group of rocks from Blair Point occurring under Group 19. Rock A-1184 does not agree well with any of the 18 groups, although the root-mean-square index from the Roza is 1.27. Because of significant errors in the Blair Point measurements,

the assignment is uncertain. Rock A-4016 does not agree with any of the listed groups. It forms a group of its own, Wahluke, along with Rock A-4017 on the chart in Volume I, Page 43, ARH-ST-137.⁽¹⁾

It again should be noted that this study arrived at correlations based solely on statistical evaluation of certain geochemical data. When the geochemical data are combined with paleomagnetic, geophysical, petrographic, and stratigraphic positions, many of the discrepancies are resolved.

CORRELATIONS BETWEEN BOREHOLE SAMPLES AND REFERENCE SAMPLES

STATISTICAL PROCEDURE

In the preceding section, it was shown that over half of the Rockwell Hanford Operations' type locality groups of analyses (Volume I, Page 43, ARH-ST-137^[1]) could be distinguished from each other by the existing chemical data alone. There were some ambiguities between the remaining groups, but these could be reduced by better or more extensive chemical measurements or other techniques such as wireline geophysics, paleomagnetism, or petrography. If all such ambiguities were removed, however, there would still remain the question as to the extent that the rather limited selections of rocks in each type locality group can identify flows at different geographic locations. This problem is affected by two main factors: the general extent of chemical homogeneity of the basalt flows at the time of emplacement; and, post-emplacement effects which may change composition.

Some of the previous measurements of the Pomona and Elephant Mountain flows bear on the first factor. The 18 samples of the Pomona analyzed at Lawrence Berkeley Laboratory⁽⁵⁾ were collected by Dr. H. U. Schmincke from an area in excess of 5,000 square miles, and the 12 Elephant Mountain samples (also collected by Dr. Schmincke) were collected from an area in excess of 2,000 square miles. The average root-mean-square deviation of the abundances

of 21 trace, minor, and major elements was 5.2 percent for the Elephant Mountain samples and 4.9 percent for the Pomona samples. These values are smaller than the Rockwell Hanford Operations' values shown in Table III, but suggest the latter may be consistent with general flow variations over an extended area.

As a method of checking this premise and the general applicability of using these chemical measurements for flow identification, the Rockwell Hanford Operations' chemical data on cores from five core holes (Figure 1) were examined. A method of analysis was employed that exploits the usefulness of the main body of chemical data without being greatly disturbed by occasional bad measurements. If the latter occur in only a few percent of the measurements, this can still cause frequent complications when 13 elements are being considered per sample. Each sample is compared with each type locality group, just as in the preceding section, except that one element is removed from the calculations. The rejected element is the one whose abundance deviates most from the group average when expressed in units of the root-mean-square deviation for that element in the group.

Some of the sensitivity for distinguishing between flows is lost, particularly when one element is responsible for most of the distinctive chemical features of a flow. This is more than compensated by the increase in reliability of the assignments. If completely reliable data were used, this rejection of an element might probably not be necessary.

RESULTS

The chemical abundance data for samples from Core Holes DDH-1, DH-2, DDH-3, DH-4 and DH-5 were treated in the same fashion as the data on the individual type locality rocks in the preceding section. The value of root-mean-square index was calculated for each of 617 borehole rocks for each of 23 groups. Root-mean-square index, as discussed previously, is an index of the deviation of

the abundances of a rock from a given chemical group. It will normally average ~ 0.85 for a group member, but there will be about a 1 percent probability that it will be as large as 1.50 and the latter value was chosen as a cut-off point for most of the data. The data are presented in graphic form in the figures in Appendix A. To facilitate reading the graphs, a variable v is plotted which is equal to 1.50 minus the root-mean-square index. Thus, $v = 0$ for values of the root-mean-square index which are equal to 1.50 or larger, and increasing values of v show increasing correlations between samples and groups. The data from DDH-1 and DDH-3 will be discussed in detail to indicate the type of information which can be obtained from major elements alone (including Ba) and with trace elements in addition. In the comparisons that follow, frequent reference is made to samples by sample number; e.g., CA-5 or A-5021. The exact location of these samples is given in the lithology logs of Volume II, ARH-ST-137.⁽¹⁾

Although Core Holes DH-4 and DH-5 were both drilled to about 5,000 feet, the graphs for Core Hole DH-4 (Figures A-7 and A-8 in Appendix A) do not extend below 2,400 feet and the graphs for DH-5 (Figures A-9 and A-10 in Appendix A) do not extend below 2,800 feet. The lower Yakima basalt flows below these depths have not been formally named at the member level, nor have type localities been assigned. They were not included in the Rockwell Hanford Operations' type locality groups of analysis in Volume I, Page 43, ARH-ST-137.⁽¹⁾ Therefore, no comparisons were made among the deeper lower Yakima basalts and the Rockwell Hanford Operations' type locality groups.

DDH-1 COMPARISONS

Figure A-1 in Appendix A shows comparisons of samples from Core Hole DDH-1 with 8 type locality groups representing upper and middle Yakima flows. Eight major elements: SiO_2 ; Al_2O_3 ; FeO ;

MgO; CaO; TiO_2 ; Na_2O ; K_2O ; and, Ba are included in the analysis. No correlation between the samples and Ice Harbor I and II flows was observed. Ward Gap shows several correlations, but crude Cr data suggest that nearly all correlations, except the uppermost two, would be eliminated if good Cr data were available. The Elephant Mountain type locality group was not included in this analysis, as the major element data available for this unit appeared more questionable than those for the other type locality groups. A composite Elephant Mountain group, however, was formed with U. S. Geological Survey and Lawrence Berkeley Laboratory data wherein the abundance of each element was normalized to the calibration of the main body of Rockwell Hanford Operations' samples with calibration factors determined in the data evaluation. As can be seen in Figure A-1 in Appendix A, the correlation of the uppermost two samples in DDH-1 with this composite group is very high. Again, good Cr data would probably eliminate most of the other correlations. The next 4 basalt samples from increasing depths in DDH-1 all show no correlation with any group. For the next 2 samples (CA-6 - 255 feet and CA-7 - 265 feet), the closest agreement is with the Pomona, although the overlap is small. This small overlap is to be expected here because the samples are from the vesicular flow top (Volume II, Page C-4, ARH-ST-137)⁽¹⁾ where compositional variations probably reflect alteration. The next group of 5 rocks is from below the vesicular top and correlate with the Pomona, except for one sample, CA-10 at 300 feet. The rocks from 475 to 600 feet correlate well with the Gable Mountain (Esquatzel), but 2 small correlations with Gable Mountain are at 200 feet and ~ 1,100 feet; trace element analysis would likely also remove these ambiguities. The next 2 samples (610 and 615 feet) do not agree with any of the type locality groups and probably represent differentiated Huntzinger. Two of the next 3 rocks from 630 to 660 feet correlate with the Huntzinger. The rock which disagrees, A-1041, is very similar chemically to the others, except for Ba and K_2O .

This may represent a difference in flow composition or, more likely, 2 bad measurements in 1 sample for which the procedures used in the analysis cannot compensate. No correlations were observed for the Wahluke. At least 9 of the next 13 rocks correlate well with the Umatilla group. The other 4 all have very high barium content, which is indicative of the Umatilla, and they also agree better with that group than any of the others. The next 2 rocks from 825 and 870 feet are from sedimentary interbeds and, thus, have essentially zero overlap with any of the type locality groups.

In Figure A-2 in Appendix A, comparisons are shown between the rocks from DDH-1 and 8 middle and lower Yakima groups. The rocks from 925 feet to 1,115 feet show varying degrees of correlation with middle Yakima groups.

The middle Yakima groups (Priest Rapids, Roza, Sentinel Gap, Sand Hollow, and Ginkgo) are chemically similar, overall, and cover the data base used in this study. Therefore, ambiguities in correlation based only on the chemical data considered in this study were expected. Paleomagnetic properties, however, permit correlations within this sequence: the Priest Rapids has a reversed polarity; the Roza is transitional; and, the Sentinel Gap, Sand Hollow, and Ginkgo have a normal polarity. Petrographic differences are also found. In practice, therefore, a multi-criteria approach is used.

DH-2 COMPARISONS

The data from Core Hole DH-2 are suspect because the material balance, which varies between 100.2 and 106.7 percent, is somewhat high. Thus, measurements of some elements or components are wrong. At least part of the errors should be in one or more of those elements whose abundances are larger than the material balance discrepancy; i.e., SiO_2 , Al_2O_3 , FeO and CaO .

Elephant Mountain, Ward Gap, and Pomona are clearly defined in Figure A-3 in Appendix A, but the Umatilla is not. The high Ba values, characteristic of the Umatilla, occur in all core samples between 180 and 360 feet, but only 2 samples give a positive indication (Figure A-3 in Appendix A). This is due principally to differences in FeO and CaO (and TiO_2 in 1 sample) between the core hole data and the Umatilla reference group. These differences may be related to the errors of measurement in DH-2 samples reflected by the material balance and, therefore, cannot be ascribed to source variations at this time. The comparisons of DH-2 samples with other reference groups are shown in Figure A-4 in Appendix A. The Priest Rapids III, II, and I groups are well defined, but cannot be distinguished from each other. There are other ambiguities in assignments, but crude Cr measurements indicate these would be greatly reduced if good Cr data were available.

DDH-3 COMPARISONS

Trace elements, as well as major elements, were measured in most of the samples from Core Hole DDH-3. The improvement due to the inclusion of trace elements is obvious, as shown in Figure A-5 in Appendix A, where the Ice Harbor I, Pomona, Gable Mountain, and Umatilla are unambiguously defined. There were no correlations between any rock from DDH-3 and the Ice Harbor II, Huntzinger, or Wahluke flows. This is not unexpected, however, because of the relatively restricted geographic distribution of these flows.

It is possible to calculate the possibility of an erroneous assignment if certain limitations or assumptions can be placed on the calculation. These are: first, the unknown rock, if it is a basalt, must conform to one of the type locality groups; second, uncertainties in the type locality values and in all measurements can be considered as Gaussian; and, third, there

are no coherences of significance (larger than measuring errors) between the abundances of the different elements used in the calculation. A failure of the third assumption will not change the sense of the calculations, but will make low correlation events appear less improbable than they are. In this procedure, the probability is first calculated for each group and each rock that a group member will have abundances deviating from the group averages as much as the unknown rock. This is the degree to which the chemical profile of a given rock overlaps a given group. Thus, for each rock, the sum of all of the probabilities for the different groups is normalized to 1, and the resulting value for each group represents the respective probability that the rock belongs to that group.

The overlap between a rock and its parent flow can be lower than expected if chemical alterations have affected the composition or if the type locality comparison group is not representative of the flow. Usually, this will not affect the sense of the calculation unless the overlap becomes so small that it is comparable with accidental overlaps with other groups. In this work only, overlaps of 10^{-10} or larger for 13 elements are considered significant.

As shown in Figure A-5 in Appendix A, core samples taken from depths of 490 to 615 feet in Borehole DDH-3 correlate well with the Pomona. The relative probabilities of these samples belonging to the different type locality groups when 13 elements are used in the classification are shown in Table V. It is seen that the possibility of an erroneous assignment is less than 1 in 10^{13} if the restrictions set on the calculation are valid. The uncertainty, however, in the value is probably at least three orders of magnitude. This type of treatment was also applied to samples which showed no correlation with any of the groups in Figure A-5 in Appendix A. The probability overlaps are tabulated in Table VI and are of the form:

TABLE V

PROBABILITY OF SELECTED SAMPLES FROM DDH-3
BELONGING TO DIFFERENT FLOWS^a

Sample Number Depth (Feet)	A-2011 500	A-2012 525	A-2013 575	A-2014 615
Group				
Ice Harbor II	10 ⁻¹¹³	10 ⁻¹¹⁶	10 ⁻¹¹⁷	10 ⁻¹¹⁷
Ice Harbor I	10 ⁻⁴¹	10 ⁻⁴³	10 ⁻⁴⁶	10 ⁻⁴⁵
Ward Gap	10 ⁻¹¹³	10 ⁻¹¹⁶	10 ⁻¹¹⁷	10 ⁻¹¹⁷
Elephant Mountain	10 ⁻¹¹³	10 ⁻¹¹⁶	10 ⁻¹¹⁷	10 ⁻¹¹⁷
Pomona	1	1	1	1
Gable Mountain	10 ⁻¹¹³	10 ⁻¹¹⁶	10 ⁻¹¹⁷	10 ⁻¹¹⁷
Huntzinger	10 ^{-24b}	10 ^{-13b}	10 ^{-14b}	10 ^{-16b}
Umatilla	10 ⁻¹¹³	10 ⁻¹¹⁶	10 ⁻¹¹⁷	10 ⁻¹¹⁷
Wahluke	10 ⁻¹¹³	10 ⁻¹¹¹	10 ⁻¹¹⁷	10 ⁻¹⁰⁵
Priest Rapids IV	10 ⁻²⁷	10 ⁻¹⁷	10 ⁻²⁴	10 ⁻¹⁶
I, II, III	10 ⁻¹¹³	10 ⁻¹¹⁶	10 ⁻¹¹⁷	10 ⁻¹¹⁷
Roza	10 ⁻¹¹³	10 ⁻¹¹⁶	10 ⁻¹¹⁷	10 ⁻¹¹⁷
Sentinel Gap/ Ginkgo	10 ⁻¹¹³	10 ⁻¹¹⁶	10 ⁻¹¹⁷	10 ⁻¹¹⁷
Sand Hollow	10 ⁻⁷⁹	10 ⁻⁶⁰	10 ⁻⁷⁵	10 ⁻⁵⁸
Rocky Coulee/ Museum	10 ⁻⁴⁶	10 ⁻²⁶	10 ⁻³⁵	10 ⁻²⁶

^aCalculation assumes all distributions are Gaussian and basalt samples must belong to one of the listed flows. Thirteen elements were used in the calculation. The probability that Pomona type locality samples would have elements deviating from the group average as much as the unknown were: 2×10^{-9} ; 7×10^{-5} ; 6×10^{-3} ; and, 10^{-2} for samples A-2011, A-2012, A-2013, and A-2014, respectively.

^bSecond most probable assignment.

TABLE VI

PROBABILITIES^a THAT GROUP MEMBERS WOULD DEVIATE IN ABUNDANCES
FROM GROUP MEANS AS MUCH AS UNKNOWN SAMPLES FROM DDH-3

(Probability = 10^{-z})

Sample Number Depth from Surface (Feet)	A-2550 300	A-2006 330	A-2008 375	A-2009 420	A-2010 470	A-2015 670	A-2016 690	A-2020 780	A-2030 1,135
Group	Values of z								
Ice Harbor II	b	41	49	35	b	b	36	b	b
Ice Harbor I		42	43	43			46		
Ward Gap		12	16	10			19		
Elephant Mountain Revised (LBL & USGS)		9 ^c 7 ^c	16 ^c 10 ^c	13 ^d 5 ^d			12 ^d		
Pomona		89	76	102			68		
Cable Mountain		16	21	20			9 ^d		
Huntzinger		89	81	98			59		
Umatilla		82	85	89			81		
Wahluke		60	62	74			40		
Priest Rapids IV		30	31	24			29		
Priest Rapids III		13	18	8 ^d			15		
Priest Rapids II		17	25	14			19		
Priest Rapids I		12	24	13			15		
Roza		17	27	22			12 ^d		
Sentinel Gap		21	28	23			10		
Sand Hollow		31	29	31			19		
Ginkgo		22	29	19			12 ^d		
Museum		50	48	46			24	60	
Rocky Coulee		68	67	76			33		

^aCalculations assume Gaussian distribution for all abundance and no coherences between elements.

^bBlanks indicate $z > 81$, the maximum cut-off when trace elements were not included.

^cThis is the highest probability for this sample and all others are over three orders of magnitude smaller.

^dThese values are the highest probabilities within a three-order-of-magnitude uncertainty.

$$\prod_{i=1}^{m-1} \left(\left(1 - 2 \int_0^{t_i} \frac{e^{-\frac{y^2}{2}}}{\sqrt{2\pi}} dy \right) / \left(2 \int_0^{t_i} \frac{e^{-\frac{y^2}{2}}}{\sqrt{2\pi}} dy \right) \right) \quad (4)$$

where m is the number of elements and t_i is the deviation of element i from the group average expressed in units of the group root-mean-square deviation for element i . The product, Π , is taken over $m-1$ elements with the smallest factor. The maximum value for any factor is cut off at 1. Values for the factors were taken from tables of the odds against the occurrence of deviations.⁽⁶⁾ Revised values for the Elephant Mountain group, as discussed in the DDH-1 section, are included in Table VI. Samples A-2005, A-2010, A-2015, A-2020, and A-2030 are from sedimentary interbeds and, therefore, have essentially zero overlap with any reference groups. Samples A-2006, A-2008, and A-2009 agree best with the revised Elephant Mountain group. As this calculation may be uncertain to three orders of magnitude, the assignment of A-2009 from the chemical evidence alone is ambiguous, with Priest Rapids III also being a possibility.

Figure A-6 in Appendix A shows the correlations between DDH-3 and 8 groups of middle and lower Yakima basalts. The Priest Rapids IV assignment is unambiguous. For rocks taken from depths of 1,290 to 2,150 feet, assignments to other middle Yakima flows are not clear cut. As stated, this is because of the overall chemical similarity among middle Yakima basalts, but with the use of a multi-criteria approach including paleomagnetism and petrography many of the correlation problems are resolved.

DH-4 COMPARISONS

Figures A-7 and A-8 in Appendix A show the correlations between the DH-4 samples taken from depths of 2,400 feet or less and upper, middle, and some lower Yakima groups. The revised Elephant Mountain abundances discussed in the section on DH-1 were included.

The trace element data in Volume II, Page C-55, ARH-ST-137⁽¹⁾ for sample A-4003 are different from those given by Tatman⁽²⁾ and appear to have transfer errors. The Tatman data were used in Figure A-7 in Appendix A. The top sample in DH-4 correlates very well with the Elephant Mountain group, although the Ward Gap group has a small correlation. Measurements of higher reliability, including additional trace elements on Ward Gap type locality material and on the core samples, might resolve this ambiguity. The next lower flow, Pomona, is very well defined. There appears some evidence for fractionation or alteration in the Huntzinger which will be discussed at the end of this section. The correlation with the Wahluke group is larger than proper, because the trace element measurements from the two DH-4 samples are the only ones available to form the reference group, and they are, coincidentally, nearly identical. The Umatilla is not detected and the next lower flow is Priest Rapids IV (Figure A-8 in Appendix A). The Priest Rapids III assignment looks moderately good, although there are small correlations with others. Nearly all of the other samples taken from the depths of 640 to 1,470 feet correlate with either the Roza, Sentinel Gap, Sand Hollow, or Ginkgo groups, but, as stated previously, more extensive trace element data might reduce and possibly eliminate some of these ambiguities. Samples taken from depths of 1,500 to 2,180 feet correlate with the Museum and Rocky Coulee groups. More and better trace element data might also distinguish between them. The samples from 1,790 to 2,145 feet also correlate well with a group (now shown in the figures) of rocks from Selah Butte for which only major element abundances were useful. This latter group comprised Samples A-1288 - A-1295 (Volume II, Table V-VI, ARH-ST-137)⁽¹⁾ and was described as "flows of the high Mg chemical type" of the lower Yakima basalts (Volume II, Page B-27, ARH-ST-137).⁽¹⁾

For 107 rocks below 2,180 feet, there were no correlations of significance for which both major and trace element data were useful, although 11 rocks (8 without trace element abundances) exhibited values of v , ($v = 1.5 \times \text{root-mean-square index}$) ranging from 0.01 to 0.37. Although DH-4 was drilled to a total depth of 4,776 feet (Volume II, Page C-102, ARH-ST-137),⁽¹⁾ the plots on Figure A-8 in Appendix A do not extend below 2,500 feet, because of the lack of designated type localities for the deeper lower Yakima flows.

The region in DH-4 between depths of 160 and 360 feet may be of geochemical interest. The abundances of all of the samples from this region are tabulated in Table VII. Two of the samples, A-4012 and A-4013, which are called Group B in the table, have a very similar chemical abundance pattern that is different from that of any of the reference groups. They are unusually abundant in MgO , Al_2O_3 , and Cr and unusually deficient in K_2O . There is no indication of this abundance pattern in data from any of the other 4 boreholes. Three samples, A-4010, A-4011, and A-4015, all have a similar chemical abundance pattern, and are called Group A in Table VII. The abundances of these samples can be mathematically related to the Huntzinger composition, Group B composition, and the Wahluke composition. For example, if magma of the Huntzinger composition fractionated to give a 30 percent component with the Group B composition, the residue would have the composition of Group A. On the other hand, the A composition pattern can also be obtained by mixing the Huntzinger (60 percent) and Wahluke (40 percent) patterns. The Huntzinger is a geographically restricted unit. Petrologic characteristics, including possible reasons for these internal compositional variations within the Huntzinger, have been recently studied.⁽⁷⁾

TABLE VII

ABUNDANCES IN CHEMICALLY ANOMOLOUS REGIONS OF DH-4

Sample Number	A-4009	A-4010	A-4011	A-4012	A-4013	A-4014	A-4015	A-4016
Depth (Feet)	160	185	200	235	275	305	340	365
Group or Pattern	<u>Pomona</u>	<u>a</u>	<u>a</u>	<u>b</u>	<u>b</u>	<u>Huntzinger</u>	<u>a</u>	<u>Wahluke</u>
Abundances: (Percent)								
SiO ₂	51	52	50	49	50	51	51	53
Al ₂ O ₃	13.3	13.6	14.1	15.6	15.7	15.1	13.9	13.6
FeO	10.8	10.8	11.1	9.8	10.1	10.7	11.5	12.2
MgO	7.4	5.8	6.1	9.2	9.0	7.6	6.0	5.3
CaO	10.2	9.0	9.0	10.3	10.6	9.7	8.8	8.1
Na ₂ O	2.4	2.4	2.3	2.2	2.2	2.4	2.4	2.8
K ₂ O	0.3	0.9	0.9	0.1	0.3	0.8	1.4	1.9
TiO ₂	1.7	1.8	1.6	1.3	1.4	1.7	1.7	1.8
In Parts Per Million								
Sc	33	27	26	30	28	26	26	25
Eu	1.6	1.8	1.8	1.1	1.0	1.4	2.0	2.0
Co	42	38	40	42	45	39	37	37
Ba	500	830	690	490	390	560	830	1,160
Cr	92	111	125	295	269	173	97	31

^aSamples A-4009, A-4010, and A-4015.^bSamples A-4012 and A-4013.

DH-5 COMPARISONS

The DH-5 correlations are shown in Figures A-9 and A-10 in Appendix A. The data used for Sc and Co in Samples A-5021, A-5022, A-5024, and A-5026 were taken from Tatman,⁽²⁾ as there were apparently typographical errors in the Sc values and one Co value given in ARH-ST-137.⁽¹⁾ The Elephant Mountain group was revised in the same manner as described for DDH-1 and part of its correlations is also shown in Figure A-9 in Appendix A. The top flow correlates well with this revised Elephant Mountain group. There are smaller correlations with the Ward Gap and Priest Rapids I, II, and III. The Priest Rapids' correlation would likely be greatly reduced if no trace elements were rejected, as the Sc abundance of these flow groups is quite different from that of Elephant Mountain. More extensive measurements of trace elements on the core samples and reference groups might distinguish much more completely between the Ward Gap and Elephant Mountain groups. Stratigraphic position, plus the paleomagnetic normal polarity of the Elephant Mountain and reversed polarity of the Priest Rapids, provides a simple means for distinguishing the Elephant Mountain and Priest Rapids. Good correlations occur for rocks between the Pomona group and rocks from depths of 340 to 460 feet in DH-5. A small correlation of 3 of these rocks with the Huntzinger would be greatly reduced if their trace elements had also been measured. The next group of rocks correlates well with the Huntzinger group. There is no evidence of the Wahluke or Umatilla group in DH-5. Two rocks from a depth of ~700 feet correlate well with the Priest Rapids IV flow. From depths of 740 to 1,680 feet, there are correlations with Priest Rapids I, II, and III, Roza, Sentinel Gap, Sand Hollow, and Ginkgo groups, but unambiguous assignments cannot be made from the existing chemical evidence alone. Better and more extensive trace element measurements might make conclusive distinctions between these groups possible. From 1,840 to 2,550 feet, nearly all rock groups correlate to some degree with the Museum and Rocky Coulee

groups. These rocks also correlate well with a group (not shown in the figures) of rocks from Selah Butte as discussed for DH-4 samples.

In DH-5, there were 14 minor correlations with those groups shown in Figure A-9 in Appendix A for 120 rocks from below 2,190 feet. There were 2 correlations with the Wahluke group, 7 with the Gable Mountain group, and 5 with the Umatilla group. For those groups shown in Figure A-10 in Appendix A, there were 2 minor correlations below 2,790 feet. Inclusions of trace element data would very likely have eliminated all of these. Although DH-5 was drilled to a total depth of 5,002 feet (Volume II, Page C-151, ARH-ST-137)⁽¹⁾ the plots on Figure A-10 in Appendix A do not extend below 2,800 feet because of the lack of designated type localities for the deeper lower Yakima flows.

APPENDIX A

FIGURES A-1 - A-10

The plotted variable v is equal to 1.5-IRMSD. Data which include trace elements are plotted as .; data which do not include such measurements are plotted as v.

FIGURE A-1
CORE HOLE CORRELATIONS WITH TYPE LOCALITY GROUPS

The plotted variable v is equal to 1.5-IRMSD. Data which include trace elements are plotted as .; data which do not include such measurements are plotted as v.

FIGURE A-2
CORE HOLE CORRELATIONS WITH TYPE LOCALITY GROUPS

The plotted variable v is equal to 1.5-IRMSD. Data which include trace elements are plotted as .; data which do not include such measurements are plotted as v.

FIGURE A-3

CORE HOLE CORRELATIONS WITH TYPE LOCALITY GROUPS

The plotted variable v is equal to 1.5-IRMSD. Data which include trace elements are plotted as .; data which do not include such measurements are plotted as v.

FIGURE A-4

CORE HOLE DH-2

CORE HOLE CORRELATIONS WITH TYPE LOCALITY GROUPS

The plotted variable v is equal to 1.5-IRMSD. Data which include trade elements are plotted as $;$; data which do not include such measurements are plotted as v .

FIGURE A-5

CORE HOLE CORRELATIONS WITH TYPE LOCALITY GROUPS

CORE HOLE DDH-3

FIGURE A-6

CORE HOLE CORRELATIONS WITH TYPE LOCALITY GROUPS

The plotted variable v is equal to 1.5-IRMSD. Data which include trace elements are plotted as .; data which do not include such measurements are plotted as v.

FIGURE A-7

CORE HOLE CORRELATIONS WITH TYPE LOCALITY GROUPS

XBL776-1077

The plotted variable v is equal to 1.5-IRMSD. Data which include trace elements are plotted as •; data which do not include such measurements are plotted as ×.

FIGURE A-8

CORE HOLE CORRELATIONS WITH TYPE LOCALITY GROUPS

CORE HOLE DH-4

The plotted variable v is equal to 1.5-IRMSD. Data which include trace elements are plotted as 'x'; data which do not include such measurements are plotted as v.

FIGURE A-9

CORE HOLE CORRELATIONS WITH TYPE LOCALITY GROUPS

The plotted variable v is equal to 1.5-IRMSD. Data which include trace elements are plotted as $\cdot$; data which do not include such measurements are plotted as v .

FIGURE A-10

CORE HOLE CORRELATIONS WITH TYPE LOCALITY GROUPS

CORE HOLE DH-5

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