Chemistry of Ash and Leachates from the May 18, 1980 Eruption of Mount St. Helens, Washington

A. Chemical and Mineralogic Aspects of Observed Fractionation of Ash from the May 18, 1980 Eruption of Mount St. Helens

B. Leachate Chemistry of Ash from the May 18, 1980 Eruption of Mount St. Helens

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March 3, 1849

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TODD K. HINKLEY, Editor

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By TODD K. HINKLEY, KATHLEEN S. SMITH,
JOSEPH E. TAGGART, JR., *and* JULIA T. BROWN

B. Leachate Chemistry of Ash from the May 18, 1980 Eruption of Mount St. Helens

By TODD K. HINKLEY *and* KATHLEEN S. SMITH

With a section on LABORATORY METHODS DEVELOPED FOR MOUNT ST. HELENS WATER AND ACID LEACHING STUDIES

By STEPHEN A. WILSON *and* CAROL A. GENT

U.S. GEOLOGICAL SURVEY PROFESSIONAL PAPER 1397

Data and interpretation,
from a large suite of
well-documented samples
from the explosive eruption

U.S. DEPARTMENT OF THE INTERIOR
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CHEMISTRY OF ASH AND LEACHATES FROM THE MAY 18, 1980
ERUPTION OF MOUNT ST. HELENS, WASHINGTON

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CHEMISTRY OF ASH AND LEACHATES FROM THE MAY 18, 1980 ERUPTION OF MOUNT ST. HELENS, WASHINGTON

CHEMICAL AND MINERALOGIC ASPECTS OF OBSERVED FRACTIONATION OF ASH FROM THE MAY 18, 1980 ERUPTION OF MOUNT ST. HELENS

By TODD K. HINKLEY, KATHLEEN S. SMITH, JOSEPH E. TAGGART, JR., and JULIA T. BROWN

ABSTRACT

We present a large body of data on major-, minor-, and trace-element compositions of whole-ash samples from the May 18, 1980 eruption of Mount St. Helens. Samples were collected from a broad downwind area during and shortly after deposition. Their postdepositional history and circumstances of collection are thoroughly documented.

The data yield a picture of distinct chemical and mineralogic fractionation within the ash-fall blanket that conforms well to expectations of either atmospheric sorting or changes in ash composition during eruption. This fractionation is manifested in the following ways.

1. In most places, the ash blanket consists of two or more strata of different density and color.
2. In general, the high-density dark particles are depleted with increasing distance from source.
3. At two sites, samples collected during time of fall in abutting time increments show a decrease through time in the concentrations of oxides MgO, CaO, TiO_2, and Fe_2O_3. These oxides are associated with the high-density particles, such as opaque minerals, pyroxene, amphibole, and calcic plagioclase. The samples also show an increase through time in the oxides SiO_2, K_2O, and Na_2O, associated with the low-density particles, such as sodic plagioclase and glass.

The range in the chemical composition of the ash blanket appears to be greater as a function of distance from source than as a function of time of fall. This suggests that atmospheric sorting processes may have caused more variation in composition of samples from the ash blanket than was caused by differences in composition of ash erupted from the vent.

INTRODUCTION

In one of the most significant geologic events of the twentieth century in the United States, the May 18, 1980 eruption of Mount St. Helens, Wash., beginning at 8:32 a.m. PDT, distributed an estimated half billion tons of air-fall tephra over a large area of Washington, Idaho, and Montana (Sarna-Wojcicki, Meyer, and others, 1981). From a geologic viewpoint, the eruption was unusual in that it was large, and it was a lateral blast (Hoblitt and others, 1981; Mullineaux and Crandell, 1981). From a social viewpoint, the eruption was of interest in that it resulted in the greatest loss of life from a volcanic eruption in United States history, and in that the ejecta fell on a populated area (Schuster, 1981; Klein, 1981; McKnight and others, 1981; Gough and others, 1981). From the viewpoint of opportunity for study, the eruption was unusual in that, in contrast to most large eruptions throughout the world, the ejecta fell on easily accessible land and not on water. Detailed study of the eruption and its ejecta may help in forecasting the nature and effects of future events (Decker, 1981).

In this report, we present a large body of data on the major-, minor-, and trace-element compositions of samples that constitute a large suite of whole-ash samples from the May 18 eruption, collected over a broad area of deposition and well documented with respect to their postdepositional history and circumstances of collection. We also describe some of the horizontal and vertical differences in composition of the depositional ash blanket from the May 18 eruption, as seen from samples collected at varying geographic locations, and from samples collected at two sites during time of fall in abutting time increments during the first 19 hours of deposition. The observed compositional variations over distance and through time are consistent with expectations of atmospheric sorting of the ash as well as with expected changes in composition of ash produced from the vent that may have occurred during the eruption.

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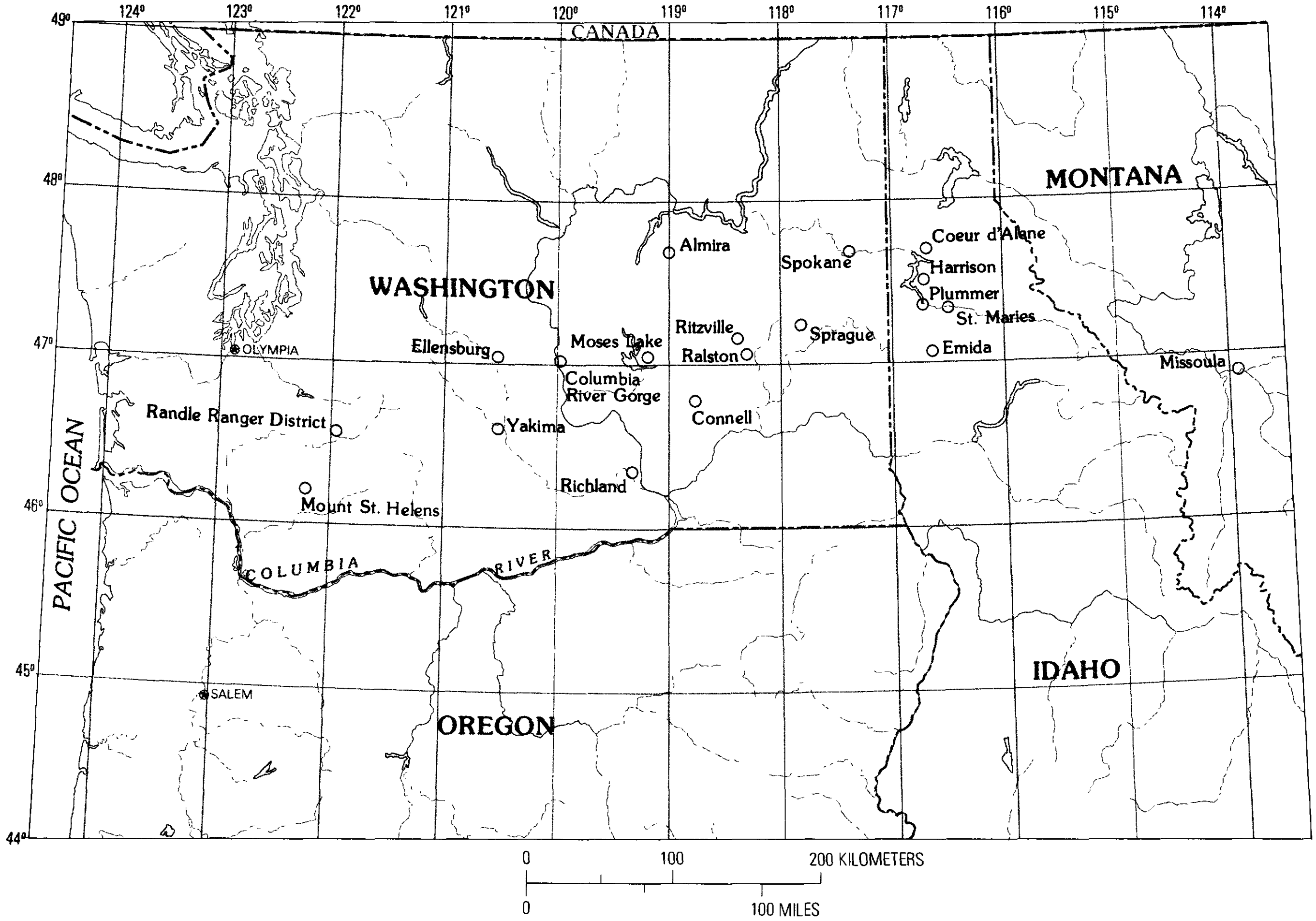


FIGURE 1.—Sampling localities, Washington, Idaho, and western Montana.

Ardith Bartel, J. S. Wahlberg, and James Baker, who worked on the X-ray analyses; F. E. Lichte and George Riddle, who worked on the inductively coupled plasma spectroscopy analyses; D. B. Hatfield, who worked on the chemical analyses; and R. E. McGregor, who managed the sample preparation. Samples collected very shortly after time of fall were provided by on-site colleagues of the U.S. Geological Survey and other organizations, and by private individuals. These include Mr. Burton, Herb Chapman, Ken Cochran, Russ Collett, Carol Connor, Robert Curry, Larry Gough, Ellen Hall, Paul Hammond, Neil Harrington, Ed Heffern, Willard Henning, Mr. Hintze, Thor Kiilsgaard, Steve Luthy, Dan Mueller, Janet Peard, Donnie Rambo, Ronald Severson, Hansford Shacklette, Wyatt Silker, Anita Tarbert, Judith Weiss, Spencer Wood, Joe Zimmer, the Montana Air Quality Bureau, and the Randle, Wash., Ranger District. Without the help of these individuals and organizations this study could not have been conducted as it was. Special thanks to Mr. and Mrs. Homer Evers of Almira, Wash., who collected and documented a set of samples in abutting time increments throughout the period of fall, and to Paul Strater of Yakima, Wash., who preserved transparent-walled cups of fallen ash for observation of contrasting strata.

SAMPLE COLLECTION

Climactic eruptive activity began at 8:32 a.m. PDT on May 18, 1980. Injection of large amounts of ash material into the atmosphere continued for about 9 hours (Christiansen and Peterson, 1981). Downwind from the volcano, the intense period of ash fall may have lasted somewhat longer than 9 hours. Samples of ash from the May 18 eruption were collected in Washington, Idaho, and western Montana (fig. 1), and Colorado and Kentucky, by resident volunteers and on-site colleagues during or immediately after deposition, and by us several weeks later. Two time-sequence sample suites (one consisting of two samples collected at Missoula, Mont., by Steve Luthy, and another of five samples collected at Almira, Wash., by Mr. and Mrs. Homer Evers) were graciously made available to us. In this report we refer to these suites as the time-sequence samples.

A complete tabulation of all chemical data from all samples, with a coded explanation of source location, exposure history, and other information, is presented in Appendix A. Of 59 original samples, 10 were split for analysis in duplicate, making a total of 69 samples.

LABORATORY METHODS

Chemical analyses were performed in U.S. Geological Survey analytical laboratories using XRF (X-ray fluorescence) spectrometry for major elements and ICP (inductively coupled plasma) spectroscopy for minor and trace elements (Taggart and others, 1981). Anionic species were determined by IC (ion chromatography). The samples were analyzed in a partially random order, so that any systematic errors, or drift in the instrument readings through a long analytical sequence, would be effectively converted into random error. Semiquantitative mineralogic analyses were made using X-ray powder diffractometry. Appendix B lists the geometric errors for reported concentrations with each element.

DISCUSSION AND RESULTS

POSTDEPOSITIONAL WIND WINNOWING OF ASH

At some sampling localities and at sufficiently long times after deposition, wind winnowing of an initially homogeneous or distinctively structured ash layer can segregate the bulk ash into physically separate fractions that are distinct in their appearances and compositions. We comment on this process here because it may have affected the composition of many samples collected for this study and for several other chemical studies of the Mount St. Helens ash that we cite. An example of the appearance of dark- and light-colored fractions of ash separated by wind winnowing on the ground is presented in figure 2. In many areas throughout the region of ash deposition, appreciable portions of the light-colored fine fraction may have been blown away before samples were collected for various investigative projects, including this one. The size and shape of the zones of light-colored, fine-grained fractions, and "salt-and-pepper," coarse-grained fractions are determined by the fine topography on the ground (vegetation in photograph), as it provides zones of higher and lower wind intensity. At sites in eastern Washington, wind-winnowed fractions were clearly distinct to a field observer. The opaque and dark minerals were strongly concentrated in the dark fraction. Plagioclase and glass were moderately enriched in the dark- and light-colored fractions, respectively, but both phases are major constituents in both fractions. Data showing the contrasting compositions of the two wind-separated fractions are presented in table 1.

FIGURE 2.—Postdepositional wind winnowing of ash. Ash is segregated by wind into light-colored, fine-grained and salt-and-pepper, coarse-grained fractions.

Samples that may have been affected by wind winnowing on the ground have not been incorporated into our summary tables that illustrate contrasts in chemical composition with varying distance from the volcano or through time of fall (tables 2–5). Samples that may have been affected by wind winnowing on the ground are identified in Appendix A by the letter "L" (indicating "late") as the initial character of their eight-character sample identifier code. Samples unaffected by wind winnowing are coded beginning with the letter "O" which indicates "original."

VARIATION IN CHEMICAL AND MINERALOGIC COMPOSITION OF ASH WITH DISTANCE FROM SOURCE AND THROUGH TIME OF FALL

We observed a systematic fractionation of the ash into layers of high-density, dark-colored particles and layers of low-density, light-colored particles. This pattern of fractionation conforms well to expectations of either atmospheric sorting (by particle density, size, and shape) or compositional changes during eruption. In general, the ash blanket consists of two or more layers of contrasting light and dark appearance. Plagioclase

TABLE 1.—*Major-element composition of dark- and light-colored fractions of ash separated by postdepositional wind winnowing*

[Fraction data in percent. Ratios for Connell site calculated from average of No. 1 and No. 2 dark-colored fraction values. LOI, loss on ignition]

Components	Connell, Wash.			Ellensburg, Wash.		Ratio--light:dark	
	Dark fraction		Light fraction	Dark fraction	Light fraction	Connell	Ellensburg
	No. 1	No. 2					
SiO_2	60.1	58.8	64.1	56.9	63.3	1.08	1.11
Al_2O_3	18.7	18.0	16.7	18.7	16.9	.91	.90
Fe_2O_3	5.6	7.1	5.2	7.3	5.5	.82	.75
MgO	2.6	3.1	2.0	3.9	2.3	.07	.59
CaO	6.4	6.3	4.7	7.1	5.0	.74	.07
Na_2O	4.4	4.2	4.5	4.1	4.4	1.05	1.07
K_2O	1.0	1.0	1.4	.72	1.34	1.40	1.86
TiO_2	.79	1.00	.73	.90	.75	.81	.83
P_2O_5	.20	.20	.20	.20	.20	1	1
MnO	.08	.09	.07	.11	.08	.82	.73
LOI	.4	.5	.6	.3	.5	.75	.6

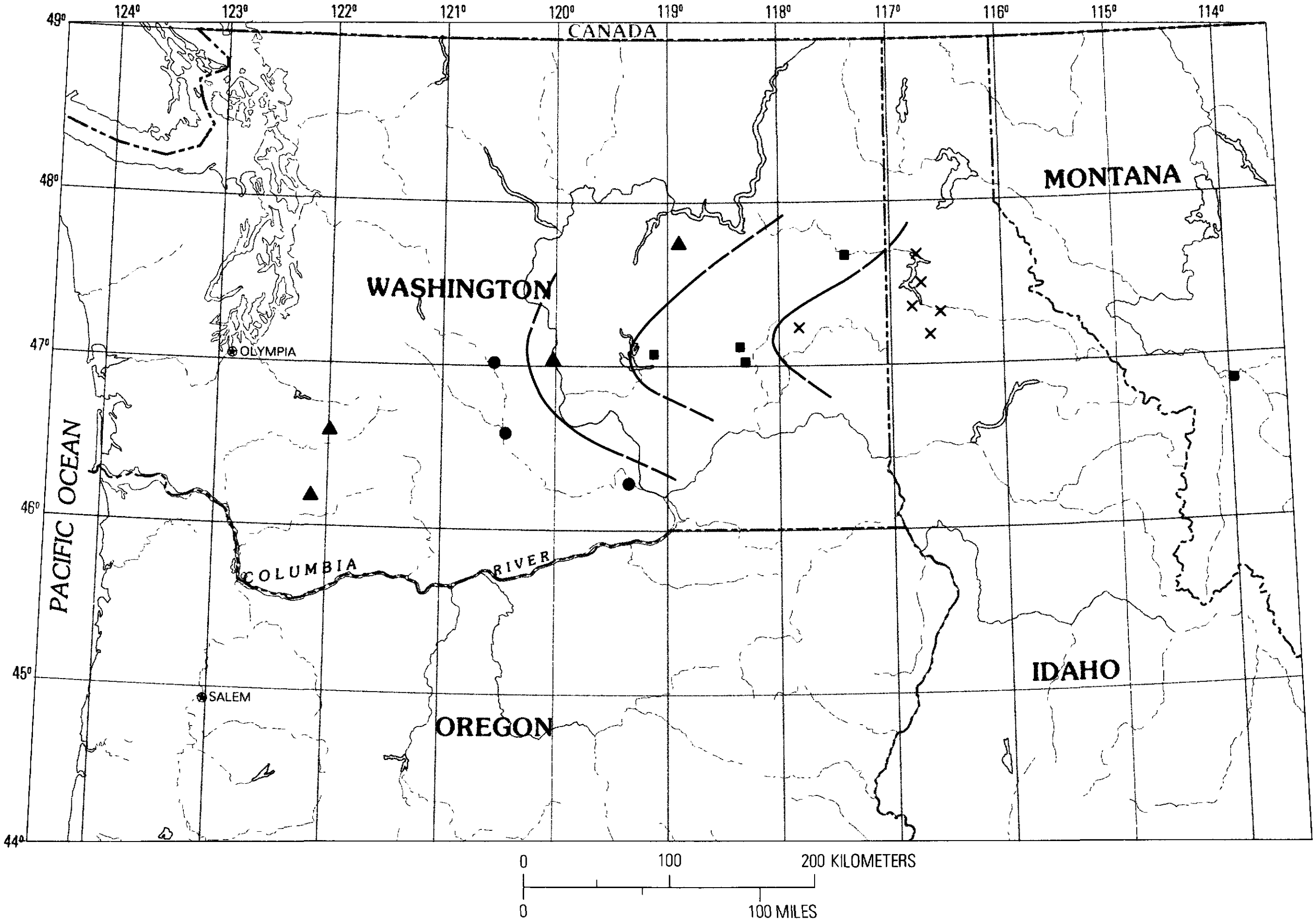
and glass were also fractionated, the heavier plagioclase being more abundant than the glass in the dark layers. Observations by Hooper and others (1980) indicated that the dark ash "is composed predominantly of plagioclase crystals * * *, glass which varies from colorless to dark brown and which usually included abundant microlites, and composite lithic fragments of plagioclase and glass. Crystals of titanium-rich magnetite make up to 5 to 10 percent (by volume), and crystals of basaltic hornblende form about one percent by volume. Occasional crystals of orthopyroxene are present. The pale ash is composed of about 80 percent clear glass, * * * plagioclase is the principal crystalline phase in this ash as well, but smaller crystals of iron oxide and hornblende are present." This fractionation is a function of both (1) increasing distance from source, as seen within the depositional blanket at each sampling locality, and (2) time of fall, as seen between the individual time-sequence samples.

The chemical composition of the ash changed systematically with distance from the volcano; particles of greater density and more ferromagnesian composition are depleted in the ash with increasing distance from the volcano. The relationship between some chemical constituents of the ash associated with the darkness and density of the particles may be seen in figure 3, which shows plots of ratios between SiO_2 (which is low in dark minerals, intermediate in plagioclase, and highest in glass) and the metal oxides Fe_2O_3 and MnO (which are abundant in dark and dense minerals). Away from the main axis of the plume (Sarna-Wojcicki, Meyer, and others, 1981), this trend of changing dark-mineral content is less distinct. Very close to the volcano (the Mount St. Helens and Randle Ranger District sites), the dumping of coarse fragments made representative sampling difficult, and samples (provided by on-site colleagues) were of widely varying appearance and composition. Data for 10 major and minor oxides in ash at eight sites at increasing distances from the volcano are presented in table 2.

Fractionation in chemical composition of the ash with distance from the volcano has been reported by others (Fruchter and others, 1980; Hooper and others, 1980). Both their work and our work demonstrate that the change in chemistry with distance from source is irregular. This irregularity could be due to any of the following.

1. Local irregularities in atmospheric transport processes such as wind directional velocity changing the trajectory of similar particles, and local winds of varying direction winnowing out finer material as the plume altitude decreased and it approached the level of the ground.
2. Changes with time in the composition of the ash plume emanating from the volcano.
3. Sampling error due largely to sampling difficulties associated with the layered compositional segregation of the ash blanket, as well as later wind winnowing of the ash as it lay on the ground.

This last consideration may have been significant when samples were collected for us by others, with the goal of obtaining material as soon as possible after deposition. Taylor and Lichte (1980) acknowledged this potential problem and urged that interpretations be based on multiple samples.



EXPLANATION

	SiO_2/Total Fe as Fe_2O_3	SiO_2/MnO
●	9–<11	590–781
▲	11–<14	>781–962
■	14–<16	>962–1,163
×	16–<19	>1,163–1,350

FIGURE 3.—Distribution of values of two chemical ratios that reflect silicic versus ferromagnesian character of the ash. Values in percent. Contours apply to values for both ratios and are approximately located; dashed where location increasingly uncertain.

There was also a modest but consistent variation in the chemistry of the ash through time of fall, at Almira and Missoula (fig. 1), where our time-sequence samples were collected. Figure 4 presents the changes in concentration of eight major oxides in the ash of the time-sequence samples from Almira and Missoula; the equivalent numerical data are presented in table 3. Fe_2O_3, MgO, and CaO decrease through time for each of these samples. The magnitudes of the decreases expressed as fractions of the maximum values are 18 percent, 26 percent, and 18 percent, respectively. The differences in the behavior of these three oxides, as influenced by atmospheric effects, are due to previously mentioned points 1 and 2. SiO_2, K_2O, and Na_2O increase through time of fall, and the magnitudes of their increases are 4.8 percent, 21 percent, and 4.4 percent, respectively. In general, the degree of chemical fractionation (compositional range) in these constituents is greater in the suite of samples collected at increasing distance from the volcano (Mount St. Helens to Missoula, table 2) than in the time-sequence sample suites collected at Almira and Missoula (table 3). This variation in degree of fractionation is shown in table 4. Only for Na_2O and CaO is the observed fractionation over distance not clearly larger than the fractionation through time of fall.

TABLE 2.—*Range in concentration of oxides with distance from source*

[Data in weight percent. All samples collected prior to first post-ash-fall rain. Fe_2O_3 is total Fe calculated as Fe_2O_3]

Sampling location	Approximate distance from Mount St. Helens (km)	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
Randle											
ODWRRR20--------	48	62.0	16.8	5.19	2.3	5.26	4.4	1.34	0.71	0.2	0.07
Randle (split)											
ODWRRR2X--------	48	62.3	17.0	5.18	2.2	5.23	4.4	1.35	.71	.2	.07
Ritzville											
ODWRZW10--------	314	66.7	16.2	4.04	1.5	4.09	4.5	1.63	.58	.2	.06
Spokane											
ODWSPK30--------	398	66.5	16.5	4.07	1.5	4.27	4.5	1.59	.58	.2	.06
Plummer											
ODIPLC20--------	426	66.9	16.0	3.78	1.3	3.85	4.6	1.69	.54	.1	.05
Emida											
ODIEMC30--------	441	67.2	16.0	3.70	1.3	3.85	4.7	1.70	.53	.1	.05
Emida (split)											
ODIEMC3X--------	441	67.4	16.0	3.71	1.3	3.86	4.6	1.70	.53	.1	.05
Coeur d'Alene											
ODICAE10--------	444	66.4	16.1	3.99	1.5	4.09	4.4	1.72	.58	.2	.05
St. Maries											
ODISMC10--------	456	67.0	16.0	3.72	1.3	3.92	4.6	1.69	.54	.1	.05
St. Maries (split)											
ODISMC1X--------	456	66.7	16.0	3.71	1.3	3.91	4.6	1.67	.53	.1	.05
Missoula											
ODMMIL40--------	631	64.6	16.5	4.22	1.6	4.58	4.4	1.53	.61	.2	.06

TABLE 3.—*Major-oxide composition of ash in time-sequence samples, Almira, Wash., and Missoula, Mont., May 18 and 19*

[Data in weight percent. Exact times of beginnings of ash fall not available. Split sample divided for analytical replication. Fe_2O_3 is total Fe calculated as Fe_2O_3]

Time of fall	Oxides that increase through time of fall			Oxides that decrease through time of fall			
	SiO_2	K_2O	Na_2O	MgO	Al_2O_3	CaO	Fe_2O_3	TiO_2
			Almira, Wash.					
Until 2 p.m. PDT May 18-	61.4	1.28	4.3	2.3	17.3	5.57	5.35	0.74
2-3 p.m. PDT------------	61.3	1.27	4.3	2.3	17.3	5.62	5.33	.74
3-4 p.m. PDT------------	61.7	1.36	4.3	2.1	16.7	5.25	5.05	.68
3-4 p.m. PDT (split)----	61.4	1.32	4.3	2.3	17.1	5.41	5.12	.70
4-6 p.m. PDT------------	62.4	1.38	4.4	2.1	16.7	5.22	5.04	.68
6 p.m. PDT May 18, until 8 a.m. PDT May 19-----	64.4	1.50	4.5	1.7	16.4	4.61	4.38	.60
			Missoula, Mont.					
Until 9 p.m. PDT May 18-	63.6	1.46	4.4	1.9	16.7	4.92	4.52	0.66
After 9 p.m. PDT May 18-	67.7	1.72	4.6	1.2	16.0	3.80	3.59	.52

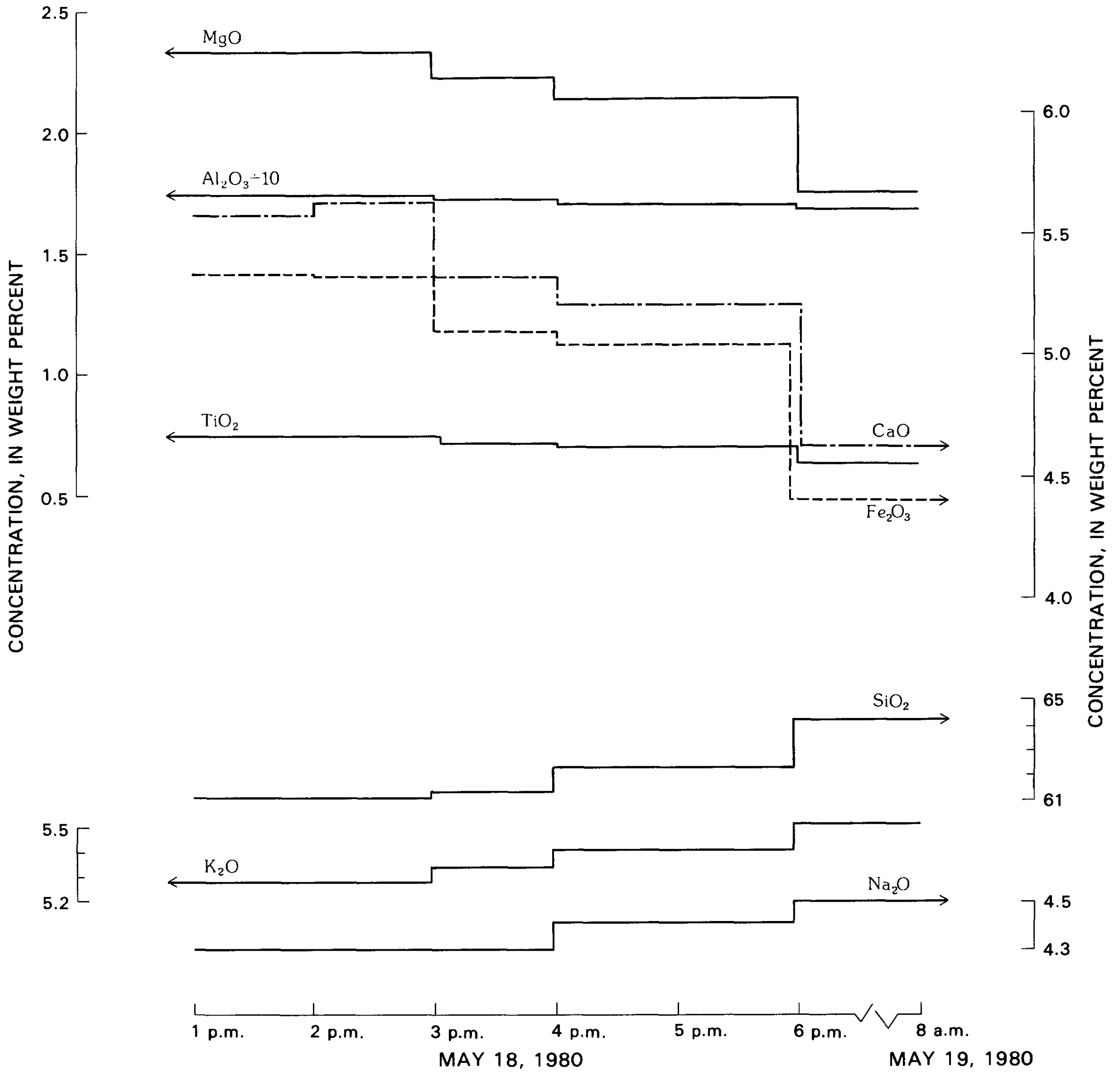


FIGURE 4.—Changes in chemical composition of ash through time of fall at Almira, Wash., and Missoula, Mont. Arrow at one end of each curve points to the appropriate scale.

Table 5 presents the data for the suite of minor and trace elements determined in the Almira and Missoula time-sequence samples, grouped by those elements that increase and those that decrease during time of ash deposition. Published data on minor and trace elements in minerals are less abundant than on major elements, and trace-element concentrations vary with mineral paragenesis. Cobalt, chromium, and nickel are associated with the early-deposited opaque minerals, manganese and zinc with pyroxene and amphibole, and strontium with plagioclase. Tabulations by Sarna-Wojcicki, Meyer, and others (1981) of composition of glass fraction and bulk ash confirmed that concentrations of barium and uranium are higher, and those of cobalt, chromium, manganese, nickel, scandium, vanadium, and zinc lower, in the glass than in the bulk ash.

Fractionation with distance (table 2) is sufficiently irregular that it may be improper to use the high and low values to define the range in a sample suite when those high and low values do not occur at or near the geographic ends of the line along which the samples were collected. Irregular values in table 2 could result from unrepresentative sampling of the stratified ash blanket, either before or after wind winnowing of ash on the ground. No such problems are suspected in the time-sequence samples from Almira or Missoula. The expected analytical error of the XRF method used to

TABLE 4.—*Comparison of maximum observed chemical fractionation of ash through time of fall at Almira, Wash., and Missoula, Mont., and with distance from the volcano*

[Values are differences, in percent, between highest and lowest values, expressed relative to the high value. Fe_2O_3 is total Fe calculated as Fe_2O_3]

Components	Difference through time of fall		Maximum difference between any two sites sampled
	Almira	Missoula	
SiO_2	4.8	6.1	7.5
Al_2O_3	5.2	4.2	5.9
Fe_2O_3	18	21	28
MgO	26	37	43
CaO	18	29	26
Na_2O	4.4	4.3	4.3
K_2O	21	15	22
TiO_2	19	21	25

determine the major elements reported in table 3 for the time-sequence samples is smaller than the differences reported between the two split samples from the 3-4 p.m. PDT Almira ash sample; the differences were probably due to inhomogeneities of sample in the containers from which the aliquots were taken. Division of samples into aliquots for the XRF and ICP analytical procedures was done on the samples in their original state, without diminution and homogenization by grinding: this was so in most cases because little sample material was available, and because of initial plans for use of total sample. Imprecision of a magnitude comparable to that reported between the two splits of the 3-4 p.m. PDT sample may be inferred to occur in all of the major-element data of this report. The precision for the ICP method used to determine the minor and trace elements reported in table 5 probably is poorer than that of the XRF method used for major oxides. The differences between the duplicate analyses of the 3-4 p.m. PDT Almira sample, however, are smaller than the changes through the suite.

The Almira site, where five time-sequence samples were collected during deposition, is north of the main plume axis. As figure 3 illustrates, the ash deposited at the margins of the plume tended to be less fractionated than at nearby points on the main axis. Sarna-Wojcicki, Shipley, and others (1981) reported that dark ash (correlating with their unit 1) began to fall considerably before the light-colored ash (unit 3). In Pullman, Wash., southeast of Almira and Ritzville, dark ash fell from 2:00 p.m. PDT until between 5:15 and 5:30 p.m. PDT, when observers noted an abrupt change to a visibly lighter colored ash (Hooper and others, 1980). The known trajectory of the plume of suspended ejecta, its spatial density and composition, and meteorologic conditions during and after the eruption are discussed by others (Pollack, 1981; Hobbs and others, 1981; Danielsen, 1981; Vossler and others, 1981). A bimodality in grain-size distribution and a "secondary thickening" in the ash layers on the ground are discussed by Brazier and others (1983). The size and shape of the ash particles, the methods of determining these parameters, and the implications for atmospheric transport fractionation are discussed in detail by Zielinski and Sawyer (1981).

MINERAL CHEMISTRY INVOLVED IN FRACTIONATION

Our approach to explain the major-oxide fractionations observed in the time-sequence samples (fig. 4 and table 3) and with distance is to discuss each oxide in terms of the minerals in which it is abundant. This approach can also explain the artificial fractionations made on the Wilfley table (see "Artificial fractionation of ash samples" section) and the fractionations observed in other eruptions (see discussion of Larsson's work in "Mechanisms of fractionation of ash" section).

Fe_2O_3—The decrease in Fe_2O_3 concentration through time of fall (fig. 4) may be associated with changes in the abundance of dense magnetite ($FeO \cdot Fe_2O_3$) and ilmenite ($FeO \cdot TiO_2$), and to some extent the pyroxenes of the idealized enstatite-ferrosilite series ($MgO \cdot SiO_2$-$FeO \cdot SiO_2$), although the reported composition of the pyroxenes is closer to the magnesian end member. A calcium-free pyroxene of composition 0.8 $MgO \cdot SiO_2$-0.2 $FeO \cdot SiO_2$ has 13.5 percent FeO and 18 percent MgO.

MgO—The decrease in MgO concentration through time of fall (fig. 4) may be associated with changes in the abundance of the magnesian pyroxenes and of hornblende. The MgO contents of the five hornblendes tabulated by Deer and others (1967) are 10, 13, 15, 18, and 21 percent, indicating that hornblende, a minor constituent, may be as rich in MgO as any species in the ash.

CaO—The decrease in CaO concentration through time of fall (fig. 4) cannot be explained on the basis of changes in abundance of any single phase of extremely high CaO concentration, but must be ascribed to the net effect of several changes in mineral abundance involving both major and minor phases of the ash. The magnitude of the decrease in CaO concentration in the samples is slightly less than the decrease of Fe_2O_3 and MgO (17 percent for CaO, versus 18 percent and 26 percent for Fe_2O_3 and MgO, respectively). The possible changes in mineral abundance that could cause the

TABLE 5.—*Minor- and trace-element composition of ash in time-sequence samples, Almira, Wash., and Missoula, Mont., May 18, and 19*

[Data in ppm. Leaders (--), data not available]

Time of fall	Elements that increase through time of fall				Elements that decrease through time of fall							
	Ba	Li	U	Zr	Co	Cr	Mn	Ni	Sc	Sr	V	Zn
					Almira, Wash.							
Until 2 p.m. PDT May 18-	320	23	1.7	120	14	21	730	21	12	530	91	78
2-3 p.m. PDT------------	310	22	--	120	14	18	715	19	11	515	90	77
3-4 p.m. PDT------------	335	24	--	120	14	21	675	19	10	490	84	73
3-4 p.m. PDT (split)----	330	24	16	120	15	21	715	20	11	510	88	76
4-6 p.m. PDT------------	355	26	22	130	14	17	700	20	11	505	86	76
6 p.m. PDT May 18, until 8 a.m. PDT May 19-----	365	29	11	140	11	13	620	13	9	445	70	70
					Missoula, Mont.							
Until 9 p.m. PDT May 18-	360	25	11	150	12	21	630	19	10	470	76	70
After 9 p.m. PDT May 18-	380	30	20	150	8	8	510	7.5	8	365	51	62

observed changes with distance in CaO abundance in the ash blanket, and through time of fall, are as follows.

1. The early deposition and (or) early eruption of plagioclase relative to glass. Plagioclase and glass are much more abundant in the bulk ash than any other constituents, therefore fractionation between them could produce appreciable differences in CaO concentration within the ash blanket, limited by the differences in their CaO concentrations and by the degree of fractionation. Plagioclase of composition 50 mole percent anorthite contains about 10 percent CaO, in contrast to about 5 percent CaO in average bulk ash from Almira. All dark and opaque minerals in the ash (amphibole, pyroxene, magnetite, ilmenite) would be removed by precipitation through air in preference to plagioclase. However, plagioclase generally crystallizes earlier than glass during magmatic differentiation, and plagioclase should be preferentially deposited with respect to glass, especially pumiceous glass that contains about 2.76 percent CaO (Sarna-Wojcicki, Shipley, and others, 1981). Most plagioclase grains observed in the ash are zoned, with zones ranging in composition from 40-60 mole percent anorthite. If there is variation in whole-grain calcium content of plagioclase grains, there would be a calcium differentiation effect in the ash due to the grains' differing atmospheric settling rates, especially if the more calcic grains were larger.
2. Early crystallization or settling from air, or both, of hornblende. Hornblende is less dense than magnetite or ilmenite. Its density overlaps that of pyroxene, and it is more dense than plagioclase and glass. The five hornblendes tabulated by Deer and others (1966) contain 12, 11, 13, 5, and 13 percent CaO (order corresponds to list previously given for MgO concentrations), contrasting with 5 percent in average bulk ash from Almira. Presence of hornblende may affect concentration of CaO in the ash that was deposited either close to the volcano or moderately early in the ash blanket.
3. The early eruption or deposition from suspension in air of the CaO-poor minerals magnetite, ilmenite, and hypersthene-enstatite. Melson and Hopson (1981) gave CaO concentrations in three ilmenites from samples of the May 18 eruption as 0.11, 0.22, and 0.10 percent, and in magnetites from the same samples as 0.09, 0.12, and 0.09, respectively; Deer and others (1966) gave the CaO content of three pyroxenes of the enstatite-ferrosilite series as 0.23, 1.4, and 1.4 percent. In figure 4, the first-collected time-sequence sample from Almira appears to be slightly lower in CaO concentration than the second sample (5.57 versus 5.62 percent), whereas the CaO concentration decreases strongly through the remainder of the samples (5.33, 5.22, 4.61). This slight reversal in trend is due to the dominance of the calcium-poor minerals magnetite and ilmenite in the first-collected fraction, contrasted with the increased amount of hypersthene and calcic plagioclase in the second-collected fraction. In the subsequent fractions, which contain little of any opaque or ferromagnesian minerals, the amounts of calcic plagioclase decrease regularly. Paralleling the initial increase and subsequent steady decrease in CaO concentration in the time-sequence samples

from Almira, the same pattern occurs in the samples from both Ritzville and Ellensburg that were artificially separated on the Wilfley table (tables 6 and 7). The densest fraction of the Wilfley table separates from Ritzville (table 6) contained 1.4 percent CaO and was shown by X-ray diffraction analysis to contain only magnetite, ilmenite, and hypersthene, in order of decreasing abundance.

Al_2O_3—The decrease in Al_2O_3 concentration through time of fall (fig. 4) may be associated with the early eruption or deposition of plagioclase relative to glass. Plagioclase that is 50 mole percent anorthite has 28 percent Al_2O_3. Sarna-Wojcicki, Meyer, and others (1981) reported Al_2O_3 as 15 percent in the glass fraction of the ash near Mount St. Helens. The calcic component of plagioclase is enriched either close to the volcano or early in the time sequence, and sodic plagioclase is more abundant farther from the volcano or later in the sequence, as judged from chemistry; but because plagioclase of some type may be well distributed throughout the sequence, Al_2O_3 does not change its concentration as markedly as other major oxides discussed in the following. Sarna-Wojcicki, Meyer, and others (1981, table 82) reported aluminum concentrations in glass of 14.7 and 13.8 percent, when expressed as Al_2O_3. The Al_2O_3 concentration of the bulk ash containing the latter glass was given as 16.8 and 16.0 percent, in two splits. This is about 22 and 16 percent more aluminum in the bulk ash than in the glass, in the two splits, respectively.

TiO_2—The decrease in TiO_2 concentration through time of fall (fig. 4) may be associated with the early settling or eruption of ilmenite, $FeO \cdot TiO_2$.

Concentrations of three major oxides increase through time of fall in the time-sequence samples—SiO_2, K_2O, and Na_2O. The magnitude of the increases as fractions of the maximum values are 4.7, 15, and 4.4 percent, respectively. The increases in all three oxides are consistent with preferential mineral deposition from air in the following order: opaques (magnetite and ilmenite), ferromagnesian silicates (pyroxene and hornblende), plagioclase, and glass. For SiO_2 the concentration would be anticipated to increase at each succession in the sequence of phases just listed, and the same should be true for Na_2O, although the increases in Na_2O through the mineral series are less even. K_2O is concentrated in the glass phase and nearly absent from all of the others, except for a probable fraction of 1 percent in hornblende. This known contrast in K_2O concentration between glass and all other phases is consistent with the greater observed magnitude of fractionation for K_2O through time of fall in the time-sequence samples than for SiO_2 or Na_2O.

ARTIFICIAL FRACTIONATION OF ASH SAMPLES

Samples of bulk ash from Ritzville and Ellensburg, Wash., were separated by water winnowing on a Wilfley table into fractions of different particle density to determine whether a hypothesis of physical winnowing of a source ash of uniform composition would be consistent with the observed fractionation of the ash over distance or through time of fall. Separation was not done on the time-sequence samples of ash from Almira or Missoula because of insufficient sample. Using artificial separation, we wanted to obtain a suite of samples that would have a greater compositional range than that of suites of natural samples, giving as great a separation by mineral grain types as possible, but still differentiated by a process analogous to the atmospheric processes that may have acted on the ash during deposition. Semiquantitative mineralogic analysis was done on some of these fractions and on magnetic and nonmagnetic subfractions of them. Major-oxide composition and mineralogy of the Wilfley table separates from the two sites are presented in tables 6 and 7.

More fine material was present in ash from the Ritzville area than from the Ellensburg area, and most of the fine material from both sites was lost during the separation. The Ellensburg sample was subject to greater wind winnowing on the ground, and may have lost its fine fraction before collection; the Ritzville sample was sheltered by wheat rows. In addition, it is also possible that low-level winds caused winnowing as the ash fell to the ground. Sarna-Wojcicki, Shipley, and others (1981, p. 587 and 588) observed that low-level wind vectors were "* * * 10°-90° north of the high-level wind vectors * * *" and that "Downwind in central Washington, eyewitnesses reported a sharp southern boundary to the falling ash, which was coarse to medium sand size. The fine ash was winnowed northward toward the axis of the air-fall lobe. Size analysis of ash samples confirm eyewitness observations." Several centimeters of ash were deposited on both areas. No close correspondence in character or composition of material is claimed between Ritzville and Ellensburg fractions that have the same fraction sequence number in tables 6 and 7; however, the expected changes in abundance of high- and low-density minerals (and glass) are observed through the sets of subsamples that were collected in succession from the Wilfley table, for both the Ritzville and Ellensburg materials. The analyses show that the ash is dominantly plagioclase (40-60 percent anorthite content) and glass, and that it has a suite of two heavy opaque minerals, magnetite and ilmenite, and two moderately heavy ferromagnesian minerals, orthopyroxene and hornblende. All mineralogic determinations of this study were done on Wilfley table fractions rather than on any whole-ash samples, in order to minimize mineral interference effects.

MECHANISMS OF FRACTIONATION OF ASH

In our work, we have observed two modes of natural fractionation (with distance from source, and through time of fall) and one kind of artificial fractionation (water winnowing on a Wilfley table) of the Mount St. Helens ash. Also available to us is a set of photographs (fig. 5) showing the appearance of the density stratification in the ash as seen through the transparent walls of nearly cylindrical plastic cups into which ash fell at Yakima, Wash. These samples were preserved and photographed by Paul Strater. The complexity of the stratigraphy in these well-preserved samples may indicate that in some localities air-fall deposition was more variable than outlined by Sarna-Wojcicki, Meyer, and others (1981) and Waitt and Dzurisin (1981). The strong visible contrasts between alternating strata indicate either that the atmospheric sorting effects during time of fall were strong and rather oscillatory, or that there were strong (and oscillatory) changes in ash composition from the volcano, or that there was great overhead wandering of a plume differentiated into lateral zones of contrasting composition.

Hooper and others (1980), Taylor and Lichte (1980), Fruchter and others (1980), and Sarna-Wojcicki, Meyer, and others (1981) have all discussed aspects of the observed differentiation of the ash blanket on the ground. In accounting for the differentiation, some authors favored changes in the composition of the material produced from the volcano and others favored atmospheric sorting. Hooper and others (1980) proposed that the bimodal nature of the ash implies two separate source materials, the dark ash possibly derived from a part of the old volcanic cone dispersed in the initial explosive event, and the pale ash representing new magma. Taylor and Lichte (1982) said that evidence seen by them implies that differentiation of the ash occurred after eruption as the ash travelled eastward through the air. Fruchter and others (1980) wrote that general compositional trends are evident with increasing distance from the volcano, especially with respect to silica, iron, calcium, magnesium, titanium, and manganese. They cited a variability in proportions of glass and crystalline species in samples from various locations. Their main ash composition tables are arranged by increasing distance from the volcano. Sarna-Wojcicki, Meyer, and others (1981) discussed both possible sorting mechanisms as well as separate compositional stages of the eruption.

FIGURE 5.—Depositional stratigraphy of ash in transparent-walled collection vessels. Photography by Paul Strater.

TABLE 6.—*Major-element and mineralogic composition of Wilfley table ash fractions, Ritzville, Wash.*

[Data in weight percent. Mineral composition determined by X-ray diffraction. Value for Fe_2O_3 in most dense fraction (in parentheses) is semiquantitative. All mineral data are semiquantitative. Fe_2O_3 is total Fe calculated as Fe_2O_3. Leaders (--), data not available; n.d., mineral not detected; tr, trace amount; P, parameter present in unknown amount; (P), parameter probably present; U, undifferentiated fraction; M, magnetic subfraction; N, nonmagnetic subfraction; LOI, loss on ignition]

Components		Most dense fraction<---------------------------------->Least dense fraction						
		1	2	3	4	5	6	7
SiO_2		13.0	61.6	67.9	71.2	--	69.7	71.6
Al_2O_3		3.33	19.6	16.1	16.2	--	15.4	15.9
Fe_2O_3		(64.3)	4.18	3.32	3.15	--	3.05	3.03
MgO		3.52	1.69	1.10	1.04	--	.99	1.00
CaO		1.44	6.33	3.70	3.43	--	3.04	2.99
Na_2O		.75	4.57	4.59	4.66	--	4.58	4.65
K_2O		.24	1.10	1.73	1.81	--	1.92	1.93
TiO_2		13.6	.61	.47	.44	--	.42	.41
P_2O_5		.64	.15	.15	.15	--	.13	.13
MnO		.44	.05	.05	.04	--	.05	.05
LOI		[1]-1.88	.48	.67	.60	--	.93	.65
Total		99.38	100.16	99.78	100.72	--	100.21	102.34
Percent of total recovered		.17	51.8	28.9	9.3	3.0	2.05	4.84
Magnetite	U	50-57	[2]tr	tr	n.d.	n.d.	(P)	n.d.
	M	--	15-20	--	--	--	--	--
	N	--	tr	--	--	--	--	--
Ilmenite	U	35-47	[2]n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	M	--	n.d.	--	--	--	--	--
	N	--	n.d.	--	--	--	--	--
Orthopyroxene	U	8	[2]20-30	n.d.	n.d.	n.d.	n.d.	n.d.
	M	--	n.d.	--	--	--	--	--
	N	--	n.d.	--	--	--	--	--
Hornblende	U	n.d.	[2]20-30	n.d.	n.d.	n.d.	n.d.	n.d.
	M	--	n.d.	--	--	--	--	--
	N	--	n.d.	--	--	--	--	--
Plagioclase	U	n.d.	[2]tr	14	15	10.5	12	10
	M	--	17-21	--	--	--	--	--
	N	--	40	--	--	--	--	--
Quartz	U	n.d.	[2]n.d.	1	1	1.3	0.7	0.7
	M	--	1-2	--	--	--	--	--
	N	--	5-10	--	--	--	--	--
Glass	U	n.d.	[2]n.d.	P	P	P	P	P
	M	--	n.d.	--	--	--	--	--
	N	--	n.d.	--	--	--	--	--

[1] This value represents an increase on ignition and indicates a change in the oxidation state of the iron species.

[2] This set of values represents a subfraction with specific gravity greater than 2.85.

TABLE 7.—*Major-element and mineralogic composition of Wilfley table ash fractions, Ellensburg, Wash.*

[Data in weight percent. Due to inadequate sample size, fractions 4 and 5, and 6 and 7, were combined for analyses. Mineral composition determined by X-ray diffraction. All mineral data are semiquantitative. Fe_2O_3 is total Fe calculated as Fe_2O_3. Leaders (--), data not available; n.d., parameter not detected; tr, trace amount; P, parameter present in unknown amount; (P) parameter probably present; U, undifferentiated fraction; M, magnetic subfraction; N, nonmagnetic subfraction; LOI, loss on ignition]

Components		Most dense fraction<-----------				----------->Least dense fraction
		1	2	3	4 and 5	6 and 7
SiO_2		47.4	58.8	63.1	68.1	--
Al_2O_3		6.8	20.9	--	15.1	--
Fe_2O_3		24.4	5.41	4.06	4.26	--
MgO		13.6	3.24	1.78	1.29	--
CaO		4.25	7.64	6.22	3.10	--
Na_2O		1.48	4.35	4.37	4.53	--
K_2O		.35	.70	1.11	1.88	--
TiO_2		2.72	.69	.55	.66	--
P_2O_5		.64	.14	.17	.22	--
MnO		.42	.08	.06	.07	--
LOI		.28	.26	.45	.87	--
Total		102.34	102.21	101.77	99.98	--
Percent of total recovered		15.8	70.8	13.2	0.13 and 0.03	0.11 and 0.01
Magnetite	U	--	9	6	(P)	n.d.
	M	21	--	15	--	--
	N	n.d.	--	4	--	--
Ilmenite	U	--	n.d.	n.d.	n.d.	n.d.
	M	(P)	--	n.d.	--	--
	N	n.d.	--	n.d.	--	--
Orthopyroxene	U	--	(P)	(P)	n.d.	n.d.
	M	P	--	(P)	--	--
	N	P	--	(P)	--	--
Hornblende	U	--	4	n.d.	3	4
	M	n.d.	--	n.d.	--	--
	N	19-20	--	n.d.	--	--
Plagioclase	U	--	67	32	26	32
	M	n.d.	--	26	--	--
	N	P	--	51	--	--
Quartz	U	--	2-3	2-3	2	0.7
	M	n.d.	--	tr	--	--
	N	n.d.	--	2	--	--
Glass	U	--	n.d.	n.d.	P	n.d.
	M	n.d.	--	n.d.	--	--
	N	n.d.	--	n.d.	--	--

Larsson (1937) carefully documented compositional differences in the ash deposited over a broad region after the eruption of the Chilean volcano Quizapu. Samples collected from an irregular array of geographic points rather than in a strict distance progression from the source were arranged in an order yielding a progression of compositional changes attributable to fractionation by either atmospheric winnowing or by changes in ash composition during eruption. His data are presented in table 8. Larsson attributed the entire observed effect to the atmospheric mechanism and seemingly regarded it only as a scientific curiosity with some interesting implications that the observed fractionation is similar to what might be expected of magmatic differentiation. He stated (p. 46, provisional translation by Ray E. Wilcox): "If the differentiation * * *[of the Quizapu ash] is compared with a corresponding magmatic variation diagram, for the normal magma of the calc-alkalic suite, it is interesting to find a correlation between them, even as to some details. Indeed, the active agent of differentiation, gravitation, is the same in both cases. That which in the one case is brought about in a short time in an especially fluid medium requires a much longer time in the second case in a very viscous medium." Larsson discussed in some detail the presumed changes in mineralogic abundance that are expected to cause the measured changes in chemical composition.

In the present study, our observations of fractionation with distance and through time of fall, the Wilfley table water-winnowing data, and the stratigraphic record observed in plastic cups are all consistent with fractionation due to either changes in magma composition or atmospheric sorting. If, as would be consistent with the simplest conceptual model, we postulate that most of the chemical progression in the time-sequence samples were due to a compositionally variable source, and most of the changing chemistry with distance were due to atmospheric sorting, it would follow from the magnitude of range in our data for the two types of sample suites that atmospheric sorting processes were of greater importance in fractionating the ash.

TABLE 8.—*Chemical variation with eolian fractionation in ash from eruption of Quizapu in South America, 1932*

[Data in weight percent. Modified from Larsson (1937), by permission; 1a and 1b are from the same site; higher-number sites have smaller depositional thicknesses on the ground (Larsson's identifying codes). Leaders (--), data not available]

Components	Sites				
	1a	1b	2	3	4
SiO_2	63.79	64.55	67.45	69.78	70.20
TiO_2	.78	.72	.45	.46	.60
Al_2O_3	16.20	15.61	17.28	15.44	14.86
Fe_2O_3	2.92	1.77	1.37	.75	.96
FeO	1.40	2.06	.90	1.59	1.26
MnO	.11	.13	.09	--	.06
MgO	1.06	1.28	1.05	.60	.54
CaO	3.87	3.06	3.15	2.12	1.88
Na_2O	5.91	6.87	4.76	4.41	4.46
K_2O	2.83	3.37	3.20	3.91	4.43

SUMMARY

1. The air-fall tephra samples of this study are extremely well documented, and represent a favorable geographic array. Most samples were collected very shortly after time of fall. Whole-rock chemical analyses were performed with care and by appropriate and reliable methods. The samples and the data derived from them are appropriate for further study of this important eruption and for comparison with other air-fall tephra blankets.
2. In most places, the ash blanket consists of two or many more strata of different density and color, and in some localities the stratigraphy resulting from air-fall deposition may have been more variable than reported by others.
3. The dense, dark particles are, in general, depleted with increasing distance from source.
4. The range in the chemical composition of the ash blanket is greater, although much less regular, as a function of distance from source than as a function of time of fall. This suggests that atmospheric sorting processes played a stronger role in differentiating the tephra blanket than did change in composition of material ejected from the source.

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APPENDIXES A AND B

APPENDIX A.—COMPLETE TABULATION OF ANALYTICAL RESULTS FOR WHOLE ASH

[Major and minor elements in whole-ash samples, reported as oxides, were determined by X-ray fluorescence spectrometry after sodium metaborate fusion. Trace elements in whole-ash samples were determined by inductively coupled plasma spectroscopy after hydrofluoric acid digestion. These techniques are described by Taggart and others (1981)]

Coding key for eight-character sample identifiers for ash samples analyzed is as follows:

Character 1.—O="original," collected by on-site colleagues immediately after deposition
L="later," collected by authors weeks after deposition

Character 2.—D=not rained on before collection ("dry")
R=exposed to rain before collection ("rain")

Character 3.—Initial of State in which sample was collected: W=Washington, I=Idaho, C=Colorado, M=Montana, and K=Kentucky

Characters 4 and 5.—City or town or other name for locality:

AL=Almira
CA=Coeur d'Alene
CO=Connell
CR=Columbia River basin
DE=Denver
EL=Ellensburg
EM=Emida
GL=Glasgow
HA=Harrison
HE=Helena
LE=Lewistown
MC=Miles City
MI=Missoula
ML=Moses Lake
PL=Plummer
RA=Rest area, 18 miles east of Ellensburg
RI=Richland
RL=Ralston
RR=Randle Ranger District
RZ=Ritzville
SG=Sprague
SH=Mount St. Helens
SM=St. Maries
SP=Spokane
UC=Union City
YK=Yakima
YV=Yakima Valley

Character 6.—Collector of sample:

B=Mr. Burton
C=Russ Collett
E=Ellen Hall
H=Ed Heffern
K=Thor Kiilsgaard
L=Steve Luthy
M=Dan Mueller
P=Paul Hammond
Q=Air Qual. Bur.
R=Ken Cochran
S=Wyatt Silker
T=Anita Tarbert
V=Homer Evers
W=Willard Henning
X=Hansford Shacklette
Y=Donnie Rambo
Z=Kathleen Smith

Character 7.—Sample number of sub-location number, if more than one sample was collected by a single collector at the site identified by characters 4, 5, and 6.

Character 8.—An "x" indicates that sample is one member of a duplicate pair (analytical split). In each duplicate pair one sample is labelled "x", the other "o". All samples not split for duplicate analyses are labelled "o".

BULK ANIONS

[Values in ppm]

Sample	Cl	F	NO_3	PO_4	SO_4	Sample	Cl	F	NO_3	PO_4	SO_4
ODWALV10	1,000	280	<500	2,500	8,000	LRWRZZ10	540	240	<500	2,200	700
ODWALV20	1,800	300	<500	2,500	8,200	LRWRZZ20	460	270	<500	2,100	800
ODWALV30	2,200	350	<500	2,800	11,000	LRWRZZ2X	1,200	250	<500	2,000	800
ODWALV3X	940	340	<500	2,500	9,500	ODIPLC20	1,000	290	<500	2,100	1,200
ODWALV40	1,000	320	<500	1,800	10,000	LRIHAZ10	1,300	230	<500	2,100	400
ODWALV50	2,000	280	<500	2,400	5,200	ODICAE10	760	250	<500	2,200	2,000
ODWRZY10	1,100	300	<500	2,100	1,600	ODIEMC3X	200	260	<500	2,100	1,300
ODWRZY1X	1,200	220	<500	2,200	1,500	ODISMC10	1,100	250	<500	2,100	1,300
ODWRZW10	920	310	<500	2,100	2,300	ODISMC1X	920	280	<500	2,000	1,500

BULK OXIDES

[Values in percent. LOI, loss on ignition. Fe_2O_3 is total Fe calculated as Fe_2O_3]

Sample	Latitude	Longitude	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	LOI
LRWSHP10	46.20	122.19	62.8	17.4	4.97	2.2	5.19	4.4	1.33	0.64	0.1	0.07	0.41
LRWSHP20	46.20	122.19	62.3	17.3	4.83	2.2	5.17	4.4	1.32	.65	.1	.07	.39
LRWSHP30	46.20	122.19	62.3	17.3	5.10	2.4	5.35	4.4	1.34	.70	.2	.07	.49
LRWSHP40	46.20	122.19	62.9	17.5	4.94	2.3	5.34	4.4	1.32	.66	.1	.07	.66
LRWSHP50	46.20	122.19	64.3	17.4	4.97	2.2	5.15	4.4	1.35	.66	.1	.07	.48
LRWSHP60	46.20	122.19	63.2	17.4	4.99	2.2	5.26	4.4	1.33	.65	.1	.07	.15
LRWSHP70	46.20	122.19	63.8	17.4	4.60	2.0	5.01	4.5	1.38	.61	.2	.06	.54
LRWSHP80	46.20	122.19	64.0	17.4	4.48	1.9	4.97	4.5	1.31	.59	.1	.06	.75
LRWSHP90	46.20	122.19	59.7	17.7	6.28	3.3	6.05	4.2	1.03	.82	.2	.10	.68
LRWSHP00	46.20	122.19	63.2	17.5	4.75	2.0	5.17	4.4	1.28	.66	.1	.06	.64
ODWRRR10	46.54	121.96	62.0	17.0	5.22	2.3	5.33	4.3	1.30	.70	.2	.07	1.04
ODWRRR1X	46.54	121.96	61.6	17.1	5.27	2.4	5.35	4.3	1.31	.71	.2	.07	1.15
ODWRRR20	46.54	121.96	62.0	16.8	5.19	2.3	5.26	4.4	1.34	.71	.2	.07	1.20
ODWRRR2X	46.54	121.96	62.3	17.0	5.18	2.2	5.23	4.4	1.35	.71	.2	.07	1.26
ODWRRR30	46.54	121.96	63.2	16.4	4.74	2.0	4.80	4.3	1.47	.66	.2	.06	1.61
ORWRRR40	46.54	121.96	58.4	19.7	5.42	2.9	7.28	4.3	.78	.70	.2	.08	.12
ORWRRR50	46.54	121.96	64.5	16.3	4.93	2.1	4.43	4.5	1.42	.65	.1	.07	.94
LRWYVZ10	46.58	120.67	59.7	18.2	6.16	3.3	6.38	4.2	.96	.80	.2	.09	.68
LRWYVZ20	46.58	120.67	59.0	18.1	6.55	3.5	6.35	4.2	.93	.83	.2	.10	.65
LRWRAZ10	47.00	120.67	56.9	18.7	7.28	3.9	7.07	4.1	.72	.90	.2	.11	.26
LRWRAZ20	47.00	120.67	63.3	16.9	5.47	2.3	4.96	4.4	1.34	.75	.2	.08	.45
LRWELZ10	47.00	120.55	60.5	17.9	5.74	2.6	5.94	4.4	1.15	.85	.2	.08	.66
LRWYKZ40	46.60	120.50	66.9	15.8	3.55	1.3	3.74	4.5	1.74	.48	.1	.05	1.20
LRWYKZ50	46.60	120.50	66.9	15.7	3.88	1.4	3.68	4.5	1.76	.52	.2	.06	1.89
LRWCRZ10	47.00	120.00	63.8	16.7	5.27	2.1	4.77	4.4	1.42	.73	.2	.07	.66
LRWCRZ20	47.00	120.00	63.5	16.7	5.42	2.1	4.86	4.4	1.39	.75	.2	.07	.65
ODWRIS10	46.29	119.28	60.4	17.4	5.96	2.7	5.75	4.3	1.22	.87	.2	.08	.71
LRWMLZ10	47.13	119.28	65.7	16.2	4.43	1.6	4.22	4.5	1.59	.64	.2	.06	.71
LRWMLZ1X	47.13	119.28	65.5	16.3	4.51	1.6	4.27	4.5	1.58	.65	.1	.06	1.10
LRWMLZ20	47.13	119.28	65.5	16.3	4.45	1.6	4.24	4.5	1.58	.64	.2	.06	.95
LRWMLZ2X	47.13	119.28	65.4	16.1	4.51	1.6	4.23	4.5	1.58	.66	.2	.06	.86
LRWMLZ30	47.13	119.28	65.7	16.2	4.36	1.5	4.15	4.5	1.60	.62	.2	.06	.56
LRWMLZ40	47.13	119.28	65.6	16.2	4.37	1.6	4.17	4.5	1.58	.62	.1	.06	.54
ODWALV10	47.71	118.94	61.4	17.3	5.35	2.3	5.57	4.3	1.28	.74	.2	.07	1.32
ODWALV20	47.71	118.94	61.2	17.3	5.33	2.3	5.62	4.3	1.27	.74	.2	.08	1.20
ODWALV30	47.71	118.94	61.7	16.7	5.05	2.1	5.25	4.3	1.36	.61	.2	.07	1.55
ODWALV3X	47.71	118.94	61.4	17.1	5.12	2.3	5.41	4.3	1.32	.70	.3	.07	1.48
ODWALV40	47.71	118.94	62.4	16.7	5.04	2.1	5.22	4.4	1.38	.68	.2	.07	1.46
ODWALV50	47.71	118.94	64.4	16.4	4.38	1.7	4.61	4.5	1.50	.60	.2	.06	1.08
LRWCOZ10	46.66	118.86	60.1	18.7	5.61	2.6	6.40	4.4	1.03	.79	.2	.08	.38
LRWCOZ1X	46.66	118.86	58.8	18.0	7.09	3.1	6.33	4.2	.99	1.00	.2	.09	.54
LRWCOZ20	46.66	118.86	64.1	16.7	5.21	2.0	4.70	4.5	1.44	.73	.2	.07	.58
LRWCOZ30	46.66	118.86	64.7	13.3	6.29	1.8	3.02	2.2	2.03	1.07	.2	.11	4.98
ODWRZY10	47.13	118.38	65.8	16.1	4.07	1.5	4.08	4.5	1.62	.58	.1	.05	.72
ODWRZY1X	47.13	118.38	66.5	16.2	4.09	1.4	4.10	4.5	1.62	.58	.2	.06	1.00
ODWRZW10	47.13	118.38	66.7	16.2	4.04	1.5	4.09	4.5	1.63	.58	.2	.06	.68
ODWRZW20	47.13	118.38	68.8	15.5	3.27	1.1	3.29	4.6	1.84	.45	.1	.05	.92
LRWRZZ10	47.13	118.38	66.1	16.1	4.14	1.4	4.04	4.6	1.62	.60	.2	.06	.76
LRWRZZ20	47.13	118.38	66.8	16.4	4.25	1.5	4.08	4.6	1.61	.61	.2	.06	.70
LRWRZZ2X	47.13	118.38	66.0	16.2	4.30	1.5	4.15	4.5	1.59	.62	.1	.06	.52
LRWRLZ10	46.98	118.34	65.6	16.1	4.34	1.5	4.09	4.5	1.60	.62	.1	.06	.75
LRWRLZ20	46.98	118.34	66.1	16.3	4.35	1.5	4.15	4.6	1.62	.63	.2	.06	.50
LRWSGZ10	47.30	117.97	67.3	16.0	3.87	1.3	3.91	4.6	1.69	.56	.2	.05	.65
LRWSGZ20	47.30	117.97	66.7	16.0	3.83	1.3	3.92	4.6	1.69	.55	.1	.05	.64
ORWSPT10	47.66	117.43	65.9	16.7	4.23	1.6	4.57	4.5	1.53	.59	.2	.05	.91
ODWSPK10	47.66	117.43	62.1	16.9	4.98	2.1	5.27	4.4	1.36	.68	.3	.07	1.05
ODWSPK20	47.66	117.43	66.4	16.2	3.94	1.4	4.14	4.5	1.62	.56	.2	.05	.71
ODWSPK30	47.66	117.43	66.5	16.5	4.07	1.5	4.27	4.5	1.59	.58	.2	.06	1.30
ODIPLC20	47.34	116.89	66.9	16.0	3.78	1.3	3.85	4.6	1.69	.54	.1	.05	.81
LRIHAZ10	47.45	116.78	66.2	15.8	3.65	1.2	3.78	4.5	1.67	.53	.1	.05	1.82
ODICAE10	47.68	116.78	66.4	16.1	3.99	1.5	4.09	4.4	1.72	.58	.2	.05	1.05
ODIEMC30	47.12	116.60	67.2	16.0	3.70	1.3	3.85	4.7	1.70	.53	.1	.05	.78
ODIEMC3X	47.12	116.60	67.4	16.0	3.71	1.3	3.86	4.6	1.70	.53	.1	.05	.76
ODISMC10	47.31	116.56	67.0	16.0	3.72	1.3	3.92	4.6	1.69	.54	.1	.05	.75
ODISMC1X	47.31	116.56	66.7	16.0	3.71	1.3	3.91	4.6	1.67	.53	.1	.05	.89
ODMMIL10	46.87	113.98	63.6	16.7	4.52	1.9	4.92	4.4	1.46	.66	.2	.06	1.06
ODMMIL20	46.87	113.98	67.7	16.0	3.59	1.2	3.80	4.6	1.72	.52	.1	.05	.76
ODMMIL30	46.87	113.98	64.6	16.4	4.28	1.7	4.58	4.5	1.55	.61	.2	.06	1.06
ODMMIL40	46.87	113.98	64.6	16.5	4.22	1.6	4.58	4.4	1.53	.61	.2	.06	.99

BULK CATIONS

[Values in ppm, except those labelled in pct]

Sample	Ag	Al pct	Au	B	Ba	Be	Ca	Cd	Ce	Co	Cr	Cu	Dy	Er	Eu	Fe pct	Ga	Ge	Hf	Ho	In	K pct	La pct	Li	Mg pct	Mn
LRWSHP10	<7.8	10.1	5.2	<11.1	310	0.85	3.4	<0.32	14	13	10	40	9	0.3	<0.5	3.7	23	30	<11	1.3	<5	1.1	16	21	1.2	690
LRWSHP20	<.1	9.9	3.0	<13.8	310	.87	<3.4	.14	14	14	14	43	11	1.1	<.1	3.7	22	27	<1	.6	8	1.2	19	23	1.2	710
LRWSHP30	<1.6	9.9	5.1	<3.9	310	.86	3.4	<.26	15	14	17	41	11	1.2	<1.0	3.6	23	30	<8	1.1	17	1.2	16	21	1.3	710
LRWSHP40	<6.2	9.9	3.9	<13.2	310	.89	3.4	<.29	12	13	14	39	10	1.0	.2	3.6	20	27	<7	.7	2	1.2	18	21	1.2	690
LRWSHP50	<3.7	9.7	4.2	<13.2	310	.88	3.3	.06	16	13	10	39	9	.7	<.5	3.6	24	29	<4	1.0	2	1.2	17	22	1.2	690
LRWSHP60	<1.7	9.7	3.4	18.8	300	.85	3.3	<.08	13	13	6	41	11	.3	<.6	3.5	22	25	<3	.7	7	1.1	15	22	1.2	670
LRWSHP70	<5.1	9.9	4.8	1.1	320	.85	3.3	<.40	14	12	4	39	9	.6	<.8	3.4	24	27	<4	.7	16	1.2	15	22	1.1	650
LRWSHP80	<1.9	9.5	4.4	17.1	290	.80	3.2	<.30	11	11	7	31	9	1.5	<1.1	3.3	25	26	<3	.8	3	1.1	14	23	1.0	610
LRWSHP90	<5.6	9.9	5.6	<19.7	250	.72	4.0	<.26	13	19	37	35	12	1.2	<1.9	4.5	26	41	<13	1.0	7	.8	14	18	1.6	890
LRWSHP00	<9.9	10.0	4.7	<1.0	290	.84	3.4	<.01	12	13	8	37	8	.4	<.9	3.5	23	26	<9	1.1	<9	1.1	14	23	1.1	640
ODWRRR10	3.1	9.7	3.5	91.5	320	.89	3.4	<.15	15	15	12	46	11	.4	<.4	3.7	23	30	<6	1.1	<1	1.1	17	23	1.2	710
ODWRR1X	<9.4	9.5	2.9	44.8	310	.92	3.4	<.34	13	14	17	47	8	<.4	<.8	3.7	19	26	<8	.5	<13	1.2	16	22	1.2	710
ODWRRR20	<4.2	10.2	5.0	2.6	340	.95	3.6	<.26	17	15	12	52	11	1.0	<1.1	4.1	24	31	<3	.7	10	1.3	18	26	1.3	760
ODWRRR2X	<9.3	9.7	5.6	<8.6	320	.85	3.4	<.18	16	14	17	47	11	.9	<.6	3.8	21	31	<11	.6	<7	1.2	17	24	1.2	720
ODWRRR30	<7.1	9.3	4.4	.7	350	.94	3.2	<.37	18	12	16	49	9	.7	<.7	3.4	25	22	<3	1.2	8	1.3	19	25	1.0	630
ORWRRR40	<5.6	11.3	5.5	<13.4	220	.62	4.9	<.35	8	16	21	35	10	<.2	<3.0	4.1	24	36	<4	.3	<13	.7	12	16	1.5	750
ORWRRR50	<.50	9.4	3.7	7.6	550	.86	3.0	.11	15	13	8	42	10	1.0	<1.5	3.5	22	26	<6	1.1	9	1.2	15	26	1.1	690
LRWYVZ10	<7.4	10.4	5.0	<4.7	250	.66	4.3	<.30	12	19	19	44	11	0	<2.2	4.6	22	38	<12	.8	2	.8	14	17	1.7	930
LRWYVZ20	<7.2	10.1	5.5	<6.3	240	.65	4.2	<.27	11	20	20	45	11	.3	<2.7	4.7	25	41	<9	1.3	9	.8	14	18	1.7	940
LRWRAZ10	<7.9	10.5	5.4	269.8	320	.50	4.6	<.50	6	21	16	40	12	.2	<3.0	5.1	25	44	<10	.6	<7	.6	12	15	1.9	990
LRWRAZ20	<7.3	9.5	4.6	10.9	310	.85	3.3	<.02	15	14	12	49	12	.7	<1.0	3.8	23	31	<7	1.3	5	1.2	16	24	1.2	740
LRWELZ10	<6.5	10.0	4.8	7.2	400	.82	3.8	<.06	13	15	24	38	12	1.0	<1.1	4.0	23	30	<5	.9	3	1.1	15	20	1.3	760
LRWYKZ40	4.9	8.9	2.1	<11.5	410	1.10	2.6	<.20	16	8	10	54	9	1.1	<.7	2.7	21	17	<4	.4	5	1.7	18	28	.7	520
LRWYKZ50	1.2	9.0	3.7	10.6	410	1.08	2.6	.31	18	9	11	57	12	1.9	<.3	2.9	19	17	<5	.7	7	1.7	19	29	.8	580
LRWCRZ10	<7.9	9.3	3.5	<12.3	320	.80	3.2	<.31	14	14	12	43	11	.6	<.9	3.7	23	27	<8	1.2	<2	1.2	16	25	1.1	690
LRWCRZ20	<8.7	9.4	3.7	<14.9	320	.73	3.2	<.14	14	14	14	45	9	<.3	<1.6	3.8	19	23	<7	.3	<13	1.2	16	24	1.1	700
ODWRIS10	<4.9	9.9	4.5	<11.1	300	.75	3.8	<.25	13	16	45	48	11	.4	<1.4	4.3	23	30	<8	.9	<8	1.1	15	22	1.4	780
LRWMLZ10	<2.8	8.2	3.4	<14.0	330	.78	2.6	<.47	15	10	8	40	8	.1	<1.8	3.0	18	18	<7	.8	10	1.1	15	24	.8	550
LRWMLZIX	<5.5	9.2	4.5	<10.2	360	.93	2.9	<.14	18	10	10	48	11	1.9	<.7	3.3	24	19	<9	1.3	2	1.4	18	26	.9	600
LRWMLZ20	<3.2	9.2	3.6	<16.2	360	.91	2.9	<.18	15	10	9	48	8	.7	<.7	3.3	22	21	<6	.6	<11	1.4	18	27	.9	600
LRWMLZ2X	<22.1	9.1	2.3	3.5	370	.92	2.8	<.79	15	10	10	48	2	<3.3	<3.6	3.3	20	18	<23	.3	<55	1.4	17	27	.9	590
LRWMLZ30	<.6	9.2	3.8	<15.5	370	.99	2.8	<.34	16	10	12	45	10	1.4	<.7	3.2	24	22	<6	.7	3	1.5	19	27	.9	600
LRWMLZ40	<8.6	9.5	2.6	6.6	380	.97	2.9	.01	15	11	9	49	9	.2	<.3	3.4	20	19	<1	.8	<11	1.5	17	28	.9	610
ODWALV10	<7.0	10.0	4.4	64.3	320	.90	3.8	<.21	17	14	21	46	9	.6	<1.8	4.0	27	31	<6	.8	<5	1.1	17	23	1.3	730
ODWALV20	<8.8	9.8	4.1	7.3	310	.84	3.6	<.28	14	14	18	46	9	<0	<1.1	3.9	20	25	<8	.3	<6	1.0	16	22	1.2	720
ODWALV30	<5.7	9.7	3.4	39.5	340	.90	3.4	<.02	15	14	21	50	10	.5	<1.1	3.7	21	26	<3	.5	<4	1.2	18	24	1.1	680
ODWALV3X	4.9	9.9	5.4	18.6	330	.96	3.6	.18	18	15	21	48	15	2.4	<.1	3.8	26	34	5	.9	24	1.3	19	23	1.2	720
ODWALV40	<2.4	10.0	5.0	3.6	350	1.02	3.6	.06	19	14	17	53	12	1.4	<.4	3.8	25	30	<4	1.5	21	1.2	19	26	1.2	700
ODWALV50	<7.3	9.6	4.2	<8.7	370	.99	3.2	<.26	18	11	13	48	8	.4	<.7	3.4	25	23	<9	1.2	<5	1.3	19	29	1.0	620
LRWCOZ10	<5.3	10.4	4.8	6.9	260	.74	4.2	<.35	9	15	18	37	10	.3	<1.9	4.0	22	33	<8	.2	6	.9	13	19	1.4	730
LRWCOZ1X	<11.2	10.4	5.5	101.8	360	.69	4.3	<.41	11	20	18	48	12	<.3	<2.4	5.2	25	35	<8	1.5	10	.8	15	19	1.6	900
LRWCOZ20	<3.8	9.5	5.2	<.1	340	.92	3.2	.14	16	14	14	46	12	1.5	<.7	3.7	24	28	0	1.3	21	1.3	17	25	1.1	680
LRWCOZ30	<5.8	7.2	4.4	<16.8	660	1.15	2.0	<.02	43	16	41	26	15	3.0	.8	4.2	18	21	<4	1.3	17	1.8	40	26	1.0	1,010
ODWRZY10	<6.2	9.0	2.1	<3.6	360	.95	2.8	<.48	14	9	9	46	7	.1	<.8	3.0	18	18	<7	.3	<9	1.5	17	27	.8	570
ODWRZY1X	<6.3	9.7	3.7	<7.6	390	1.01	2.9	<.32	16	10	9	49	9	.2	<1.1	3.2	23	20	<6	.7	<10	1.5	18	29	.8	610
ODWRZW10	<5.5	9.2	3.5	<.7	380	1.02	2.8	<.11	16	10	9	47	9	.7	<1.2	3.0	20	19	<4	.2	<9	1.6	18	29	.8	570
ODWRZW20	<6.7	8.8	2.2	<2.3	410	1.11	2.3	.07	16	7	6	45	7	<.1	<.6	2.5	18	15	<4	.3	<27	1.7	21	31	.6	510
LRWRZZ10	<5.0	9.2	3.5	4.1	370	1.02	2.7	<.29	15	10	12	45	10	1.5	<.5	3.0	22	17	<3	.2	3	1.5	18	29	.8	570
LRWRZZ20	<6.2	9.2	2.6	<17.5	360	.96	2.8	<.06	15	10	21	45	7	<.2	<.7	3.1	20	16	<2	.5	<17	1.5	18	27	.8	570
LRWRZZ2X	<1.6	9.5	4.0	<13.4	380	.99	2.9	<.24	16	10	10	45	10	1.2	<.2	3.3	22	21	<5	.5	4	1.5	19	29	.9	600
LRWRLZ10	<7.6	9.3	2.8	<12.3	370	.95	2.8	<.39	16	10	12	45	8	.3	<.9	3.2	19	18	<11	.7	<13	1.5	17	27	.9	590
LRWRLZ20	<6.5	9.1	3.5	<14.9	360	.90	2.8	<.03	15	10	10	48	9	.4	<.7	3.2	23	19	<9	.5	<5	1.4	18	27	.9	590
LRWSGZ10	1.1	7.8	2.9	<13.2	330	.86	2.3	<.47	15	8	7	40	7	1.2	<1.0	2.6	19	13	<2	.8	11	1.2	16	24	.6	480
LRWSGZ20	<1.7	9.1	3.5	<14.4	380	1.03	2.7	<.07	16	8	10	45	10	2.0	<.5	2.9	19	19	<4	.6	15	1.5	18	28	.7	550
ORWSPT10	1.0	9.3	2.7	<6.9	350	.96	3.0	<.23	16	10	11	43	9	.9	<.9	3.1	22	19	<1	.5	<5	1.3	17	24	.9	560
ODWSPK10	0	9.7	6.0	.1	330	.94	3.4	<.24	18	13	23	49	13	1.8	<1.5	3.7	26	28	<5	1.3	8	1.3	18	24	1.1	670
ODWSPK20	<1.3	9.6	1.3	21.9	390	.98	2.9	.01	14	9	9	47	9	.9	<.4	3.1	16	16	<5	<.1	<9	1.5	18	29	.8	580
ODWSPK30	<6.8	9.1	5.1	<12.7	360	1.03	2.8	<.24	16	9	9	45	8	.3	<.7	3.0	19	18	<4	.7	2	1.4	17	27	.8	560
ODIPLC20	<3.5	8.9	1.5	<7.5	370	1.03	2.6	<.11	14	8	7	45	8	.8	<1.1	2.7	20	13	<3	.2	<15	1.5	17	28	.7	530
LRIHAZ10	<2.8	8.7	3.1	<9.7	370	.98	2.5	<.19	16	8	7	42	9	.7	<.4	2.6	20	18	<6	.7	<5	1.5	18	27	.7	510
ODICAE10	.9	9.9	5.1	<10.8	870	1.28	3.0	.16	25	10	12	49	11	1.8	.6	3.3	28	24	<2	1.6	13	1.6	24	34	.9	610
ODIEMC30	<4.4	9.1	2.1	<8.8	390	1.04	2.6	.06	15	8	8	45	9	.7	<.8	2.8	19	17	<4	<.1	<6	1.6	20	29	.7	530
ODIEMC3X	<1.1	9.3	4.0	<12.3	400	1.09	2.7	<.25	18	9	9	46	10	1.5	<.4	2.9	24	17	<1	1.0	4	1.5	19	30	.7	550
ODISMC10	<10.9	9.1	2.9	<14.5	390	1.01	2.7	<.45	14	8	9	45	7	<1.0	<1.2	2.8	20	17	<8	.4	<20	1.6	18	28	.7	540
ODISMC1X	<7.2	9.0	3.4	<11.9	380	.98	2.6	<.31	15	8	9	42	7	1.0	<.4	2.8	21	16	<3	.7	<5	1.5	18	29	.7	540
ODMMIL10	<4.8	9.9	3.5	.8	360	1.00	3.3	<.02	17	12	21	51	10	1.1	<.2	3.4	23	25	<4	1.3	<5	1.3	19	25	1.1	630
ODMMIL20	<3.4	8.8	4.0	<3.6	380	1.01	2.5	<.22	19	8	8	44	8	.7	<.8	2.7	23	18	<5	1.3	5	1.4	18	30	.7	510
ODMMIL30	1.4	9.4	3.9	13.8	360	.98	3.1	<.14	18	11	17	48	9	1.7	<.7	3.2	21	24	<7	1.2	11	1.3	19	26	.9	590
ODMMIL40	<.9	9.0	3.0	<11.1	350	.93	3.0	<.10	17	11	15	42	8	.9	<1.1	3.1	23	20	<2	1.0	11	1.2	17	25	.9	550

BULK CATIONS—Continued

[Values in ppm, except those labelled in pct]

Mo	Na pct	Nb	Nd	Ni	P pct	Pb	Pr	Rh	Sb	Sc	Se	Sm	Sn	Sr	Tb	Th	Ti	Tm	U	V	W	Y	Yb	Zn	Zr
0.2	3.7	3.7	9.1	11	0.067	7.6	0.7	4.0	6.0	10	13	0.2	0.3	510	2.0	<3.3	0.41	2.2	8.6	88	5.0	17	1.4	76	110
.9	3.7	4.0	6.8	13	.068	7.1	<1.9	4.0	6.3	11	11	2.7	.3	510	7.4	<2.7	.42	2.7	<8.2	89	.2	16	1.4	76	110
<.4	3.6	5.2	10.1	16	.071	5.0	1.1	4.0	4.9	11	3	2.1	<.1	510	6.5	<.6	.43	2.4	7.2	89	<5.9	17	1.4	74	120
<.2	3.6	4.8	5.5	13	.067	8.2	<0	4.0	5.6	11	8	1.0	<2.0	510	4.7	<4.4	.42	1.9	<.3	89	<3.1	16	1.3	74	110
.5	3.6	4.5	6.8	12	.068	7.2	<.5	4.0	5.9	11	13	2.4	.9	490	7.9	<2.1	.41	2.2	<1.4	87	2.6	17	1.3	75	110
<.3	3.6	3.6	6.2	11	.065	7.2	1.2	3.9	5.1	11	6	2.2	<1.3	490	5.4	<1.5	.39	2.8	<1.5	84	<7.7	16	1.4	74	110
.7	3.7	4.5	8.7	8	.062	9.5	.9	4.0	<.8	10	13	1.0	1.4	490	3.8	<2.4	.37	1.9	23.8	80	<4.0	16	1.3	71	120
.8	3.6	3.8	7.0	8	.059	8.3	2.5	3.9	5.9	9	10	1.3	3.0	470	5.0	<0	.35	2.2	23.7	75	1.8	14	1.2	68	120
<.3	3.5	5.1	5.8	21	.071	5.6	1.2	3.9	5.1	14	15	1.0	14.7	550	7.6	<2.4	.50	1.7	10.3	111	<3.0	17	1.3	86	100
.9	3.7	4.3	2.8	10	.061	7.2	<.7	4.0	3.9	11	17	<.1	1.3	490	1.2	<1.9	.40	1.4	6.7	86	<3.4	16	1.2	69	120
.2	3.6	3.8	6.7	18	.083	5.6	2.3	4.0	3.8	11	16	1.1	<4.2	490	8.2	<2.5	.43	2.3	<3.6	87	<3.2	18	1.4	75	120
.1	3.5	4.7	5.9	17	.081	6.4	<3.5	3.9	.0	11	5	.1	.3	490	4.7	<3.9	.43	1.8	<7.6	87	<4.5	18	1.4	75	120
.6	3.8	6.0	13.6	19	.089	4.5	<.7	4.3	6.6	12	8	3.1	<1.5	520	5.4	<2.1	.48	3.3	<5.6	96	<4.5	20	1.6	85	130
.9	3.6	5.3	5.9	17	.083	<.8	4.0	5.1	11	11	11	1.1	<.5	500	5.0	<3.2	.45	2.6	<8.3	90	<1.8	19	1.5	79	120
1.1	3.6	5.4	11.6	15	.088	13.2	<.5	4.0	5.8	10	8	2.3	<1.3	440	4.1	<1.5	.39	2.6	7.5	74	<6.4	18	1.3	75	130
.6	3.6	4.7	1.7	22	.062	7.1	.2	4.0	3.1	13	13	<.2	<.7	680	3.5	<4.0	.44	1.8	<.1	98	3.5	14	1.2	73	70
<.9	3.7	3.3	8.0	9	.064	17.0	2.3	4.0	6.3	10	<2	2.4	<.9	430	7.6	<.5	.35	2.4	15.7	77	<7.7	15	1.4	75	130
<.2	3.5	4.8	2.7	19	.078	6.1	<2.4	3.9	3.6	14	9	.5	<.6	600	6.5	<3.5	.50	1.5	<5.6	113	.1	16	1.4	88	90
.1	3.4	4.9	4.9	21	.079	6.2	<0	3.9	2.7	14	8	<.2	<1.2	580	6.5	<2.3	.52	1.3	13.0	116	<5.6	17	1.2	101	90
<.6	3.4	4.5	<3.4	20	.076	5.0	<3.6	3.8	<.8	16	11	<1.1	<.7	630	2.8	<3.3	.52	.8	<13.4	133	<10.3	16	1.2	93	70
<.4	3.6	3.7	8.0	13	.076	9.6	2.6	4.0	8.4	11	14	2.8	.9	470	11.0	<1.3	.45	2.4	13.9	100	.6	17	1.5	83	130
.2	3.5	5.3	10.2	20	.078	7.9	.4	4.0	1.1	12	2	.5	<2.7	550	7.5	<2.4	.51	2.7	<8.3	100	<5.3	18	1.6	80	110
1.0	3.7	3.8	11.0	10	.072	21.1	<1.5	4.0	4.4	8	11	3.2	<.6	370	4.1	<1.7	.30	3.0	<7.9	48	<3.7	17	1.5	76	150
1.0	3.7	3.9	14.8	12	.079	47.3	3.9	3.9	10.5	9	2	5.4	1.4	360	4.1	2.7	.31	3.6	8.3	53	1.2	18	1.5	98	160
.7	3.6	4.5	6.0	13	.074	7.4	<.6	4.0	2.3	10	17	.7	<.7	450	7.2	<.1	.45	2.3	7.4	100	<5.3	17	1.3	79	130
<.2	3.6	4.2	5.3	13	.074	4.9	<4.3	4.0	.4	11	2	2.1	<1.5	460	9.1	<3.4	.45	2.8	<14.3	100	<8.0	17	1.4	82	120
.6	3.6	6.4	7.7	32	.081	7.9	<1.5	4.0	7.5	12	5	1.8	1.7	520	8.1	<2.7	.52	2.8	<3.2	107	<3.0	19	1.4	90	120
<.3	3.3	3.5	7.0	9	.064	4.9	<1.1	3.6	1.5	8	1	2.1	<1.4	370	6.4	<1.3	.36	3.0	<4.2	71	<10.1	16	1.2	65	130
.9	3.7	3.9	11.0	10	.071	11.9	.6	4.0	5.4	9	4	3.0	<.4	410	8.7	.7	.38	2.9	24.8	75	3.7	17	1.3	70	140
.7	3.7	4.2	10.1	9	.071	5.5	<.8	4.0	4.0	9	11	.1	1.4	410	2.8	<2.3	.40	3.0	<3.8	77	2.7	18	1.3	71	140
.3	3.6	3.6	1.3	7	.068	6.9	<8.5	3.8	<3.7	9	9	<4.7	.7	400	<3.9	<9.8	.38	1.3	<13.5	72	<16.1	17	1.0	69	140
1.0	3.7	4.6	12.5	10	.070	10.5	1.9	4.1	5.6	9	11	2.8	1.7	410	5.0	.0	.38	3.2	12.6	72	6.1	17	1.4	73	150
.4	3.9	4.5	8.6	9	.074	8.5	<.5	4.2	3.5	9	3	2.2	.4	420	6.8	<1.3	.40	3.2	<5.8	77	4.6	18	1.5	72	150
.3	3.7	5.8	7.1	21	.087	7.2	<2.2	4.1	4.9	12	6	.1	1.4	530	5.8	<2.3	.47	2.5	1.7	91	<6.6	19	1.5	78	120
<.2	3.6	4.9	8.4	19	.084	5.8	<5.2	4.0	.4	11	12	.8	<1.7	520	8.0	<4.1	.46	2.7	<16.3	90	<8.0	18	1.4	77	120
.04	3.6	6.3	8.0	19	.091	6.3	<3.1	4.0	2.5	10	4	2.0	<.4	490	7.3	<3.7	.43	3.0	<11.6	84	<1.2	19	1.4	73	120
1.9	3.7	5.9	14.8	20	.089	12.3	5.0	4.1	12.4	11	13	6.4	3.5	510	12.3	.0	.45	3.4	16.2	88	3.3	19	1.6	76	120
1.1	3.8	6.2	10.8	20	.095	11.7	3.1	4.2	3.6	11	12	2.3	.5	500	9.3	<1.3	.45	2.9	21.5	86	1.9	20	1.7	76	130
.8	3.8	5.4	10.7	12	.081	10.8	<.1	4.1	3.4	9	7	<.8	<.7	450	9.3	<.5	.39	2.7	10.8	70	<2.5	19	1.3	70	140
<.3	3.6	4.3	1.9	17	.073	5.9	<3.6	4.0	3.0	12	12	1.3	<2.0	590	9.6	<3.8	.47	1.7	<20.9	107	4.5	16	1.4	76	100
<.8	3.6	5.3	2.2	21	.084	5.2	<4.7	4.1	1.7	14	8	<.6	<1.8	590	2.8	<3.7	.64	1.8	<.4	154	<8.5	20	1.6	95	100
1.4	3.7	5.2	10.4	14	.074	10.7	3.5	4.1	5.9	11	14	3.6	.2	450	10.8	1.2	.45	2.6	9.8	96	9.5	18	1.4	78	130
<.2	1.9	5.2	32.1	19	.087	14.7	2.2	2.4	6.9	15	2	7.0	.1	320	12.6	8.3	.59	5.0	<9.1	128	<.2	29	2.5	97	110
.4	3.7	3.6	4.4	9	.069	7.3	<2.3	4.0	2.6	8	10	.5	.3	400	8.1	<1.8	.36	2.7	<4.5	65	<1.7	17	1.4	68	150
.9	4.0	4.7	8.5	10	.073	8.4	<1.5	4.3	4.5	9	12	3.4	<2.1	420	5.8	<1.2	.38	3.1	7.4	69	2.8	18	1.4	78	160
.2	3.8	3.7	12.3	10	.070	7.9	<2.2	4.1	2.4	8	9	2.4	<1.6	400	<.5	<1.8	.36	3.2	<8.1	63	<1.2	17	1.6	67	150
.4	3.8	3.6	6.0	7	.064	9.8	<2.9	4.0	1.5	7	9	2.3	<1.7	340	6.0	<3.1	.28	3.2	<9.5	38	<6.5	17	1.4	62	170
.5	3.7	3.5	7.8	9	.068	8.5	.8	4.1	6.2	8	10	3.4	<2.0	400	7.6	<1.4	.36	3.0	6.2	67	<5.0	17	1.5	69	150
.6	3.7	4.0	8.7	9	.068	7.7	<.7	4.0	.7	9	11	.9	2.7	400	2.4	<3.3	.36	2.6	4.3	69	<3.0	17	1.3	69	150
1.2	3.9	5.2	14.5	10	.073	9.7	.4	4.2	8.8	9	13	1.9	.1	420	9.0	<1.4	.40	3.0	5.9	76	2.7	18	1.3	72	150
.2	3.7	4.0	8.0	10	.070	6.2	<3.3	4.1	4.7	9	3	.1	<2.7	410	<1.5	<3.7	.39	2.8	<12.8	75	<8.7	17	1.2	71	150
.2	3.7	4.2	8.1	10	.069	5.6	<1.1	4.0	<.3	9	11	.9	.2	400	6.8	<2.3	.38	3.3	<2.5	73	2.6	17	1.1	72	140
.4	3.2	3.5	7.7	7	.062	4.7	1.2	3.5	2.3	7	3	2.2	<1.0	330	4.6	<.4	.31	2.9	5.0	54	<10.5	15	1.1	58	130
.1	3.7	3.6	11.6	8	.070	9.8	.3	4.1	3.6	8	2	3.7	<.1	390	3.7	1.4	.34	3.4	9.9	59	4.7	17	1.3	68	150
.2	3.6	3.3	10.9	11	.073	13.4	<.8	3.9	5.5	9	12	1.7	.5	430	6.3	<1.9	.30	3.1	<5.0	57	<2.8	16	1.5	66	120
<.03	3.6	4.5	15.3	17	.085	10.6	4.3	4.0	3.6	11	12	6.3	1.1	490	8.5	1.0	.43	3.3	26.9	82	<7.9	19	1.6	76	120
.4	3.9	4.4	8.4	11	.076	8.0	<4.2	4.2	9.3	9	8	2.3	.2	420	.6	<4.8	.36	4.1	<28.4	62	.1	18	1.5	68	160
.7	3.7	4.2	10.4	10	.072	6.7	<.4	4.0	3.4	9	9	2.5	.1	410	8.2	<2.6	.34	2.8	<9.3	59	<6.3	17	1.5	64	140
1.0	3.7	3.9	10.5	7	.065	6.9	<.8	4.0	2.1	7	9	2.5	.2	370	6.4	<1.9	.32	2.7	<4.7	52	1.1	16	1.4	65	150
.5	3.6	4.7	9.6	7	.066	8.1	<1.5	3.9	<.3	8	8	1.7	2.4	360	6.3	<.1	.31	3.0	4.2	51	8.2	16	1.3	63	150
2.0	3.9	5.2	19.4	10	.078	31.3	5.3	4.3	9.0	10	13	4.0	4.9	430	7.0	1.7	.36	3.5	37.2	65	8.5	19	1.8	77	150
.5	3.8	3.1	10.0	8	.068	9.4	<1.4	4.1	<.2	8	0	2.4	<.6	380	4.4	<2.8	.32	2.9	<11.3	53	<3.5	17	1.5	64	150
1.3	3.9	4.4	12.9	9	.070	9.2	2.7	4.3	4.9	8	6	3.6	<1.3	390	9.0	1.1	.34	3.3	4.8	55	7.6	18	1.5	67	160
1.0	3.8	4.1	10.7	6	.067	9.5	<3.3	4.0	3.6	8	7	<1.3	<.1	390	.5	<4.1	.33	2.9	2.0	54	<3.8	17	1.3	65	160
.4	3.8	4.0	12.2	8	.068	9.2	<2.9	4.1	2.5	8	4	<.1	1.9	380	3.2	<3.4	.33	3.2	<4.1	55	3.8	16	1.4	65	150
.6	3.8	5.8	13.9	19	.085	9.7	1.0	4.2	7.9	10	12	2.2	3.6	470	9.6	<2.8	.42	3.2	10.9	76	<6.4	19	1.6	70	150
.7	3.7	3.7	9.7	8	.065	9.8	<.5	4.0	6.5	8	4	1.5	1.0	360	1.8	<.8	.31	2.9	19.9	51	<5.6	17	1.4	62	150
.2	3.7	5.3	14.2	16	.080	12.5	.8	4.1	5.0	10	12	2.3	0	430	7.6	<1.9	.39	3.0	13.8	67	<1.3	18	1.5	67	150
.1	3.5	4.3	11.6	14	.075	8.7	1.6	3.9	5.3	9	13	3.1	.6	420	7.7	.2	.35	3.1	5.0	63	<1.0	17	1.3	65	140

APPENDIX B.—ESTIMATE OF ANALYTICAL ERROR IN CHEMICAL CONCENTRATION DATA FOR WHOLE ASH

Analytical precision is estimated by the geometric error for each chemical species determined. The geometric error is the antilog of the log standard error, and is calculated from the logarithms of the differences in measured concentrations between samples that are members of pairs of analytical replicates (splits). The use of logarithmic data minimizes the perturbing effect of uncommon, extreme-value data upon the final value of the error parameter. The number of sample pairs from whose data the error parameter calculation was made are also listed in the appendix.

Geometric error was calculated from concentration values of 10 pairs of samples. For samples with qualified values (below detection limit, where only an upper limit is given), a value of 0.7 times the detection limit was substituted and used in the calculation. The number of pairs free of qualified values is given in the table.

WHOLE-ASH CHEMICAL ANALYSES

[LOI, loss on ignition. Fe_2O_3 is total Fe calculated as Fe_2O_3]

Chemical species	Geometric error	Number of pairs
X-ray fluorescence		
SiO_2	1.01	10
Al_2O_3	1.01	10
Fe_2O_3	1.05	10
MgO	1.05	10
CaO	1.01	10
Na_2O	1.01	10
K_2O	1.01	10
TiO_2	1.05	10
P_2O_5	1.33	10
MnO	1.05	10
LOI	1.18	10
Ion chromatography		
Cl^-	1.60	4
F^-	1.08	4
PO_4^{-3}	1.03	4
SO_4^{-2}	1.23	4
Inductively coupled plasma spectroscopy		
Al	1.04	10
Au	1.32	10
B	2.12	3
Ba	1.08	10
Be	1.06	10
Ca	1.04	10
Ce	1.11	10
Co	1.08	10
Cr	1.22	10
Cu	1.08	10
Dy	1.41	10
Er	2.60	5
Fe	1.07	10
Ga	1.14	10
Ge	1.11	10
Ho	2.50	9
In	2.75	2
K	1.07	10
La	1.06	10
Li	1.04	10
Mg	1.05	10
Mn	1.06	10
Mo	2.96	8
ICP--Continued		
Na	1.03	10
Nb	1.16	10
Nd	1.76	10
Ni	1.12	10
P	1.05	10
Pb	1.30	10
Rh	1.04	10
Sb	4.70	8
Sc	1.06	10
Se	2.17	10
Sm	3.55	7
Sn	4.25	2
Sr	1.04	10
Tb	1.88	9
Ti	1.08	10
Tm	1.24	10
U	2.98	1
V	1.10	10
Y	1.06	10
Yb	1.08	10
Zn	1.07	10
Zr	1.04	10

Leachate Chemistry of Ash from the May 18, 1980 Eruption of Mount St. Helens

By TODD K. HINKLEY *and* KATHLEEN S. SMITH

With a section on LABORATORY METHODS DEVELOPED FOR MOUNT ST. HELENS WATER AND ACID LEACHING STUDIES

By STEPHEN A. WILSON *and* CAROL A. GENT

CHEMISTRY OF ASH AND LEACHATES FROM THE MAY 18, 1980
ERUPTION OF MOUNT ST. HELENS, WASHINGTON

U.S. GEOLOGICAL SURVEY PROFESSIONAL PAPER 1397-B

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LEACHATE CHEMISTRY OF ASH FROM THE MAY 18, 1980 ERUPTION OF MOUNT ST. HELENS

By TODD K. HINKLEY and KATHLEEN S. SMITH

ABSTRACT

We present and interpret a large body of chemical leachate data from a large number of ash samples from the May 18, 1980 eruption of Mount St. Helens, Wash. The postdepositional history and circumstances of collection and storage of the samples are well documented. We performed leach treatments on 39 ash samples with both near-neutral (deionized water) and low-pH (0.01 F H_2SO_4) solutions, using a 4-hour leaching time with a 14:1 solution-to-ash ratio; deionized water and acid leach treatments were done on separate sample aliquots rather than in sequence on the same aliquots. The near-neutral treatments may approximate natural conditions of exposure to rain, soil solutions, and ground water, and the low-pH treatments may approximate exposure to the very thin zones of soil solution surrounding plant roots. The purpose of the treatments was to gain information on the amounts, compositions, and removal sequences of materials on and within the grains of tephra, and to gain insights into the processes of formation of the tephra grains as they emerged from the volcano and were transported through the air.

The deionized water leach treatment removed material as follows. Of the metals, Ca, Na, Mg, K, Si, Mn, Ba, and Sr were removed in greatest absolute amounts, but Ni, Co, Mn, and Ca were removed in greatest fractions of their whole-ash contents. About half of the total Cl^- and SO_4^{-2} was removed, much less of total F^-, and almost no PO_4^{-3}. The soluble material in the deionized water leachate, and the material removed by rain in the field, was composed of electrically equivalent amounts of the major cations and anions found in common salts, suggesting that it may represent a layer of material that mantles grains of igneous material, but is distinct from them in composition and solubility. Nearly the same amounts of most cations and anions were readily removed by leach treatments of widely varying water to ash ratios, and by rain in the field, indicating presence of a definite quantity of easily dissolved surficial material.

Larger fractions of whole-ash contents of elements were put into solution by the 4-hour acid leach treatment than by the deionized water leach treatment, but the increases in the amounts were different for various elements. The most abundant elements in the acid leachate were Ca, Fe, Al, Na, P, K, Mg, and Si. The acid leach removed slightly more Cl^- and SO_4^{-2}, somewhat more F^-, and much greater amounts of PO_4^{-3} than did the deionized water leach. Much of the acid-soluble material probably came from surficial material coating primary igneous grains but, unlike the deionized water leach solute, anions were insufficient to electrically balance the cations in the acid leach solute. Exchange reactions, in which protons displaced cations from grain surfaces, were evidently a source of cations to the acid leach solution. Increased pH values after the completion of leach treatment show that the quantities of electrical equivalents of protons consumed accounted for a large fraction of the excess cations put into solution.

There are highly significant positive and negative statistical correlations between Ca, Si, and Na in the whole ash (elements indicative of lithologic type) and amounts of leachable species removed by the water and acid leach treatments. Dark-colored ash (high Ca, Fe, Mg; low Si, Na) released a greater amount of material to leaching treatments than did light-colored ash (high Si, Na; low Ca, Fe, Mg).

Much material initially present on the ash as soluble salts was released to the water and soil environments in a single pulse shortly after deposition of the ash blanket. If one or two pore volumes of interstitial solution from the ash were added to the solution present in a typical soil, there would be a net increase in concentrations of some elements that are either innocuous or beneficial to plant nutrition (K, Mg, Cu, Fe, and Zn), and either a net decrease or no large change in concentrations of some elements of "environmental concern" (Ba, Na, and Mo). The chemistry of some small bodies of water may have been more significantly altered after the ash fall, and some biotas may have been affected. A suite of elements similar in proportions to those yielded by acid leach treatment may be expected to be released over long periods of time in the low-pH zones near plant roots.

Species determined were removed from ash by water leach treatment in greater amounts than are reported in soils literature to be removed from common soils by similar treatment. However, repeated leach treatments of ash samples removed smaller amounts of solute than did the first treatment, whereas amounts of solutes from repeated extractions of soils are reported to change little. Analytical splits of ash samples yielded leach solutions of more consistent composition than splits of soil samples commonly do. This may be because ash is a simpler material than soil and lacks the clays, organic materials, oxide and hydroxide coatings, and long development histories of most soils.

INTRODUCTION

The May 18, 1980 eruption of Mount St. Helens, Wash., deposited an estimated half billion tons of air-fall tephra over large areas of the States of Washington, Idaho, and western Montana (Sarna-Wojcicki, Shipley, and others, 1981). Almost immediately after deposition, substances began to be leached from the ash by rain, soil solution, bodies of water, and the action of plant roots.

The present investigation of the leachate chemistry of the ash had two purposes. One was to determine the identity, amount, and sources of the leachable chemical substances likely to be yielded by the ash. The other was to provide a body of information to aid the work of others on the interaction of the ash particles with gaseous or aerosol phases that may condense upon them during times of eruption and atmospheric transport, possibly forming water-soluble coatings on grain surfaces and in interstices.

We performed leaching experiments on selected samples of the ash in the laboratory using both deionized water and dilute solutions of strong acid. The deionized water leaches were intended to approximate conditions in the field under which the ash would be washed by rain or soaked by soil solution at near-neutral pH, after incorporation of ash into soil. The acid leaches were intended to more closely approximate conditions in the microzones surrounding plant roots where pH values can be low (pH 2 to pH 4).

ACKNOWLEDGMENTS

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SAMPLE COLLECTION AND TREATMENT

A large number of ash samples from the May 18, 1980 eruption of Mount St. Helens was obtained over a wide area of deposition, from on-site colleagues and volunteers during or immediately after deposition, and by the authors several weeks later. A map of sampling localities is included as figure 1, chapter A, of this volume. We carefully documented the collection and storage procedures and the postdepositional history for each sample, anticipating that the leachable chemical characteristics of ash samples could be easily altered in a short time following deposition. Whenever possible, samples were put into clean tightly sealed plastic or glass jars at the time of collection and kept in them, undisturbed, until aliquots were taken for analytical preparation.

Large numbers of the samples represent the three following natural groupings: (1) ash that fell at progressively increasing distances from the source; (2) ash from the same location before and after rainfall; and (3) ash that was collected during successive time increments (referred to herein as time-sequence samples) at single sites. Suites of five samples from Almira, Wash., and two samples from Missoula, Mont., represent the time-sequence samples. The Almira samples were carefully collected on a plastic table cloth and transferred and sealed into sterile glass jars at successive time intervals throughout the ash fall. Due to this careful and expedient collection procedure, the Almira ash did not have any contact with soil and little postdepositional contact with the atmosphere. Because of the uniquely favorable and well-documented circumstances of collection of the samples from Almira, they are, despite their paucity, treated in much of this report as yielding results of quality and importance equal to those of other more numerous pre-rain samples used in this study.

We used 39 samples for the deionized water and acid leach studies. These were selected from 69 samples (59 originals plus 10 analytical duplicates) that were analyzed for whole-ash chemical composition and discussed in chapter A of this volume. In the present study, the leachate anions were determined by IC (ion chromatography) and the cations by ICP (inductively coupled plasma) spectroscopy. Specific laboratory methods and IC techniques are described in the "Laboratory methods" section of this report. A complete tabulation of all chemical and leachate data for individual samples, with an explanation of source location, exposure history, and other information, is given in Appendix C.

The samples were analyzed in a partially random order, so that systematic error (such as "machine drift") through the analytical sequence would be largely converted to random error. However, samples belonging to a natural subset or grouping, such as the time-sequence sample suite for Almira, Wash., were placed fairly close to each other in the analytical queue, to minimize drift in accuracy between samples whose values would be compared.

LABORATORY METHODS DEVELOPED FOR MOUNT ST. HELENS WATER AND ACID LEACHING STUDIES

By S. A. Wilson and C. A. Gent

INTRODUCTION

The purpose of this work was to develop general laboratory methods for quantifying trace levels of anions and cations (using IC [ion chromatography] and ICP-AES [inductively coupled plasma-atomic emission spectroscopy], respectively) under specific environmental conditions for the Mount St. Helens ash samples. These data are important in understanding the intricate associations between anions and cations, and are critical in assessing the long-and short-term impacts of the eruption on the environment.

To properly simulate environmental effects, two leaching solutions were selected to approximate conditions to which the ash material would have been subjected. The first solution tested was deionized water, which is believed to model the effect of rain or river water on the ash. The second solution was sulfuric acid, which was selected because significant quantities of acidic gases (SO_2, H_2S) emanated from the volcano prior to, during, and after the eruption (Casadevall and others, 1981; Evans and others, 1981). The combination of these acidic gases with atmospheric moisture will result in the formation of sulfuric acid. The effect of sulfuric acid is significant because it will impact the ash directly through changes in pH or exchange reactions, which will affect the extraction of selected anions and cations.

A second reason for the use of a sulfuric acid leach solution deals with the chemistry occurring at the plant root–soil interface. It is suggested that various organic acids are extruded at the root surface, which is in direct contact with the soil (Rovira and Davoy, 1971). These organic acids are important in the mobilization of nutrients, using chemical processes such as complexation or pH changes. Although sulfuric acid does not mimic all of these chemistries, it may serve as a useful model for the effect of acidity on the transport of nutrients from the ash.

Although the two solutions cannot approximate every environmental condition to which the ash would have been subjected, they point out the accessibility of ions to two important chemical conditions.

EXPERIMENTAL PROCEDURES

LEACHING STUDIES

Initial studies conducted to optimize experimental conditions used samples collected in early Mount St. Helens eruption studies (Taylor and Lichte, 1980). The samples used were collected from Sunnyside, Anthanum, and Spokane, Wash., as well as Spaulding, Idaho. Details of their collection are reported by Taylor and Lichte (1980). Later experiments involving nitric acid leaches included a sample from Almira, Wash.

In investigations using deionized water and sulfuric acid, a half gram of ash material was placed in a 60-mL polyethylene bottle, and 7 mL of leaching solution (water or acid) was added. The bottle was sealed and placed on a Lab-Line junior orbit shaker[1] operating at 150 rpm. The solution was shaken for 4 hours, after which the solution was filtered using a 0.2 micron teflon filter. The filtered solution was split into two aliquots for IC and ICP-AES analyses. Water leach solutions for ICP-AES analysis were acidified with 1 mL of 6 *M* HNO_3 and stored in teflon test tubes.

ION CHROMATOGRAPHIC CONDITIONS

IC analyses used Dionex models 12S and 16 ion chromatographs. Instrument parameters were 100-mL injection loop, 138-mL/hr eluent flow rate, 0.003 *M* $NaHCO_3$-0.0024 *M* Na_2CO_3 eluent, 3-100 μS full scale settings, 3×250 mm S-1 anion separator columns, 3×150 mm S-1 anion precolumns, and a 6×250 mm anion suppressor column. Chromatograms were recorded using a Houston omniscribe strip chart recorder. Standards were prepared in deionized water or acid to match the sample matrix. Deionized water standards and solutions obtained using deionized water leaches were spiked with a concentrated sodium carbonate-bicarbonate solution to match the chromatographic eluent. This spike addition was necessary to eliminate a water dip interference on chloride determinations.

Sulfate extraction studies conducted on an Almira, Wash., sample used a 0.009 *M* HNO_3 extracting solution. The resulting solutions were analyzed using identical instrument parameters except for the use of S-2 anion precolumns, S-2 anion separator columns, and an eluent of 0.003 *M* Na_2CO_3 and 0.0015 *M* NaOH.

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[1] Any use of trade names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY CONDITIONS

ICP-AES analyses were performed using a Jarrell Ash Model 11760 Plasma Atomcomp ICP-AES. The 62-channel system was equipped with a modified Babbington nebulizer and a Gilson peristaltic pump for sample and internal standard delivery. Instrument parameters, wavelengths, and precision values for the analysis of the Mount St. Helens ash have been reported (Taggart and others, 1981).

pH STUDIES

All pH measurements were obtained using a Beckman model 4500 digital pH meter and an Orion combination pH electrode. The system was calibrated at 25 °C using pH 4 and pH 7 buffers. All solutions were filtered prior to a pH measurement. In extraction versus time experiments for deionized water, pH values were recorded at 1-, 4-, and 20-hour intervals. In sulfuric acid leach experiments, samples were selected for pH measurement following a 4-hour extraction.

ACCURACY AND PRECISION

Errors associated with the analysis of each element are reported in Appendix D. In ICP-AES studies involving total elemental analysis, the accuracy of the analytical procedure was tested using U.S. Geological Survey rock standard G-2. Samples of G-2 were prepared for analysis using the standard acid digestion procedure. The resulting solutions were analyzed at the beginning and end of each group of Mount St. Helens samples. Other studies have reported ±10 percent accuracy for ICP-AES analysis of whole-rock samples of Mount St. Helens ash (Taggart and others, 1981). Cation leachate studies should produce comparable accuracy and precision values.

Precision values for whole-rock and extractable anion concentrations were estimated in two separate studies. Precision estimates for anion concentrations in whole-rock analyses by IC were based on previous investigations (S. A. Wilson and C. A. Gent, unpub. data, 1982, 1983). On the basis of these studies a recommended value of ±10 percent is considered conservative for the total anion analyses. Precision values for anion determination in the extraction study were based on repetitive analysis of an Almira, Wash., sample. On the basis of these studies a precision value of 4 percent was observed for the anions examined.

DISCUSSION AND RESULTS

Laboratory methods used in this study were designed to examine the effect of leaching solution composition and time of extraction on the removal of ions from the ash. Design of an optimized experimental procedure was based on anion data accumulated using IC. It was assumed that cations would have similar extraction trends as the anions. Initial experiments examined the effect of solution composition on anion extraction. In these studies a Richland, Wash., ash sample was leached with deionized water and 0.01 *M* and 0.1 *M* sulfuric acid solutions for 1 hour. The results are presented in figure 6. There was a significant increase in the amount of anions extracted using the acid solutions compared to the water leach. In addition, there was a slight increase in extractable anions as the acid concentration increased from 0.01 *M* to 0.1 *M* sulfuric acid. On the basis of these observations, a 0.01 *M* acid concentration was selected for the general laboratory procedure, since it is probably a better model for acid extraction than the 0.1 *M* acid leach.

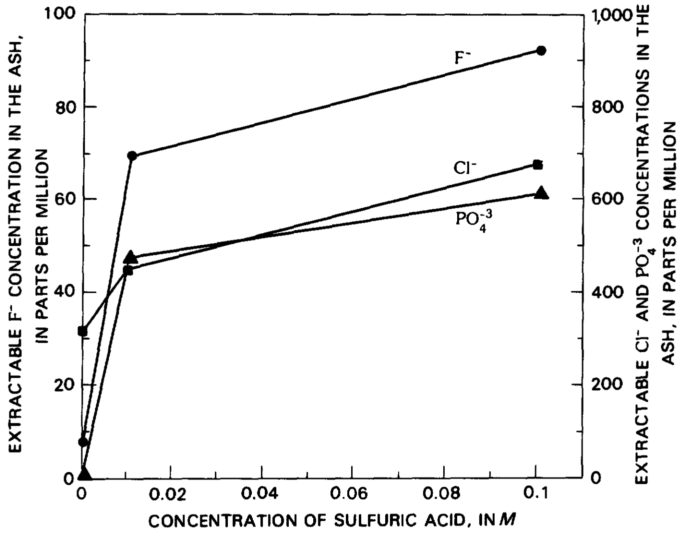

FIGURE 6.—Effect of acid concentration on the extraction of F^-, Cl^-, and PO_4^{-3} from the ash using deionized water (0 *M* H_2SO_4) and 0.01 and 0.1 *M* H_2SO_4 and a 1-hour extraction time. Sample collected at Richland, Wash.

A second set of experiments designed to evaluate the optimum extraction time was conducted using 1-, 4-, and 20-hour leaching periods. Results of the extractions using deionized water and sulfuric acid are presented in figures 7 and 8, respectively. These data indicate that the major changes in extractable anion concentrations occur in the period between 1 and 4 hours. Because of these observations, the large number of samples, and the need for rapid sample analysis, a 4-hour leach interval was used in all subsequent studies.

A comparison of extractable anion concentrations using deionized water and 0.01 *M* sulfuric acid leaches is presented in table 9 for a Missoula, Mont., sample. It is apparent that the acid leach extracted substantially more F^- and PO_4^{-3} than did the water leach. This increased extraction may be due to an exchange process in which SO_4^{-2} ions, or changes in pH, affect the solubility of specific compounds. The greater PO_4^{-3} extraction is especially significant as it can affect soil fertility by making PO_4^{-3} more accessible to plants. An examination of the Cl^- data in table 9 reveals a different trend than that seen for PO_4^{-3} and F^-. The lack of a major increase in extractable Cl^- was attributed to the presence of water-soluble chloro compounds such as sodium chloride or hydrochloric acid. These compounds would not need any exchange process or pH change to release Cl^- into solution.

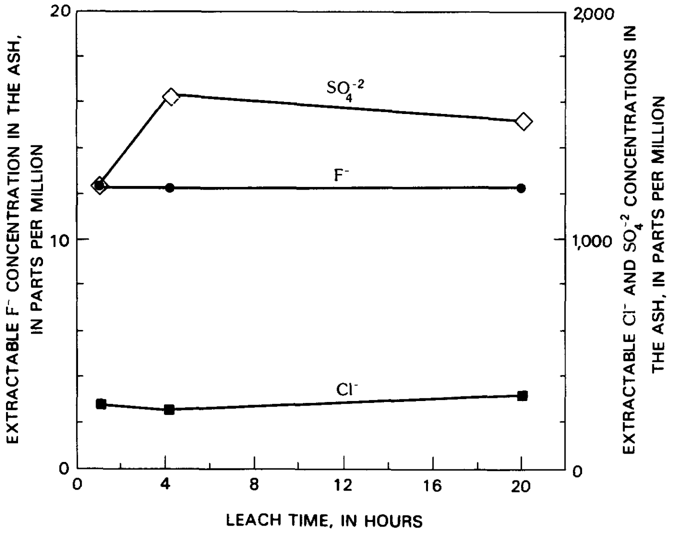

FIGURE 7.—Effect of leach time on the extraction of F^-, Cl^-, and SO_4^{-2} from the ash using deionized water. Sample collected at Spaulding, Idaho.

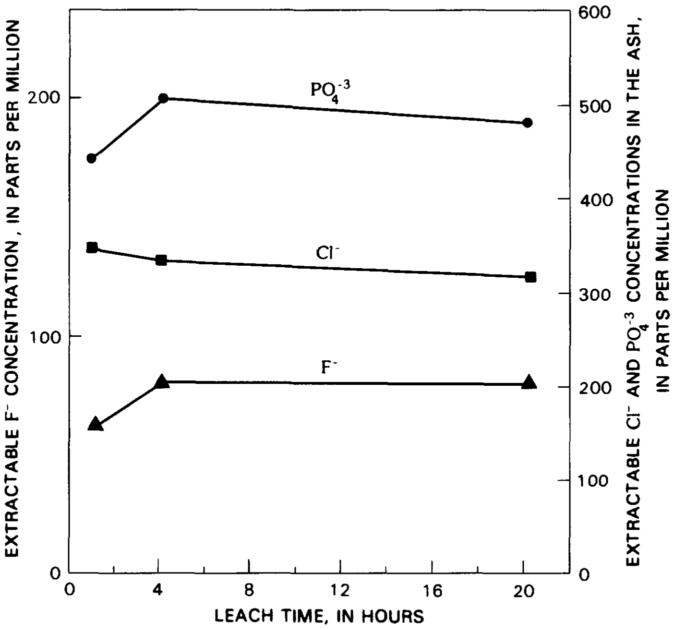

FIGURE 8.—Effect of leach time on the extraction of F^-, Cl^-, and PO_4^{-3} from the ash using 0.01 *M* H_2SO_4. Sample collected at Spaulding, Idaho.

Information on the extractability of sulfate in an acid leach was not possible using the standard sulfuric acid extraction procedure. As a result, a modification to the acid extraction procedure was devised for an Almira, Wash., sample, using a 0.02 *M* nitric acid solution. Results are presented in table 10.

TABLE 9.—*Concentration of anions extracted from the ash using deionized water and 0.01* M *H_2SO_4 leaching solutions and a 4-hour extraction time*

[Sample collected at Missoula, Mont. Leaders (--), data not available due to nature of leaching solution]

Anion	Concentration of extracted anions (in ppm)	
	Deionized water leach	0.01 M H_2SO_4 leach
F^-	19	100
Cl^-	830	910
PO_4^{-3}	50	600
SO_4^{-2}	4,000	--

TABLE 10.—*Concentration of anions extracted from the ash using deionized water, 0.01* M *H_2SO_4, and 0.02* M *HNO_3 leaching solutions and a 4-hour extraction time*

[Sample collected at Almira, Wash. Leaders (--), data not available due to nature of leaching solution]

Anion	Concentration of extracted anions (in ppm)		
	Deionized water leach	0.01 M H_2SO_4 leach	0.02 M HNO_3 leach
F^-	25	84	80
Cl^-	670	860	800
PO_4^{-3}	50	1,300	1,200
SO_4^{-2}	2,900	--	3,800

As seen in previously discussed studies comparing deionized water and acid leaches, the nitric acid leach extracted significantly more anions from the ash than did the deionized water leach. The nitric acid data mimic the sulfuric acid data and support the theory that anions are present in the ash material as adsorbed (water soluble) or chemically associated (ion exchange or precipitated) ions. This chemical association with the ash is apparently acid independent as the F^-, Cl^-, and PO_4^{-3} concentrations are similar in both the nitric acid and sulfuric acid leaches. Extrapolating the results of the acid extractions to a soil environment containing certain organic acids, one could anticipate similar extraction phenomena. This would result in the gradual mobilization of ions long after the water-soluble ions have been removed.

As indicated previously, investigators have found acidic gases in the volcanic plume during the eruption. These acidic gases could condense on the ash and undergo subsequent neutralization or dissolution reactions. If these reactions are only partially complete, then there should be residual acid present on the ash. This residual acid could participate in subsequent reactions, and be monitored by changes in pH.

To examine this possibility, pH data were accumulated during extraction time studies involving the deionized water leach of various ash samples. The results for selected samples are presented in table 11.

TABLE 11.—*Changes in pH observed during ash extraction using deionized water leaching solution and 1-, 4-, and 20-hour extraction times*

[Leaders (--), data not available due to nature of leaching solution]

Sampling sites	Observed pH changes		
	1-hour extraction	4-hour extraction	20-hour extraction
Sunnyside, Wash.-	3.83	4.87	7.13
Ahtanum, Wash.---	3.63	4.01	6.58
Kalispell,Mont.--	3.72	6.70	7.69
Spalding, Idaho--	4.17	4.87	7.06
Spokane, Wash.---	--	4.87	6.67

The recorded pH increased significantly as the extraction proceeded from 1 to 20 hours. This pH change can be attributed to an initial release of acidic material adsorbed onto the surface of the ash, lowering the solution pH. The subsequent increase in pH is the effect of a slow ion exchange or neutralization process that removes protons from solution. This removal of protons should be accompanied by increases in cation or anion concentrations in solution (2–3 ppm in solution). Although the neutralization or ion exchange affects may be slight, the variation in pH can have important implications for other solution reactions such as solubility or complexation.

The pH studies were later extended to sulfuric acid extraction studies to see if similar pH changes occurred. In these studies, samples were leached with 0.009 *M* sulfuric acid and the final pH values were compared to a blank run simultaneously. A pH change from 2.0 to 2.8 was observed for the Ritzville, Wash., sample, which is typical of the change seen for other samples tested. This change in pH indicates that even under acidic conditions, neutralization or ion exchange reactions are occurring, which contribute to the ability of the acid leach to extract greater amounts of ions than the water leach.

SUMMARY

Procedures developed for leaching studies involving Mount St. Helens ash were based on initial experiments using IC. Leaching experiments conducted with deionized water, sulfuric acid, and nitric acid monitored the extraction of F^-, Cl^-, PO_4^{-3}, and SO_4^{-2} using S-2 and S-3 anion separator columns. These initial studies were designed to establish optimum experimental conditions, such as extraction intervals and leach solution concentrations.

Information accumulated during these initial experiments demonstrated the greater extraction efficiency of the acid leaches compared to the deionized water leach. This is especially significant in the case of F^- and PO_4^{-3}. In addition to significant changes in anion extractions, important pH changes were also noted in both the acid and water extractions. These pH changes are useful in explaining some of the chemical processes observed during the experiments.

BACKGROUND AND LITERATURE DISCUSSION

Several researchers have recently documented the presence of water-soluble material on freshly erupted volcanic ash (Taylor and Stoiber, 1973; Rose and others, 1973, 1978, 1980; Rose, 1977; Smith, 1980; Smith and others, 1981; Smith, Zielinski, and Rose, 1982; Smith, Zielinski, and others, 1982). In these studies, fresh ash samples were subjected to a water wash and the resulting leachates were generally found to contain Ca, K, Mg, Na, Cl^-, F^-, and SO_4^{-2} with lesser amounts of Al, B, Ba, Br, Cu, Fe, Mn, Se, Si, and Zn. Models have been developed to explain the presence, distribution, and chemical makeup of these water-soluble materials.

Oskarsson (1978, 1980) proposed a model based on the existence of three distinct temperature-dependent reaction regimes within an eruption cloud. Each regime accounts for a specific type of reaction involving acid magmatic gases (such as SO_2, HCl, and HF). The characteristics and processes of the three regimes are as follows.

1. At the high temperatures that prevail during degassing of magma in the eruption vent or in the core of an eruption cloud, aerosol salt particles, primarily halides and sulfates, may form. The temperature limit for this salt formation process depends on the melting point of the particular salt being formed. These aerosol salt particles can be transported as suspended load. The presence of aerosol salt particles adhering to fresh ash from volcanoes in Central America has been confirmed by the use of scanning electron microscopy and energy dispersive X-ray analysis (Rose and others, 1973, 1980; Smith, Zielinski, and others, 1982). Naughton and others (1974) collected sublimates from directly above a lava fountain and found salt components consisting of chlorides, fluorides, and sulfates of the alkali metals and calcium.
2. In Oskarsson's intermediate temperature regime (below about 700 °C), surface adsorption of gaseous halogen acids (primarily HCl and HF) onto solidified silicate material may take place.
3. In the lowest temperature regime (below 338 °C), sulfuric acid is stable and may condense as an aerosol by the following reactions:

$$SO_{2(g)} + \tfrac{1}{2}\,O_{2(g)} = SO_{3(g)}$$

$$SO_{3(g)} + H_2O_{(g)} = H_2SO_{4(l)}.$$

Subsequently, at temperatures below 120 °C, halogen acids are stable and may condense. Upon further cooling, acid condensates absorb water vapor to form dilute acids. These acid condensates may coat ash particles.

Another model for the formation of soluble materials on ash particles, proposed by Rose (1977), involves the scavenging of acid aerosol droplets (primarily H_2SO_4 and some HCl) by ash particles. In this process, scavenged droplets of dilute acid may leach soluble elements from the glass and mineral grains of the ash, leaving coatings of water-soluble material on their surfaces. Acid aerosol scavenging should be most active at intermediate distances from the source, where the number of acid particles is at a maximum, and least active both in the immediate vicinity of the vent, where aerosol droplets have not yet condensed from gases, and at greater distances from the vent, where the aerosol is dispersed (Rose, 1977). The acid aerosol scavenging theory may provide a useful explanation for observations made in a study by Rose and others (1973), in which the amount of water-soluble material associated with the ash decreased with increasing distance from the source, despite the fact that ash collected far from the source was fine grained, and hence had a larger surface area. They also noted that ash particles from the final stages of a pyroclastic eruption were coated by the largest amount of water-soluble material. Rose and others (1980) and Smith, Zielinski, and others (1982) have confirmed the presence of acid coatings on ash particles using scanning electron microscopy on small particles (<25 μm in diameter) directly sampled by aircraft in volcanic eruption clouds.

In another prevalent model, Taylor and Stoiber (1973) suggested that, upon decrease of pressure and temperature after an eruption, volatile compounds, such as the halides of Cu, K, Na, and Zn, condense as water-soluble coatings on ash particles. A combination of this condensation process and acid aerosol scavenging by ash particles may be analogous to fumarolic incrustation formation processes described by Stoiber and Rose (1974).

The relative contributions of the aforementioned models and processes to resolving the formation mechanisms for soluble components associated with volcanic ash is, as yet, unclear. This may be attributed to the complexity and range of conditions possible in an eruption cloud.

Enrichment of certain elements in the water-soluble components associated with volcanic ash has been reported in the literature. Smith (1980) performed aqueous extractions of filters used to collect aerosols from volcanic eruption clouds. He calculated the enrichment factors for these water-soluble elements and found that Cd, Cu, Pb, V, Zn, Cl^-, F^-, and probably S (as sulfate) were enriched in the water-soluble component relative to the composition of bulk ash.

Several elements reported to be associated with volcanic ash are the same as those reported to be enriched in studies of atmospheric particulates not directly associated with volcanic activity. Zoller and others (1974), Duce and others (1975), and Maenhaut and others (1979) sampled aerosols in remote areas far from cities, whereas Miklishanskiy and others (1977, 1978) sampled city air. These studies all produced comparable results: enrichment of the aerosols with respect to a similar suite of elements (Ag, As, Au, Br, Cd, Cu, Hg, In, Pb, Sb, Se, V, W, and Zn) in comparison to baseline crustal rock and seawater abundances. Several researchers have found this similar suite of elements to be abundant in atmospheric particles from active volcanic regions (Cadle and others, 1979; Mroz and Zoller, 1975; Lepel and others, 1978). There is a general similarity between the results of these studies, and some authors proposed that volcanism may be an important source of the reported enrichment of several elements in atmospheric particulates not directly associated with volcanic activity (Duce and others, 1975).

RESULTS AND DISCUSSION

In the following sections we discuss the amounts of material removed from different types of ash samples (1) by the two artificial leach treatments used in this study, (2) by other commonly used leaching techniques, and (3) by rain. Then we attempt to evaluate the nature and sources of the material removed from the ash samples by the leaching solutions, paying detailed attention to the implications of the electrochemical relationships in the leachates.

AMOUNTS OF MATERIAL REMOVED BY WATER AND ACID LEACHING TREATMENTS

Table 12 presents data on the amounts of chemical species removed by the deionized water and acid leach treatments for ash samples from Washington, Idaho, and Montana, and for time-sequence samples from Almira, Wash., none of which had been rained on at the time of collection. All leachate amounts presented in the tables and text of this report are as micrograms of element (or species) per gram of ash (ppm ash). The most abundant species in the deionized water leachate were: SO_4^{-2} (represents 800–2,900 ppm ash), Ca (550–1,000 ppm ash), Cl^- (480–670 ppm ash), Na (320–440 ppm ash), Mg (60–100 ppm ash), K (60–100 ppm ash), NO_3^- (80–100 ppm ash), Si (20–30 ppm ash), Mn (9–17 ppm ash), and F^- (13 ppm ash). This ranking of species in order of abundance corresponds with that found by Smith, Zielinski, and Taylor (1982) for fresh Mount St. Helens ash.

Those species present in the greatest amounts in the acid leachate were: SO_4^{-2} (1,200–3,900 ppm ash), Ca (1,700–2,700 ppm ash), PO_4^{-3} (900–1,300 ppm ash), Fe (470–760 ppm ash), Cl^- (530–820 ppm ash), Al (450–570 ppm ash), Na (440–530 ppm ash), P (360–470 ppm ash), K (340–510 ppm ash), Mg (320–490 ppm ash), and Si (220–290 ppm ash). Fe and Al concentrations were below the analytical limit of detection in solutes of the deionized water leach treatment, yet were among the most abundant elements in the acid leachate. All removed in greater amounts by the acid leach treatment than by the deionized water treatment.

The two leach treatments removed chemical species in different percentages of their whole-ash contents (table 12). A large percentage of the leachable amounts of the anions Cl^- and SO_4^{-2} was dissolved by the water leach; that is, the harsher acid leach removed only slightly more of these species than did the water leach. However, in the case of the minor anion F^-, the acid solution removed several times more than the deionized water leach. As for PO_4^{-3}, the deionized water leach removed no detectable amount, whereas it was removed by the acid leach in amounts equal to about 50 percent of its whole-ash content.

The rankings of chemical species (orders of abundance) in the leachates were different between the two leach treatments. Table 13 is a ranking of the abundances of chemical species removed by deionized water and acid leaches as a percentage of the total amount present in the ash. The equivalent information is presented graphically in figure 9. Ni, Co, Mn, and Ca lead the ranking for elemental species in the deionized water leach, having been removed in amounts representing about 2–6 percent of their totals. The alkali and alkaline earth metals Li, Na, and K, and Mg, Sr, and Ba, respectively, were all removed in lesser fractions, but in amounts greater than 0.4 percent of their totals. V, La, Y, Cu, Zn, Fe, Al, and Si were removed by deionized water leach in fractions of their whole-ash totals smaller than 0.6 percent. This information is consistent with that presented by Dethier and others (1981) for Mount St. Helens ash.

For the most part, whole-ash fractions of elements released by the acid leach treatment are larger than those released by the deionized water leach treatment, but the range in magnitude of acid leach values is great (table 13). There is a group of elements that is removed from the ash much better by acid than by water, and another suite removed more nearly equally by the two leach treatments. Cu, Fe, Zn, Al, La, Y, and PO_4^{-3} are removed by acid leach in amounts more than a factor of 24 times greater than amounts removed by deionized water leach. For Si, V, Mn, K, Ca, Mg, Sr, Li, Ni, Co, and Na, the factor is smaller, ranging from about 10 times more for Si to about unity for Ni, Co, and Na. Barium concentrations are generally less in the acid leach solution, probably because its solubility is controlled by the presence of sulfate. This separation of elements into two groups is clear from figure 9.

We expect that, in a natural setting, amounts of elements leached by our deionized water treatment would be removed in the surface environment before the ash was exposed to harsher leaching solutions, such as

TABLE 12.—*Average amounts of components removed from the ash by water and acid leaching solutions*

[Values for Washington, Idaho, and Montana are an average of analyses of 19 samples taken at varying distances from volcano (Randle, Ritzville, and Spokane, Wash.; Coeur d'Alene, Emida, and St. Maries, Idaho; Missoula, Mont.); except that only nine samples were used for Cl^-, F^-, NO_3^-, PO_4^{-3}, and SO_4^{-2}. Of these samples, some are members of closely spaced pairs, considered to be "sampling replicates." Values for Almira, Wash., are an average of five time-sequence samples, plus one sample analyzed in duplicate, for a total of six samples; each was collected and sealed immediately after fall. Averages include some analyses of both splits of single samples. Values determined by inductively coupled plasma spectroscopy unless otherwise noted: star (*), determined by X-ray fluorescence. Specific conductance of water leach solution equals 0.39 micromhos/cm for the Washington, Idaho, and Montana samples[1], and equals 0.65 micromhos/cm for the Almira, Wash. samples. Leaders (--), value not determined; n, number of samples analyzed]

Components	Washington, Idaho, and Montana pre-rain ash samples					Almira, Wash., pre-rain ash samples				
	Whole-ash content	Amount removed as ppm of whole ash		Amount removed as a percentage of amount of element in whole ash		Whole-ash content	Amount removed as ppm of whole ash		Amount removed as a percentage of amount of element in whole ash	
		Water leach	Acid leach	Water leach	Acid leach		Water leach	Acid leach	Water leach	Acid leach
			n=19					n=6		
Al	*8.7 pct	<10	450	<0.01	0.51	*9.0 pct	<10	570	<0.01	0.6
Ba	390 ppm	4.3	2.0	1.1	.51	340 ppm	4.8	2.2	1.4	.7
Ca	*3.2 pct	550	1,720	1.7	5.4	*3.8 pct	1,030	2,700	2.7	7.0
Co	10.8 ppm	.28	.35	2.6	3.2	13.7 ppm	.33	.58	2.4	4.2
Cu	47 ppm	<.1	7.2	<.2	15	49 ppm	<.1	5.6	<.2	11
Fe	*3.0 pct	<10	470	<.03	1.6	*3.5 pct	<10	760	<.03	2.2
K	*1.3 pct	57	340	.4	2.6	*1.1 pct	100	510	.9	4.6
La	18 ppm	<.1	2.4	<.6	13	18 ppm	<.1	3.7	<.5	21
Li	27 ppm	[1].26	[1].50	1.0	1.9	24 ppm	.52	.97	2.2	4.0
Mg	*1.0 pct	58	320	.6	3.2	*1.29 pct	103	490	.80	3.8
Mn	*.045 pct	8.7	42	1.9	9.3	*.054 pct	16.5	74	3.1	14
Na	*3.3 pct	320	440	1.0	1.3	*3.2 pct	440	530	1.4	1.7
Ni	12 ppm	.7	[1].5	5.8	4.2	19 ppm	.75	1	3.9	5.3
P	*.078 pct	<10	360	<1.3	47	*.095 pct	<10	470	<1.1	49
Si	*30. pct	[1]20	220	.007	.07	*29. pct	30	290	.01	.10
Sr	430 ppm	2.1	5.3	.5	1.2	500 ppm	3.7	7.8	.74	1.6
V	69 ppm	[1].17	1.2	.25	1.7	85 ppm	.18	1.6	.2	1.9
Y	18 ppm	<.1	2.4	<.6	13	19 ppm	<.1	3.5	<.5	18
Zn	71 ppm	<.1	4.2	<.1	5.9	75 ppm	<.1	4.9	<.1	6.5
			n=9					n=6		
Cl^-	[2]1,130 ppm	480	530	43	47	1,490 ppm	670	820	45	55
F^-	270 ppm	13	48	5.0	18	310 ppm	13	77	4.2	25
NO_3^-	<500 ppm	[1]77	[1]54	--	--	<500 ppm	[1]97	[1]87	--	--
PO_4^{-3}	2,100 ppm	<150	900	<7.1	43	2,420 ppm	<150	1,290	<6.2	53
SO_4^{-2}	1,540 ppm	800	[4]1,200	52	[4]75	8,650 ppm	2,870	[3]3,850	33	[3]38

[1] When appropriate, individual samples registering below instrumental detection limit were assigned values 0.7 times the detection limit and then used with other values to obtain average.

[2] Average of eight samples.

[3] Average of one sample and its analytical duplicate for HNO_3 leach.

[4] Sample from Ritzville, Wash., for HNO_3 leach.

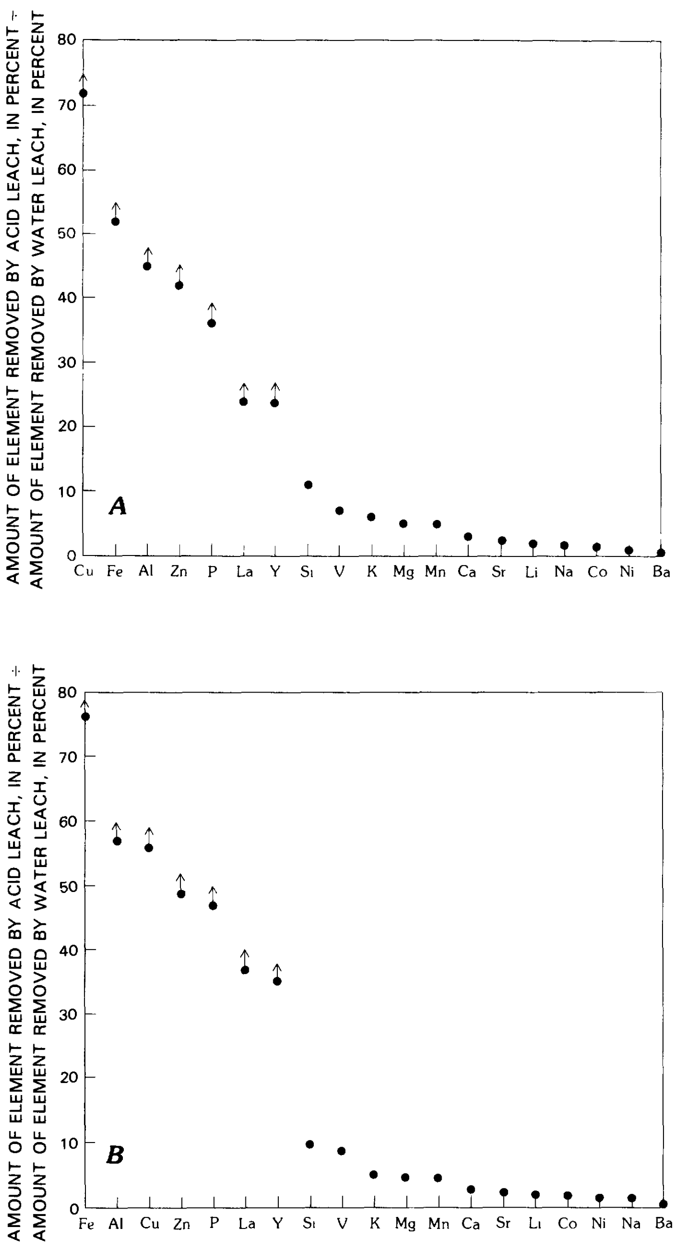

FIGURE 9.—Ordered plots of ratios (amount of element removed by acid leach ÷ amount of element removed by water leach) for two suites of ash samples not affected by rain on the ground. Plotted points represent average values for *A*, 19 samples from Washington, Idaho, and Montana, and *B*, six samples from Almira, Wash. Order of elements is slightly different for the suites. Arrows pointing upward indicate that water leach values are lower limits.

TABLE 13.—*Ranking of abundance of chemical species removed from the ash by water and acid leaches, as percent of total whole-ash content*

[Data in percent. Sample descriptions and original data presented in table 12. n, number of samples averaged. Starred (*) values represent an average of nine samples]

Water leach				Acid leach			
Wash., Idaho, and Mont. (n=19)		Almira, Wash. (n=6)		Wash., Idaho, and Mont. (n=19)		Almira, Wash. (n=6)	
Ni	5.8	Ni	3.9	Cu	15	La	21
Co	2.6	Mn	3.1	La	13	Y	18
Mn	1.9	Ca	2.7	Y	13	Mn	14
Ca	1.7	Co	2.4	Mn	9.3	Cu	11
Ba	1.1	Li	2.2	Zn	5.9	Ca	7.0
Li	1.0	Ba	1.4	Ca	5.4	Zn	6.5
Na	1.0	Na	1.4	Ni	4.2	Ni	5.3
Mg	.6	K	.9	Co	3.2	K	4.6
Sr	.5	Mg	.8	Mg	3.2	Co	4.2
K	.4	Sr	.74	K	2.6	Li	4.0
V	.25	V	.2	Li	1.9	Mg	3.8
La	<.6	La	<.5	Fe	1.6	V	1.9
Y	<.6	Y	<.5	Na	1.3	Na	1.7
Cu	<.2	Cu	<.2	Sr	1.2	Sr	1.6
Zn	<.1	Zn	<.1	Al	.51	Ba	.7
Fe	<.03	Fe	<.03	Ba	.51	Al	.6
Al	<.01	Al	<.01	Si	.07	Si	.1
Si	.007	Si	.01	V	1.7	Fe	2.2
SO_4^{-2}	*52	Cl^-	45	Cl^-	*47	Cl^-	55
Cl^-	*43	SO_4^{-2}	33	PO_4^{-3}	*43	PO_4^{-3}	53
F^-	*5.0	F^-	4.2	F^-	*18	F^-	25
PO_4^{-3}	*<7.1	PO_4^{-3}	<6.2				

acid leach treatment of this study). Thus, in some cases, our deionized water leach concentrations should be subtracted from our acid leach concentrations before the data are applied to projected natural situations. However, the overall contribution of chemical species to the soil-plant system by the ash may commonly be equal to the maximum removable amounts presented in this study (amount removed by acid leach treatment). If the deionized water leach solute concentrations for each element are subtracted from acid leach solute concentrations, the ranked order of element concentrations is nearly the same as for acid leach.

POSSIBLE SOURCES, NATURE, AND SOLUBILITY OF MATERIAL REMOVED BY LEACHING TREATMENTS

The possible sources of material removed by leach solutions are the following: (1) various amorphous or soluble coatings present on igneous surfaces; (2) particles of igneous minerals and volcanic glass; (3) older mineral and lithic material from the volcanic cone; or (4) combinations of these. Readily soluble surficial deposits on ash particles may have formed from fluid or gaseous phases during suspension of the particles in air, or may have resulted from the in-situ leaching of the particles by adsorbed acids (as was described in the "Background and literature discussion" section of this report). Smith and others (1981) reported that water-soluble surface deposits of freshly erupted volcanic ash from several different eruptions were important in the initial release of B, Ba, Cd, Cu, F^-, Pb, and Zn from ash to aqueous solution, but that Li, Si, U, and V were released to solution less rapidly, primarily through the dissolution of glass. Smith, Zielinski, and Taylor (1982) found similar results for fresh Mount St. Helens ash. Soluble anions in ash from both before and after the May 18, 1980 eruption of Mount St. Helens have been discussed in the literature (Stoiber and others, 1980, 1981). A 2-year weathering study of the Mount St. Helens volcanic ash has been conducted by White and others (1986).

Defining the relative contributions of the possible sources of solute to different leaching solutions is of interest because soluble salts are likely to be removed from the ash and released to soil and hydrologic environments by a single rainfall event at the beginning of the weathering history of the deposited ash. The mineral grains would be broken down and their constituents released more slowly in the plant-root environment.

The following kinds of information may help distinguish whether single species, or groups of species, in the solutes from the two leach treatments have soluble surficial materials or igneous mineral phases as their primary sources.

1. Whether a species is readily removed by mild leach solution.
2. Whether there are great differences between amounts of species removed by treatments with widely varying solution:ash ratios.
3. Whether the cations removed from the ash are electrically balanced by anions associated with common salts; alternatively, whether it appears that hydronium ions from the leaching solution have replaced cations from mineral grain surfaces such that, in the solute, these cations are in excess of salt-associated anions removed from the ash.
4. Whether there are significant correlations between certain cations and anions in the leachate solutions such that cation-anion associations might be inferred.
5. Whether there is wide variation in leach solute composition from sample to sample for such key ratios as Ca/Sr. This ratio would be expected to be fairly consistent for solute derived from a homogeneous assemblage of igneous phases.
6. Whether there is a great difference between amounts of species removed from ash by deionized water and acid leach treatments.

These points will be discussed in order in the following sections.

SPECIES READILY REMOVED BY DEIONIZED WATER LEACHING TREATMENTS AND BY RAIN

The rapid release of a species to a mild leaching solution such as deionized water, or the ready removal of an element from the ash by rain, would indicate that the major source of the element was water-soluble surficial material. The alkali and alkaline earth metals Li, Na, and K, and Mg, Ca, Sr, and Ba, respectively, (and possibly also Mn, Co, and Ni), all removed by water leach in amounts greater than 1/2 percent of their whole-ash totals (tables 12 and 13), may be important constituents of the readily soluble surficial coatings on volcanic ash particles. The anions SO_4^{-2} and Cl^- (and possibly NO_3^-), removed in amounts of as much as about 50 percent of their whole-ash totals, are major constituents of the water-soluble surficial material.

Daily rainfall records for the Ellensburg, Moses Lake, and Ritzville, Wash., sites are summarized in table 14, where the data are presented in inches, as published (National Oceanic and Atmospheric Administration, 1980a, b). About 0.8 inches (2 cm) of rain fell at Ellensburg, about 2 inches (5 cm) at Ritzville, and about 4 inches (10 cm) at Moses Lake during the month-long interval between deposition and collection of those samples of ash affected by rainfall on the ground. On May 30, 1980, 2.25 inches (6 cm) fell at Moses Lake, the greatest one-day precipitation at any site in the State during that month.

TABLE 14.—*Daily rainfall at ash collection sites in Washington State during the time interval between deposition and collection of some ash samples*

[Data in inches; 1 in.=2.54 cm. Leaders (--), no rainfall. No rain fell on omitted dates. From National Oceanic and Atmospheric Administration (1980a, b)]

	Ellensburg	Moses Lake	Ritzville
May 21	0.01	--	--
May 22	--	--	0.22
May 23	.04	--	--
May 25	--	0.05	--
May 26	.07	.40	.69
May 27	.10	.52	.44
May 28	.01	.09	--
May 30	--	2.25	--
June 9	.04	--	--
June 12	.01	--	--
June 13	.18	.42	.30
June 14	.12	.05	.04
June 15	--	--	.02
June 16	--	.19	--
June 17	.20	--	.05
Total-	0.78	3.97	1.76

Ash that lay on the ground in the field for several weeks before collection contributed smaller amounts of certain chemical species to the water and acid leaches than did ash collected immediately after deposition. We believe that washing by rainfall removed appreciable amounts of these chemical species from the ash that was collected several weeks after deposition. The amounts of elements removed by rain were evaluated by observing the differences in amounts extracted from suites of pre-rain and post-rain samples from approximately the same locations. Within broad limits, rainfall apparently removed most species in about the amounts suggested by deionized water leaching experiments. Table 15 presents data for anions removed by both water and acid leach treatments from pre-rain and post-rain ash samples from Idaho and from Ritzville, Wash. Table 16 presents similar data for cations.

Judging from the data of the water leach, rain apparently removed large amounts of Cl^- and SO_4^{-2} (table 15); Cl^- was removed to the greatest extent. Estimates could not be made for NO_3 due to imprecise data. The cation data for the water leach treatment (table 16) show that appreciable percentages of water-leachable Li, Na, K, Mg, Ca, Sr, and Mn were removed by rain. Mn and K were removed to the greatest extent. The amount of rainfall that came into contact with the ash between times of deposition and collection was clearly less than the 14:1 deionized water-to-ash ratio (by weight) used in the laboratory treatment. Also, the contact time of the rain water with the ash particle surfaces was probably quite short due to the permeable nature of the ash blanket. And, the 4-hour agitation time used in the laboratory was most likely a more rigorous treatment than the ash was subjected to in the field. Therefore, the similarity in amounts of material removed from pre-rain samples by the water leach treatment and from post-rain samples by rain suggests that there was a discrete and limited amount of soluble material on the ash that was susceptible to removal by even a slight exposure to water.

Judging from the data of the acid leach, a harsher treatment that removes larger quantities of material

TABLE 15.—*Effect of rain on amounts of anions removed from the ash by water and acid leaches*

[Values in ppm removed from whole rock unless otherwise noted. All determinations by ion chromatography. Leaders (--), estimates were not made because of imprecise data. Values in parentheses are results of duplicate analyses, performed on split of original sample. When appropriate, individual samples (starred (*)) registering below instrumental detection limit were assigned values 0.7 times the detection limit and then used with other values to obtain average]

	Water leach species				Acid leach species			
	F^-	Cl^-	NO_3^-	SO_4^{-2}	F^-	Cl^-	NO_3^-	PO_4^{-3}
Ritzville, Washington								
Pre-rain samples:								
ODWRZY10 (ODWRZY1X)----	20 (10)	580 (560)	180 (<50)	870 (820)	48 (48)	750 (680)	65 (<50)	900 (830)
ODWRZW10---------------	14	480	<50	1,000	52	290	78	900
Average--------------	15	525	--	925	50	505	--	885
Post-rain samples:								
LRWRZZ10---------------	10	15	160	380	46	41	<50	850
LRWRZZ20--(LRWRZZ2X)---	7 (6)	16 (18)	<50 (56)	87 (110)	41 (42)	42 (46)	53 (<50)	830 (880)
Average--------------	8	16	--	240	45	45	--	855
Summary:								
Approximate difference between pre- and post-rain averages---	7	510	--	685	5	460	--	30
Approximate percent of available amount removed by rain------	50	95	--	75	10	90	--	<5
Idaho								
Average, pre-rain samples (four original samples; two analyzed in duplicate)--------	13	440	*87	700	48	500	*55	910
Post-rain sample (one sample)---------	3	17	<50	32	36	6	<50	750

TABLE 16.—*Effect of rain on amounts of cations removed from the ash by water and acid leaches*

[Values in ppm removed from whole rock unless otherwise noted. All determinations by inductively coupled plasma spectroscopy. NA, estimates not available because cations were present in concentrations below the analytical detection limit. Leaders (--), estimates were not made because of imprecise data. Values in parentheses are results of duplicate analyses, performed on split of original sample. When appropriate, individual samples (starred (*)) registering below instrumental detection limit were assigned values 0.7 times the detection limit and then used with other values to obtain average]

	Ca	Mg	Na	K	B	Co	Ni	Mn	Li	Sr	Cu	Zn	P
Water leach													
Ritzville, Washington													
Pre-rain samples:													
ODWRZY10(ODWRZY1X)-----	380 (360)	60 (50)	350 (340)	54 (51)	8.0 (12.9)	0.2 (0.3)	0.7 (0.5)	7.1 (5.8)	0.2 (0.1)	1.6 (1.5)	NA	NA	NA
ODWRZW10---------------	410	40	280	40	9.7	.2	.9	6.1	.2	1.7	NA	NA	NA
Average--------------	390	48	313	46	10	.2	.8	6.3	.2	1.6	NA	NA	NA
Post-rain samples:													
LRWRZZ10---------------	100	<10	80	<10	8.4	.2	.6	.5	<.1	.4	NA	NA	NA
LRWRZZ20(LRWRZZ2X)-----	35 (70)	<10 (10)	80 (80)	<10 (10)	11.9 (10.0)	.3 (.2)	.8 (.6)	.3 (.7)	<.1 (<.1)	.2 (.3)	NA	NA	NA
Average--------------	76	--	80	--	10	.2	.7	.5	--	.3	NA	NA	NA
Summary:													
Approximate difference between pre- and post-rain averages---	300	>40	230	>40	0	0	.1	6	>.1	1.3			
Approximate percent of available amount removed by rain------	75	80	75	90	0	0	15	95	50	80			
Idaho													
Average, pre-rain samples (four original samples; two analyzed in duplicate)--------	340	40	263	38	8.9	0.3	0.7	5.5	*0.2	1.5	NA	NA	NA
Post-rain sample (one sample)---------	120	30	90	30	11.7	.3	.7	3.6	<.1	.8	0.5	NA	NA
Acid leach													
Ritzville, Washington													
Pre-rain samples:													
ODWRZY10(ODWRZ1X)------	1,300 (1,300)	270 (280)	480 (500)	280 (290)	7.7 (7.6)	0.3 (0.4)	0.3 (0.4)	32 (33)	0.7 (0.6)	4.5 (4.3)	6.7 (6.6)	2.7 (2.5)	310 (320)
ODWRZW10----------------	1,400	220	410	220	6.2	.2	.3	28	<.1	4.2	7.2	2.4	340
Average--------------	1,350	248	450	253	6.9	.3	.3	30	*.4	4.3	6.9	2.5	328
Post-rain samples:													
LRWRZZ10---------------	1,100	240	220	245	5.4	.2	<.1	21	.3	3.3	6.7	1.9	310
LRWRZZ20(LRWRZZ2X)-----	1,000 (1,000)	240 (230)	210 (200)	245 (230)	9.1 (6.6)	<.1 (.2)	.2 (.6)	21 (22)	.1 (.3)	3.0 (3.0)	7.0 (6.4)	2.2 (2.3)	310 (320)
Average--------------	1,050	238	213	241	6.6	--	--	21	.25	3.2	6.7	2.1	313
Summary:													
Approximate difference between pre-and post-rain averages---	300	10	240	10	.3	>0	>0	10	.15	1.1	.2	.4	15
Approximate percent of available amount removed by rain-----	20	5	55	5	5	>0	>0	35	40	30	5	15	5
Idaho													
Average, pre-rain samples (four original samples; two analyzed in duplicate)--------	1,350	213	391	220	7.1	0.2	*0.24	28	0.2	4.4	8.2	4.7	340
Post-rain sample (one sample)---------	910	200	160	207	7.9	.4	<.1	17	.2	3.0	5.3	2.6	220

from the ash than the water leach, rain was potent enough to have leached about half of the Na, a third of the Li, Mn, and Sr, a quarter of the Ca, and a measureable amount of the Zn, Mg, B, K, Cu, and P available to the acid leach treatment (table 16). The anion data for the acid leach treatment (table 15) suggest that a large amount of Cl^- and a measureable amount of F^- were removed by rain. It is unclear whether appreciable amounts of NO_3^- and PO_4^{-3} were removed by rain because of imprecision in the data. SO_4^{-2} values were not available for these samples due to the use of H_2SO_4 as the leaching acid.

Of the four metals that yielded the greatest percentages of their total whole-ash concentrations to the deionized water leach (Ni, Co, Mn, and Ca) and of the six species that yielded the greatest percentages to the acid leach (La, Y, Mn, Cu, Ca, and Zn), as was shown in table 13, only Mn and Ca appear to have been removed in appreciable amounts during exposure in the field.

AMOUNT OF MATERIAL REMOVED USING DIFFERING AMOUNTS OF LEACHING SOLUTION RELATIVE TO THE AMOUNT OF ASH

Table 17 presents data on amounts of selected elements removed from fresh ash by the following three treatments: (1) the 4-hour 14:1 deionized water-to-ash ratio (by weight) leach extraction of the present study; (2) a 4-hour single-pore-volume deionized water column leach done by Taylor and Lichte (1980); and (3) a 24-hour 4:1 deionized water-to-ash ratio (by weight) leach extraction done by Smith, Zielinski, and Taylor (1982). Also presented for later discussion are data by Bradford and others (1971) for amounts of these same selected elements removed from common soils by the saturated paste method. Analytical methods differ in these studies and, for that reason, comparisons of analytical data must be made only broadly, with proper allowances for relative error.

Table 17 shows that amounts removed from ash of the four major alkali and alkaline earth elements of interest (Na, K, Mg, and Ca) are similar in both the "large-solution-volume" (14:1 deionized water-to-ash ratio, by weight) leach extraction and the "small-solution-volume" (single-pore-volume and 4:1 deionized water-to-ash ratio, by weight) experiments. The amounts removed in the "large-solution-volume" study are consistently slightly larger for the four metals, but the differences between the amounts removed in the "large-solution-volume" study versus the "small-solution-volume" studies are much smaller than the differences between the volumes of water relative to ash. This similar removal between the three studies suggests that a reservoir of water-soluble material is present as surficial coatings on the grains. Subsequent successive single-pore-volume leaches performed by Taylor and Lichte (1980) did not yield much more material to solution; only Ca, Si, and SO_4^{-2} were removed in significant amounts upon further leaching. The soluble surficial material seems to be rapidly and almost completely dissolved by both the "large-solution-volume" and the "small-solution-volume" leaches in a 4-hour period.

The trace alkali metal Li and the minor alkaline earth metal Sr adhered to the same pattern as the major metals previously discussed. Barium concentrations are dissimilar in the leach studies of ash, suggesting that Ba, the least soluble of the alkali and alkaline earth metals determined, may be reaching its saturation, as controlled by SO_4^{-2}, in the "small-solution-volume" leaches. If so, much more Ba should be removed in the "large-solution-volume" leach experiment, in which there is about 13–14 times more water to hold the Ba, than in the "small-solution-volume" leach experiment and, in fact, the data indicate that about 50 times more Ba was removed. The numerical magnitude of the factor may be a result of analytical error, due to low concentrations or different analytical techniques, or a result of complications in the amounts and identities of the anions present. Observed solubility products for $BaSO_4$ are about 1.5×10^{-8} and 2.5×10^{-9} for the "small-solution-volume" and "large-solution-volume" leach studies, respectively (using raw concentrations). Both products are larger than published saturation values for these ions. Amounts of Cu, Mn, and Si removed from the ash are also similar in the different studies. Boron values from the studies do not agree and may be a reflection of the determination difficulties for this element.

The evidence from comparing the results of the studies by Taylor and Lichte (1980) and Smith, Zielinski, and Taylor (1982) with those of the present study suggest that readily soluble surficial deposits on grains, rather than igneous mineral phases, are the primary sources of material in the deionized water leach solutes.

ELECTRICAL ION BALANCE IN THE LEACHATE SOLUTIONS

The electrical ion balance between cations and anions given up to solution by the ash may give information about the sources of material soluble to leach treatments of varying stringency. Table 18 presents electrical ion balance values for groups of samples in which material was removed by deionized water treatment or by rain. In deionized water leachates from samples collected immediately after deposition,

TABLE 17.—*Comparison of amounts of elements removed from the ash by large and small volumes of water, and from common soils by the saturated paste method*

[All values in ppm of whole rock removed by the leach treatment. Values for leach method of this study were determined by inductively coupled plasma spectroscopy; values for column leach method of Taylor and Lichte (1980) were determined by spark source mass spectrometry; values for study of soils by Bradford and others (1971) were determined by conventional emission spectrometry. Samples of the present study were collected at varying distances from Mount St. Helens (Randle, Ritzville, and Spokane, Wash.; Coeur d'Alene, Emida, and St. Maries, Idaho; Missoula, Mont.). Samples of study by Taylor and Lichte (1982) were collected in Spokane, Wash., and Helena and Kalispell, Mont. Samples of study by Smith, Zielinski, and Taylor (1982) were collected at varying distances from volcano. All samples were collected before being wetted by rain. Soil samples of study by Bradford and others represent 30 California soils of varying type. Original values for materials reported by Taylor and Lichte, Smith and others, and Bradford and others were in form of leach solution concentrations; soil values were converted to units of this table after consultation with G. R. Bradford. When appropriate, individual samples (starred (*)) registering below instrumental detection limit were assigned values 0.7 times the detection limit and then used with other values to obtain mean. n, number of samples analyzed. Leaders (--), not available because of qualified data. Data in parentheses are semiquantitative. ND, not determined]

Element	14:1 water:ash leach of present study (n=19)		Single-pore-volume column leach of Taylor and Lichte (1980) (n=3)		4:1 water:ash leach of Smith, Zielinski, and Taylor (1982) (n=19)		Common soils reported by Bradford and others (1971) (n=30)		
	Mean	Range	Mean	Range	Mean	Range	Mean	Median	Range
Al	--	all <10	(0.38)	(0.17-(0.58)	ND	ND	0.16	<0.04	<0.04-0.24
B	9.4	3.3-15.4	.79	.44-1.08	ND	ND	1.2	<.04	<.04-10.4
Ba	4.3	2.2-6.7	.08	.07-.11	.15	.01-.24	.1	.04	<.02-.48
Ca	551	280-1,100	266	263-267	440	108-800	51	24	.4-372
Co	.28	.2-.4	.04	.03-.06	.02	0-.07	.02	.004	<.004-.06
Cu	*.09	<.1-.3	.15	.09-.2	.16	0-.48	.02	.01	<.004-.08
Fe	--	all <10	.09	.06-.11	.38	0-.48	.02	.01	<.004-.32
K	57	35-98	(47)	(41)-(58)	ND	ND	8.0	4.0	.28-51.2
La	*.07	<.1-.1	(.01)	(.002)-(.02)	ND	ND	ND	ND	ND
Li	*.26	<.1-.6	.3	.26-.33	.21	.01-.52	.04	.02	<.01-.43
Mg	58	30-100	56	52-63	48	13.6-84	15	5.0	.16-160
Mn	8.7	2.9-18	9.5	7-12.8	7.6	.8-13.2	.07	<.004	<.004-.38
Mo	--	all <.05	.01	.004-.02	.01	0-.06	.3	<.004	<.004-8.8
Na	322	140-520	275	235-325	264	84-440	210	18	.36-7,680
Ni	.7	.2-1.0	(.24)	(.03)-(.58)	ND	ND	.01	<.004	<.004-.04
P	--	all <10	.05	.01-.11	ND	ND	ND	ND	ND
Si	*20	<10-30	20	17-22	19	15-26	2.0	1.4	.08-9.6
Sr	2.1	1.0-3.8	1.5	1.2-1.7	1.8	.4-2.9	.37	.07	<.04-4.16
V	*.17	<.1-.3	*.0007	<.0006-.0012	.0012	0-.03	.03	.004	<.004-.48
Y	--	all <.1	.002	.0012-.0029	ND	ND	ND	ND	ND
Zn	--	all <.1	.28	.09-.42	2.0	.07-27	.03	.02	.004-.16

summed electrical equivalents of major cations measured (Na^+, K^+, Mg^{++}, Ca^{++}, and Mn^{++}) are nearly identical to those of anions measured (F^-, Cl^-, NO_3^-, PO_4^{-3}, and SO_4^{-2}), indicating dissolution of ionic salts. The data indicate slight excess of cation equivalents in water leach treatment solutes, about 1 percent in one group (19 samples from Washington, Idaho, and Montana) and about 7 percent in the other (6 samples from Almira, Wash.). The values in table 18 are averages for groups of samples rather than for a leach treatment of a single sample. Details of cation-anion electrical balances for water leach solutes from five selected single samples are presented in table 19. Values for cation-anion balance were calculated from data yielded by two independent analytical procedures (IC for anions and ICP for cations). The slight electrical deficiency of anions relative to cations may be a result of analytical or other error, presence of anions that we did not consider, ion-exchange reactions between hydronium ions in the leaching solution and surface cations on mineral grains (Petrovic and others, 1976), slight dissolution of mineral phases, or a combination of these. Anions such as OH^-, negatively charged silicon species, HCO_3^-, and CO_3^{-2} can be associated with the dissolution of minerals or glass but, because of the proton condition (near-neutral pH), it is not possible that any of those species are abundant in the water leach solutes. Replacement of cations from surfaces of grains of minerals or glass by hydronium ions of the deionized water leach solution of near-neutral pH could have had only a small effect; however, if a solution were CO_2 buffered, more hydronium ions could be available. The cation NH_4^+ was not measured. Taylor and Lichte (1980) reported NH_4^+ concentrations to be low in their water leach solute. Organic acids and ligands may have some importance in influencing the cation-anion balance, depending on the degree of exposure of the ash to burned organic materials. Organic species in ash leachates are discussed by McKnight and others (1981).

TABLE 18.—*Electrical balances of cation and anion equivalents in deionized water leach solutes and in material apparently removed from the ash by rain*

[Data in milliequivalents per 10^3 g ash. Amounts of ions removed by rain were inferred from differences in water leach availability from three samples collected before and three samples collected after exposure to rain at same location. ND, not detected; n, number of samples averaged]

Material removed by water leach from ash samples not exposed to rain							
Wash., Idaho, and Mont. (n=19)				Almira, Wash. (n=16)			
Cation		Anion		Cation		Anion	
Na^+	14.0	F^-	0.6	Na^+	19.1	F^-	0.7
K^+	1.5	Cl^-	13.2	K^+	2.6	Cl^-	18.9
Mg^{++}	4.8	SO_4^{-2}	30.2	Mg^{++}	8.5	SO_4^{-2}	59.7
Ca^{++}	27.5	PO_4^{-3}	ND	Ca^{++}	51.3	PO_4^{-3}	ND
Mn^{++}	.3	NO_3^-	.9	Mn^{++}	.6	NO_3^-	1.6
Total	48.1		44.9		82.1		80.9

Material apparently removed from ash samples by rain			
Ritzville, Wash.			
Cation		Anion	
Na^+	10.6	F^-	0.4
K^+	<1.0	Cl^-	14.8
Mg^{++}	<3.3	SO_4^{-2}	14.7
Ca^{++}	15.7	PO_4^{-3}	ND
Mn^{++}	.2	NO_3^-	.1
Total	<30.8		30.0

For the material apparently removed by rain in the field (table 18, six samples from Ritzville, Wash.: three collected before rain, three collected after rain), the electrical ion balance is also close. We have previously commented on the possible relative stringencies of the rain and the deionized water leach treatments. Rain apparently removed one-third to one-half of the

TABLE 19.—*Electrical balances of anion and cation equivalents in deionized water leach solutes from selected ash samples*

[Data in milliequivalents per 10^3 g ash. ODWALV30 and ODWALV3X are analytical replicate splits from Almira, Wash. ODWRZY10 is from Ritzville, Wash. These three samples were collected before exposure to rain. LRIHAZ10 and LRWRZZ2X are from Harrison, Idaho, and Ritzville, Wash., respectively; both were exposed to rain before collection]

	ODWALV30	ODWALV3X	ODWRZY10	LRIHAZ10	LRWRZZ2X
F^-	0.6	1.3	1.1	0.16	0.32
Cl^-	22	19	16	.5	.5
PO_4^{-3}	<4.7	<4.7	<4.7	<4.7	<4.7
SO_4^{-2}	73	60	18	.7	2.3
NO_3^-	<.8	5.5	2.9	<.8	.9
Total	<101	< 91	<43	<6.9	<8.7
Ca^{++}	60	55	19	6	3.5
Mg^{++}	10	9	5	2.5	.8
Na^+	22	20	15	3.9	3.5
K^+	2.9	2.7	1.4	.8	<.3
Mn^{++}	.7	.7	.3	.1	.03
Fe^{++}	<.4	<.4	<.4	.4	<.4
Si^{4+}	4.3	4.3	1.4	2.8	2.8
Al^{3+}	<1.1	<1.1	<1.1	<1.1	<1.1
Total	<101	<93	<44	<18	<12

equivalents that would have been available to the water leach treatment. The preceding lines of evidence indicate that the sources of solute in the water leach and the rain leach are principally surficial deposits of readily soluble salt materials rather than primary igneous grains.

The relationships between electrically charged species in the acid leach solution are different from those in the water leach solution. Table 20 gives electrical balances in acid leach treatment solute for the same five samples for which water leach electrical balance data were presented in table 19. Table 20 also presents information

TABLE 20.—*Electrical balances of anion, cation, and proton equivalents in 0.01* F *H_2SO_4 acid leach solutes from selected ash samples*

[Data in milliequivalents per 10^3 g ash. Values in parentheses are for HNO_3 leach treatment. Leaders (--), no value was measured because of interference from the anion in leaching acid. Anion totals are approximate because SO_4^{-2} values from corresponding HNO_3 leach were substituted and used in addition; similarly, NO_3^- values from H_2SO_4 treatment were used to compute sums of anions for HNO_3 acid leach. ODWALV30 and ODWALV3X are analytical replicate splits from Almira, Wash. ODWRZY10 is from Ritzville, Wash. These three samples were collected before exposure to rain. LRIHAZ10 and LRWRZZ2X are from Harrison, Idaho, and Ritzville, Wash., respectively; both were exposed to rain before collection]

	ODWALV30	ODWALV3X	ODWRZY10	LRIHAZ10	LRWRZZ2X
F^-	4.9 (4.1)	4.4 (4.2)	2.5 (2.4)	1.9 (1.7)	2.2 (2.1)
Cl^-	26 (25)	24 (22)	21 (19)	.2 (0.8)	1.3 (1.1)
PO_4^{-3}	43 (38)	43 (38)	28 (13)	24 (15)	28 (18)
SO_4^{-2}	-- (85)	-- (75)	-- (25)	-- (10)	-- (8.3)
NO_3^-	1.8 (--)	1.6 (--)	1.0 (--)	<.8 (--)	<.8 (--)
Total--	<161 (<153)	148 (<140)	<78 (<60)	<37 (<28)	<41 (<30)
Ca^{++}	150	135	65	45	50
Mg^{++}	41	39	22	16	19
Na^+	26	23	21	7.0	8.7
K^+	14	13	7.2	5.4	5.9
Mn^{++}	2.9	2.8	1.2	.6	.8
Fe^{++}	28	27	14	13	15
Si^{4+}	43	43	26	23	26
Al^{3+}	67	63	44	39	44
Total--	<372	<346	>200	149	>169
Difference between total cations and total anions---------	211	198	122	112	128
Initial pH of solution (measured "blank" pH; 0.009 M H_2SO_4)-------	2.06	2.06	2.06	2.06	2.06
Final pH of solution (measured)-----------	2.82	2.45	2.29	2.29	2.30
Protons consumed (calculated from measured pH values)--	98	70	56	56	56
Difference between non-salt-associated cations released and protons consumed-	113	128	66	56	72
Acid-associated anions (calculated)---------	189	189	189	189	189

on the contribution of protons to the ionic electrical charge balance. This information is needed because there is a much greater abundance of protons (or hydronium ions) in solution at the lower pH values of the acid leach solution than at the near-neutral pH of the water leach solution, and the quantities of electrical charge associated with changes in proton concentration in the acid leach solution before and after treatment of the ash are considerable. Therefore, we included in table 20 information on the contribution of protons to the ionic electrical charge balance.

The acid leach treatment yielded a large excess of positive charge from the cations Ca^{++}, K^{+}, Mg^{++}, Na^{+}, Mn^{++}, Fe^{++}, Al^{3+}, and Si^{4+} over the negative charge from the anions SO_4^{-2}, Cl^{-}, PO_4^{-3}, F^{-}, and NO_3^{-}. Both Mn and Fe ions are considered to have a formal charge of (II) because they are more commonly present in the reduced state in igneous-rock minerals. Silicon is included with the cationic species in these calculations because it is likely to be present in the solute as silicic acid ($H_4SiO_4{}^{\circ}$), an uncharged species, thereby consuming hydronium ions and affecting the pH. Aluminum would most likely exist as Al^{+3} at such acidic pH values. Nitric acid leaches were done on a few samples, in addition to the sulfuric acid leaches done on the larger number of samples, in order to get information on the amounts of SO_4^{-2} removed from the ash under similar pH conditions in strong-acid solution.

The data of table 20 show that numbers of electrical equivalents of cations in solute typically exceed those of anions by about two and a half times, and that the hydronium ions consumed (determined from change in measured solution pH) typically account for only about half of that imbalance. However, the uncertainty in the results of table 20 is great because of uncertainty in the behavior, speciation, and charge of many species in the solutions. First, the number of equivalents of hydronium ions consumed were determined from measured pH values and converted to a per-gram-of-ash basis; if a calculated initial pH had been used, based on acid concentration and on the published dissociation constant for the second proton of H_2SO_4, hydronium ion consumption would have appeared to more closely bridge the excess of cation equivalents over anion equivalents. Also, the electrical sums for cations and anions were calculated without regard to speciation, and our assignment of the formal charge for an ion may be incorrect. With respect to the formal charge that we have attributed to the species listed in the tables, we do not mean to insist on the physical reality of these particular species, but rather to suggest a charge corresponding to the number of hydronium ions most probably consumed in ion-exchange reactions (or, in the case of silica, complexation reactions).

The relationships among equivalents of cations, anions, and hydronium ions moving into or out of solution during the acid leaching process suggest extensive replacement of cations on primary igneous mineral surfaces by hydronium ions of the acid leach solution. Such dissolution of many or most mineral phases contrasts with the apparent congruent dissolution of the readily soluble surficial material, which yields cations and anions to deionized water leach solution in electrically equivalent amounts. White and Claasen (1980) confirmed that, at a pH similar to the acid leach treatment in the present work, displacement of cations from rhyolitic glass is largely done by the protons in the leaching acid.

SIGNIFICANT CORRELATIONS BETWEEN CATIONS AND ANIONS IN THE LEACHATE

Results of this study indicate that there may be a direct association of Na with Cl in the readily water-soluble material that coats ash particles, and an association of both alkali and alkaline earth metals, as well as others, with SO_4. Table 21 gives a correlation matrix for species in water leachates for a group of 13 samples collected before exposure to rain. The critical values are

TABLE 21.—*Correlation matrix for species measured in water leach treatment*

[Correlation coefficients were determined for 13 ash samples collected before exposure to rain from Washington, Idaho, and Montana. No analytical duplicates or Almira, Wash., time-sequence samples were included. Only those species whose leach-solution concentrations were above analytical detection limit for all samples are included in table, unless otherwise noted: in the cases of the Si and Li analyses, two individual samples registering below the instrumental detection limit were assigned values 0.7 times the detection limit. Underlined correlation coefficients are significant at worst at the 5 percent confidence level. Cation values were determined by inductively coupled plasma spectroscopy; anion values were determined by ion chromatography]

	Ca	K	Li	Mg	Mn	Na	Si	Sr	Cl	F	SO_4
Ca	1.00	0.93	0.55	0.90	0.77	0.62	0.48	0.97	0.33	0.20	0.97
K	--	1.00	.51	.97	.86	.72	.37	.90	.43	.25	.91
Li	--	--	1.00	.52	.23	.38	.18	.52	.67	-.09	.49
Mg	--	--	--	1.00	.88	.83	.23	.91	.57	.38	.86
Mn	--	--	--	--	1.00	.81	.07	.83	.57	.42	.79
Na	--	--	--	--	--	1.00	-.09	.75	.90	.58	.56
Si	--	--	--	--	--	--	1.00	.33	-.27	-.14	.42
Sr	--	--	--	--	--	--	--	1.00	.50	.28	.95
Cl	--	--	--	--	--	--	--	--	1.00	.41	.25
F	--	--	--	--	--	--	--	--	--	1.00	.13
SO_4	--	--	--	--	--	--	--	--	--	--	1.00

0.55 at the 5 percent confidence level, and 0.68 at the 1 percent confidence level. As may be seen in the table, only Na strongly correlates with Cl, whereas Ca, Sr, K, Mg, and Mn strongly correlate with SO_4. Many metals strongly correlate with each other. These results are similar to those of Smith, Zielinski, and Taylor (1982), but contrast some with the suggestion of Taylor and Lichte (1980) that there are two classes of salts, alkali (plus ammonium) chlorides and alkaline earth sulfates, the former being the more soluble. The lack of significant correlation between anions SO_4 and Cl found by us contrasts with the highly significant correlation for this pair found by Smith, Zielinski, and Taylor (1982). In the water leach solute, there is no significant correlation with F for any of the metals listed above.

Table 22 gives the correlation matrix for species in the acid leach solution. Many metals in the acid leachates strongly correlate with PO_4 and with each other. Na and Cl again strongly correlate. SO_4 is not included in this matrix because H_2SO_4 was used as the leaching acid. No species correlate strongly with F (except Mn with a correlation coefficient of 0.71). Correlations of Cu with other species are in a sense opposite to those observed for most metals.

From the correlation matrices for species in the water and acid leach solutes, some associations may

TABLE 22.—*Correlation matrix for species measured in acid leach treatment*

[Correlation coefficients were determined for 13 ash samples collected before exposure to rain from Washington, Idaho, and Montana. No analytical duplicates or Almira, Wash., time-sequence samples were included. Only those species whose leach-solution concentrations were above analytical detection limit for all samples are included in table, unless otherwise noted: in the case of the Li analyses, one individual sample registering below the instrumental detection limit was assigned a value 0.7 times the detection limit. Underlined correlation coefficients are significant at 5 percent confidence level. Cation values were determined by inductively coupled plasma spectroscopy; anion values were determined by ion chromatography]

	Al	Ca	Co	Cu	Fe	K	Li	Mg	Mn	Na	Si	Sr	V	Y	Zn	Cl	F	PO_4
Al	1.00	0.93	0.65	-0.19	0.87	0.93	0.59	0.94	0.89	0.07	0.94	0.86	0.94	0.95	0.58	0.18	0.55	0.89
Ca	--	1.00	.40	-.15	.83	.87	.54	.88	.91	.25	.93	.96	.85	.93	.69	.27	.59	.89
Co	--	--	1.00	-.24	.71	.76	.52	.74	.58	-.36	.57	.27	.71	.61	.18	-.13	.33	.57
Cu	--	--	--	1.00	-.35	-.20	-.12	-.22	-.02	.49	-.28	-.03	-.27	-.16	-.15	.64	.27	-.19
Fe	--	--	--	--	1.00	.96	.46	.96	.92	-.06	.90	.73	.79	.81	.65	.06	.55	.77
K	--	--	--	--	--	1.00	.63	1.00	.95	.06	.91	.79	.86	.89	.59	.22	.58	.85
Li	--	--	--	--	--	--	1.00	.63	.54	.33	.53	.60	.63	.62	.23	.42	.20	.68
Mg	--	--	--	--	--	--	--	1.00	.95	.06	.92	.81	.86	.89	.60	.22	.60	.85
Mn	--	--	--	--	--	--	--	--	1.00	.25	.88	.88	.76	.85	.68	.37	.71	.80
Na	--	--	--	--	--	--	--	--	--	1.00	-.02	.44	-.08	.05	.02	.86	.29	.07
Si	--	--	--	--	--	--	--	--	--	--	1.00	.86	.87	.90	.78	.12	.46	.86
Sr	--	--	--	--	--	--	--	--	--	--	--	1.00	.73	.85	.69	.47	.62	.82
V	--	--	--	--	--	--	--	--	--	--	--	--	1.00	.96	.43	-.02	.40	.92
Y	--	--	--	--	--	--	--	--	--	--	--	--	--	1.00	.53	.12	.51	.94
Zn	--	--	--	--	--	--	--	--	--	--	--	--	--	--	1.00	.21	.32	.53
Cl	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	1.00	.33	.18
F	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	1.00	.44
PO_4	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	1.00

be inferred. Na and Cl correlate strongly in both leach treatments, suggesting presence of NaCl as a discrete substance. Ca, K, Mg, Mn, and Sr all have highly significant correlation coefficients with SO_4 in the water leach, indicating the presence of sulfate salts. These ion associations are consistent with the presence of minerals detected in posteruption alteration products by Dethier and others (1981). Grains of salt identified as NaCl and $CaSO_4$, as well as some other simple salts, have been identified on grains of ash from other eruptions (Rose and others, 1973, 1980; Smith, Zielinski, and others, 1982), but Smith, Zielinski, and Taylor (1982) did not report discrete salt crystals on Mount St. Helens ash. Al, Ca, K, Mg, Mn, Si, Sr, V, and Y all have correlation coefficients greater than or equal to 0.80 with PO_4 in the acid leach. Phosphate salts would be nearly insoluble in water but could be expected to be extensively dissolved at lower pH values. It is uncertain whether the metal-anion associations indicate the presence of discrete salts, complex mixtures of salts, or amorphous residues.

Ca/Sr RATIOS IN SOLUTES

The Ca/Sr ratios for whole ash, water leach solute, and acid leach solute are distinct, being lowest for whole ash and highest for acid leach solute. The data are presented in table 23. For samples collected before rainfall and before significant wind winnowing on the ground, there is no overlap in values for the sets of ratios for the three types of material. The three-fold-larger values of water leachate Ca/Sr ratios compared to whole-ash Ca/Sr ratios indicate that a separate and relatively more Ca-rich reservoir of material is available to form the solute. The still larger Ca/Sr values for the acid leach solute indicate that there is a strongly selective removal of Ca, relative to Sr, by proton displacement (ion-exchange reactions) at grain surfaces. The dispersions in the sets of Ca/Sr ratios for whole ash, water leachate, and acid leachate are not great; the slightly greater dispersion in the leachate ratio sets is no more than would be expected from the poorer precision (fewer significant figures) of their concentration data. Also because of poorer precision associated with small concentration values, there is slightly greater dispersion in the data sets for post-rain samples than for pre-rain samples. The small magnitudes of the dispersions indicate that the source materials for both the water leach and acid leach solutes are homogeneous and consistent in composition, almost as much as the whole ash itself.

The lower section of table 23 is presented to remind the reader of the relative masses of the three types of material: water leach solute represents about 0.1-0.2 percent and acid leach solute about 0.5-1 percent of whole ash, for pre-rain samples.

TABLE 23.—*Ca/Sr ratios in solutes, and total amounts of ash removed by leach treatments*

[Amounts of ash removed by leach treatments are expressed as ppm of whole ash, and were calculated by summing amounts of five anions (Cl^-, F^-, NO_3^-, PO_4^{-3}, SO_4^{-2}) and nine cations (Na^+, K^+, Mg^{++}, Ca^{++}, Ba^{++}, Al^{3+}, Fe^{++}, Mn^{++}, Si^{4+}) from solutes; values for SO_4^{-2} were estimated from results of a parallel acid leach treatment using HNO_3. n, number of samples analyzed]

Ca/Sr ratios in solutes

	Pre-rain samples (n=18)			Post-rain samples (n=8)		
	Mean	Range	Standard deviation	Mean	Range	Standard deviation
Whole ash--	74.2	68-78	2.6	74.4	67-80	3.8
Water leach solute---	252	200-289	28	164	>100-200	44
Acid leach solute---	326	290-360	28	348	162-471	94

Total amounts of ash removed (ppm) by leach treatments (calculated)

	Pre-rain samples (n=18)	Post-rain samples (n=8)		
	Mean	Mean	Range	Standard deviation
Water leach treatment-	1,600	480	370-860	180
Acid leach treatment-	6,700	4,150	3,400-6,050	800

AMOUNTS OF SPECIES YIELDED TO MILD AND HARSH LEACHING TREATMENTS

Those elements that most nearly yield equal amounts to the deionized water and acid treatments (fig. 9) probably have a major fraction of their leachable totals in the form of water-soluble surficial coatings. Elements that best meet this criterion are the alkali and alkaline earth metals, the transition metals Ni, Co, V, and Mn, and the anions Cl^- and SO_4^{-2}. Solubility limitations may be the controlling factor for some species concentrations. Smith, Zielinski, and Taylor (1982) ran successive 4:1 liquid-to-ash ratio (by weight) leaches on fresh Mount St. Helens ash with an initial deionized water leach followed by an acid leach of dilute HCl (pH 3.5-4.0). They found the same species (SO_4^{-2}, Ca, Cl^-, Na, Mg) to be yielded in greatest abundance to both the initial deionized water and the subsequent acid leachate, with the acid leach solute concentrations equal to about one-third those of the water leach.

Species not associated with common water-soluble salts and not detected in the present study in the water leach solution, such as PO_4^{-3}, Al, and Fe, are prominent species in the acid leach solute. By the stoichiometry of any suite of igneous phases expected to act as sources of solute, there is in the acid leach solute a deficiency of Si relative to the major cations Ca, Mg, Na, and K, whether or not the contribution of a balanced suite of cations and anions from soluble surface salts is included in the calculation. It should be noted that oxides, sulfides, and phosphates might exhibit increased solubility in acidic solutions, but would be expected to exhibit approximately congruent dissolution. The data suggest the presence of a discrete phase in the ash that is less water soluble than other materials which are well represented in the water leach solute.

CONTRIBUTION TO SOLUTE BY PRIMARY IGNEOUS GRAINS

The distribution of all elements among the various species and sizes of grains in the ash is not well known. Ni, Mn, and Co, removed by water leach in amounts representing about 2–5 percent of their whole-ash totals, are expected to be concentrated in the opaque and dark minerals of the ash, which are susceptible to rapid breakdown by weathering; however, these elements may also be present in surficial coatings.

Some ash particles are older altered grains of glass, minerals, and lithic fragments, and any of these may contribute to leach solutes in distinctive ways. Such materials, quarried from the throat of Mount St. Helens during eruption, may or may not be more easily attacked by solutions than would grains of many fresh primary species, and they may provide solute material at an unknown rate.

In mixed mineral systems, the kinetic rates of dissolution of individual constituent cations are not simple combinations of the rates of cation dissolution from the individual minerals involved. Differences in the identities and grain sizes of the minerals in the mix may control variations in the fractional removal of cations from the outer atomic layers of the mineral grains in the rock–solution system.

Many authors have recently discussed the mechanisms and kinetics of uptake of material by solutions from minerals, glasses, rocks, and soils (Lepel and others, 1978; Maenhaut and others, 1979; Naughton and others, 1974; Smith and others, 1981). Generally, in the earliest stage of dissolution, cations may be displaced by hydronium ions in the solution. Over much longer times, true congruent dissolution of minerals may occur. The amount of material in solution may be a proportion of the square root of time of exposure (parabolic dissolution curve); with such a relationship there may appear to be an initial period of rapid uptake (possibly due to very fine grain size of some particles) by the solution, followed by a later period of slower uptake during which the relation between time and amount of solute may appear to be nearly linear. The effects associated with the dissolution of feldspars in low-pH solutions, described by Busenberg and Clemency (1976), include relatively equal release of Na and Ca, moderate release of Al, and copious release of Si; these effects were not approximated during the acid leach treatment of Mount St. Helens ash in the present study. From our Mount St. Helens data, about two to four times more Ca than Na seems to be released, and large amounts of both Al and Si are released. However, the feldspar composition and mean grain size of the ash are different between the present study and that of Busenberg and Clemency.

It is worthy of consideration that important sources of many elements in the agitated leach extractions of the present study, and the column leach extractions of Taylor and Lichte (1980), may be the abundant, mineralogically unidentified ultrafine particles that are observed clinging tenaciously to the surfaces of larger grains in scanning electron microscope photographs of the Mount St. Helens ash. Most of these are probably fine fragments of minerals or glass rather than particles of the highly soluble surficial material. As proposed by Holdren and Berner (1979) and Berner and Holdren (1979), these ultrafine grains and "* * * sites of excess surface energy, such as at dislocations or similar crystal defects * * *" could be expected to supply to solution greater amounts of the elements than would larger grains, and could thus be responsible for the initial parabolic dissolution observed by many researchers over exposure times approximately the same as those of the present study.

VARIATION IN AMOUNT OF THE SOLUBLE MATERIAL

The variation in chemical and mineralogic composition of samples of whole ash and the relationship of that variation to time of fall and distance from source are discussed in Chapter A of this volume. (See also Taylor and Lichte, 1980; and Sarna-Wojcicki, Meyer, and others, 1981.) Basically, there is one end-member compositional type of Mount St. Helens ash that is dark colored, with abundant opaque and dark minerals and calcic plagioclase, phases that taken together are relatively rich in Ca, Mg, Fe, Sr, Mn, Ni, Co, and V. This dark-colored ash is abundant in the ash that fell early from the suspended plume or close to Mount St. Helens, although there appears to be considerable local variation. The other end-member compositional type is light colored, and is characterized by abundant glass and sodic plagioclase, phases rich in Si, Li, Na, and K. This light-colored ash is more abundant in ash that fell later or at greater distances from the volcano, although for these species also the relation between composition and distance from source is only general.

Various lines of evidence (composition of water leach solute, composition of material removed by rain, consistency in amounts of elements removed by procedures using varying water-to-ash ratios, and details of electrical ion balance) make it clear that a quantity of readily soluble material is present as a minor but distinct component of the ash. Ca, Na, K, Mg, Si, and Mn, in decreasing order of abundance, form the greatest bulk of cationic species in this soluble material. Their proportions in the solute remain fairly constant for all samples. However, amounts of total solute removed by a given leach treatment vary considerably.

The question arises of whether there is a simple relationship between amount of soluble material available to be dissolved from the ash, and compositional type of the ash. Observations on this possible relationship can best be made by determining statistical correlations between (1) amount of selected elements removed in leach treatments and (2) concentrations of the elements that serve to characterize the compositional type of the whole ash. Table 24 presents correlation coefficients between amounts of various species removed by leach treatments from pre-rain samples, and concentrations of three key species in whole ash. Calcium was chosen to characterize the dark-colored ash, which is rich in ferromagnesian minerals and calcic plagioclase; Na and Si were chosen to characterize the light-colored ash, which is rich in glass and sodic plagioclase. Several species show highly significant correlation coefficients between mass removed by both water and acid leach treatments and whole-ash Ca, Na, and Si. The generally strongly positive correlation coefficients between whole-ash Ca and solute species, and the negative coefficients relating Na and Si to solute species, indicate that the dark-colored ash, containing opaque and dark minerals and calcic plagioclase, yields more of most constituents of the soluble material than the light-colored ash, which contains sodic plagioclase and glass. Solute Cu is associated with the more silicic type of ash and is an exception.

TABLE 24.—*Correlations between whole-ash calcium, sodium, and silicon, and species removed by water and acid leach treatments*

[Correlation coefficients were determined for 13 ash samples from Washington, Idaho, and Montana, and for five time-sequence samples from Almira, Wash., all collected before being rained on. No analytical duplicates were included. Only those leachate species whose leach-solution concentrations were above the analytical detection limit for all samples are included in table, unless otherwise noted: one individual value below the instrumental detection limit for the Li acid leachate analyses, and two values for the Li and Si water leachate analyses, were assigned values 0.7 times the respective detection limits. Underlined correlation coefficients are significant at 5 percent confidence level. Cation leachate values were determined by inductively coupled plasma spectroscopy; anion leachate values were determined by ion chromatography; whole-ash values were determined by X-ray fluorescence]

Washington, Idaho, and Montana samples								Almira time-sequence samples			
Water leach species	Whole-ash Ca	Whole-ash Na	Whole-ash Si	Acid leach species	Whole-ash Ca	Whole-ash Na	Whole-ash Si	Acid leach species	Whole-ash Ca	Whole-ash Na	Whole-ash Si
Ca	$\underline{0.83}$	$\underline{-0.64}$	$\underline{-0.91}$	Al	$\underline{0.95}$	$\underline{-0.74}$	$\underline{-0.91}$	Al	0.19	-0.27	-0.30
K	$\underline{.79}$	$\underline{-.58}$	$\underline{-.88}$	Ca	$\underline{.90}$	$\underline{-.79}$	$\underline{-.90}$	Ca	.62	-.68	-.71
Li	.44	-.49	-.52	Co	$\underline{.67}$	-.43	-.48	Co	.79	-.50	-.65
Mg	$\underline{.66}$	-.49	$\underline{-.82}$	Cu	-.26	.44	.21	Cu	$\underline{-.96}$	$\underline{.91}$	$\underline{.95}$
Mn	.53	-.22	$\underline{-.66}$	Fe	$\underline{.89}$	$\underline{-.82}$	$\underline{-.79}$	Fe	$\underline{.94}$	-.87	$\underline{-.95}$
Na	.18	-.10	-.41	K	$\underline{.94}$	$\underline{-.77}$	$\underline{-.87}$	K	$\underline{.88}$	-.82	$\underline{-.90}$
Si	$\underline{.65}$	$\underline{-.76}$	-.52	Li	$\underline{.57}$	$\underline{-.43}$	$\underline{-.65}$	Li	.71	-.56	-.69
Sr	$\underline{.69}$	-.50	$\underline{-.81}$	Mg	$\underline{.94}$	$\underline{-.76}$	$\underline{-.88}$	Mg	$\underline{.90}$	-.84	$\underline{-.92}$
				Mn	$\underline{.88}$	$\underline{-.77}$	$\underline{-.84}$	Mn	.76	-.77	-.83
				Na	.06	-.07	-.30	Na	-.12	-.02	-.02
Cl	-.14	.16	-.07								
F	-.11	-.05	-.14	Si	$\underline{.88}$	$\underline{-.83}$	$\underline{-.84}$	Si	.75	-.68	-.78
SO_4	$\underline{.85}$	$\underline{-.57}$	$\underline{-.90}$	Sr	$\underline{.80}$	$\underline{-.70}$	$\underline{-.86}$	Sr	.53	-.59	-.63
				V	$\underline{.91}$	$\underline{-.70}$	$\underline{-.82}$	V	.69	-.62	-.72
				Y	$\underline{.94}$	$\underline{-.69}$	$\underline{-.88}$	Y	.83	-.78	-.86
				Zn	.47	$\underline{-.72}$	-.45	Zn	.74	-.78	-.82
Whole-ash Ca	$\underline{1.00}$	$\underline{-.72}$	$\underline{-.94}$								
Whole-ash Na	--	$\underline{1.00}$	$\underline{.68}$	Cl	.12	-.04	-.32	Cl	.31	-.39	-.43
				F	.52	-.23	-.45	F	-.37	.24	.30
Whole-ash Si	--	--	$\underline{1.00}$	PO_4	$\underline{.89}$	$\underline{-.66}$	$\underline{-.83}$	PO_4	.56	-.65	-.66

Table 25 presents correlation coefficients between the amount of each element removed by water or acid leach treatments and its own whole-ash concentration. The data show that the relationship defined above, between amount of soluble material and whole-ash composition, holds for both water and acid leach treatments. In the water leach treatment only those elements that are more abundant in the dark-colored ash (Ca, Mg, Sr, Mn) significantly correlate positively between amount in fresh-ash water leach solute and whole-ash concentration; those that are less abundant in the dark-colored ash (K, Na, Si, Li) either correlate negatively or show no significant correlation. In the acid leach treatment, the same relationships hold for the two groups of four elements; the additional elements Al, Fe, V, Y, and Zn, not successfully detected in the water leach treatment, are positively correlated with their own whole-ash concentrations.

OTHER EVIDENCE ON SOURCE MATERIAL FOR ACID LEACH SOLUTE

The sources of solute to acid leach treatment appear to be: (1) the same salts available to the water leach treatment (largely Cl^- and SO_4^{-2} salts); plus (2) other less easily soluble salts such as PO_4^{-3} and possibly OH^- and O^{-2} salts or amorphous material; and (3) proton-displaced surficial cations from the minerals themselves. The segregation of elements into two distinct groups in figure 9 may be used in conjunction with the acid and water correlation coefficients of table 25 and the electrical ion balance data of table 20 to give complementary information on the nature of sources of acid leach solute. The group of elements that is removed much better by acid than by water (the "high" part of the plot of fig. 9) includes Fe, Al, Y, and Zn; this suggests that a massive source of solute not available to

TABLE 25.—*Correlations between removal by water or acid leach treatments and whole-ash content for each chemical species*

[Correlations were determined on 13 ash samples (unless otherwise noted by dagger (†), which indicates five samples) from Washington, Idaho, and Montana and on five time-sequence ash samples from Almira, Wash.; all were collected before being rained on. No analytical duplicates were included. Only those leachate species whose leach-solution concentrations were above the analytical detection limit for all samples are included in the table, unless otherwise noted: individual leachate samples registering below the instrumental detection limit, two each for both Li and Si for water leach analysis, and one sample for Li for acid leach analysis, were assigned values 0.7 times the respective detection limits. Underlined correlation coefficients are significant at the 5 percent confidence level. Cation leachate values and some whole-ash values were determined by inductively coupled plasma spectroscopy; other whole-ash values were determined by X-ray fluorescence; anion leachate values were determined by ion chromatography]

Washington, Idaho, and Montana samples				Almira time-sequence samples			
Ranked species	Acid leach correlation coefficient	Ranked species	Water leach correlation coefficient	Ranked species	Acid leach correlation coefficient	Ranked species	Water leach correlation coefficient
Mg	0.93	Ca	0.83	Fe	0.96	Mg	0.64
Ca	.90	Mg	.74	Mg	.92	Ca	.58
Fe	.89	Mn	.70	V	.77	Sr	.46
Sr	.87	Sr	.67	Mn	.72	Mn	.35
Al	.86	Li	-.02	Co	.68	Li	-.68
Zn	.86	Na	-.10	Zn	.66	K	-.46
V	.67	Si	-.52	Ca	.62	Na	-.35
Y	.63	K	-.82	Cu	.51		
Mn	.62			Sr	.47		
Co	.50			Y	.25		
Cu	.41	Cl†	.92	Na	-.02	SO_4	.99
Na	-.07	SO_4†	.79	Al	-.21	F	.74
Li	-.47	F†	.78	Li	-.53	Cl	-.01
Si	-.84			Si	-.78		
K	-.89			K	-.80		
PO_4†	.79			F	.27		
Cl†	.15			Cl	.14		
F†	-.19			PO_4	-.09		

water leach becomes available to displacement by protons during the acid leach treatment. An alternate hypothesis would be that there is an additional reservoir of somewhat more resistant acid-soluble surficial salt deposits. In contrast, the elements Ni, V, and Co, which appear in the "low, flat" part of the plot of figure 9, are among the group of elements removed only moderately more successfully by acid than by water. Water leach solute data on Ni, V, and Co were not complete enough to allow calculation of correlation coefficients; but from figure 9 it can be inferred that mineral sources of these elements for acid leach treatment are probably minor and that they are largely available to both kinds of treatments as more soluble and less soluble surficial salts.

The acid leach coefficients are generally somewhat larger in magnitude than those for water leach, suggesting the following: (1) to the extent that additional salts, rather than the surfaces of the minerals themselves, are the source of acid leach solute, the salts are probably physically associated with mineral grains containing a large amount of the same elements, and (2) the salt deposits are formed by acid attack on individual grains during or shortly after air transport. This is in opposition to the alternative possibility of indiscriminate condensation of element-rich aerosols on all types of ash particles during transport from the vent.

TRENDS IN GROUPS OF ASH SAMPLES

SYSTEMATIC AND RANDOM CHANGES IN LEACHATE CONCENTRATIONS IN THE ALMIRA, WASH., TIME-SEQUENCE SAMPLES

Between samples within certain sample groups, there appear to be definite differences in the amount of some elements released to the leach treatments. This is best seen in the time-sequence samples from Almira, where there may be systematic variations in species concentrations through time of fall. Figure 10 shows variations in species concentrations for the water leach. For several leachate species, there is a striking concentration decrease from the sample representing the final collection period at the Almira site; the leachate concentrations are largest from samples representing the middle period (from 4 to 6 p.m. PDT) of ashfall collection. Silicon concentration, however, remains constant throughout the time span. Figure 11 shows similar trends for the acid leach. Acid leach Cu (not detected in water leach solute) displays behavior through time of fall that is opposite to that of other solute species. Also, F^- is abundant in solute from the initial sample. The systematic changes may indicate differences in the nature and abundance of the materials that hold and release soluble species, and these differences may be associated with time of fall, changes in the composition of the eruptive gases, changes in temperature and pressure, differing exposure times of the samples before collection, grain size (surface area), or identity of mineral species (or position in mineral solid solution series). A systematic relationship to time of production from the volcano source, rather than merely an empirical relationship to time of precipitation from the overhead plume, must be regarded as a possibility for further research.

DIFFERING AMOUNTS OF MATERIAL YIELDED TO LEACHING SOLUTIONS BY GROUPS OF ASH SAMPLES

Samples collected after exposure to rain yielded less solute to acid leach treatment than expected if it is assumed that rain should remove the same amount of material as the 14:1 (by weight) water leach treatment. This may be explained through the widely reported observation (Leifer and others, 1981) that airborne or newly fallen ash bore liquid condensates of concentrated strong acid. Moderate wetting in the field (filling of the pore volume in the ash blanket, without flushing), as by light rain, could have exposed ash particles to extensive contact with solutions whose pH approached that of the acid leach treatment of the present study. Such exposure may have made available more material (to be removed later by heavier rain) than sudden flushing by a large volume of solution of near-neutral pH, such as in the water leach treatment of the present study. Such acid condensates may have evaporated before the fall of rain, leaving a residue of altered material on grain surfaces, to be flushed away later.

The greater yield to leaching solutions of the Almira samples, compared to other samples collected before exposure to rain, might be explained by similar considerations. The Almira samples were collected on plastic sheets, and sealed in jars only minutes or hours after fall. Other pre-rain samples were collected from various surfaces and had longer exposures to air. Contact with volatile acidic condensates during the time of confinement between collection and analysis could have made the Almira samples more susceptible to dissolution during leaching experiments. It may be observed that the last-collected Almira ash sample (ODWALV50) produced, for many chemical species, the lowest solute concentrations of any Almira sample. Because of the longer time span represented by this sample it was exposed to air several times longer than any other sample in the sequentially collected suite. However, the last-collected Almira sample also differs from the others in its whole-ash chemistry; it also conforms differently than the other Almira samples to the set of strong positive and negative correlations observed between amount of solute removed by leach treatments and whole-ash chemical composition for the larger group of all samples collected before exposure to rain.

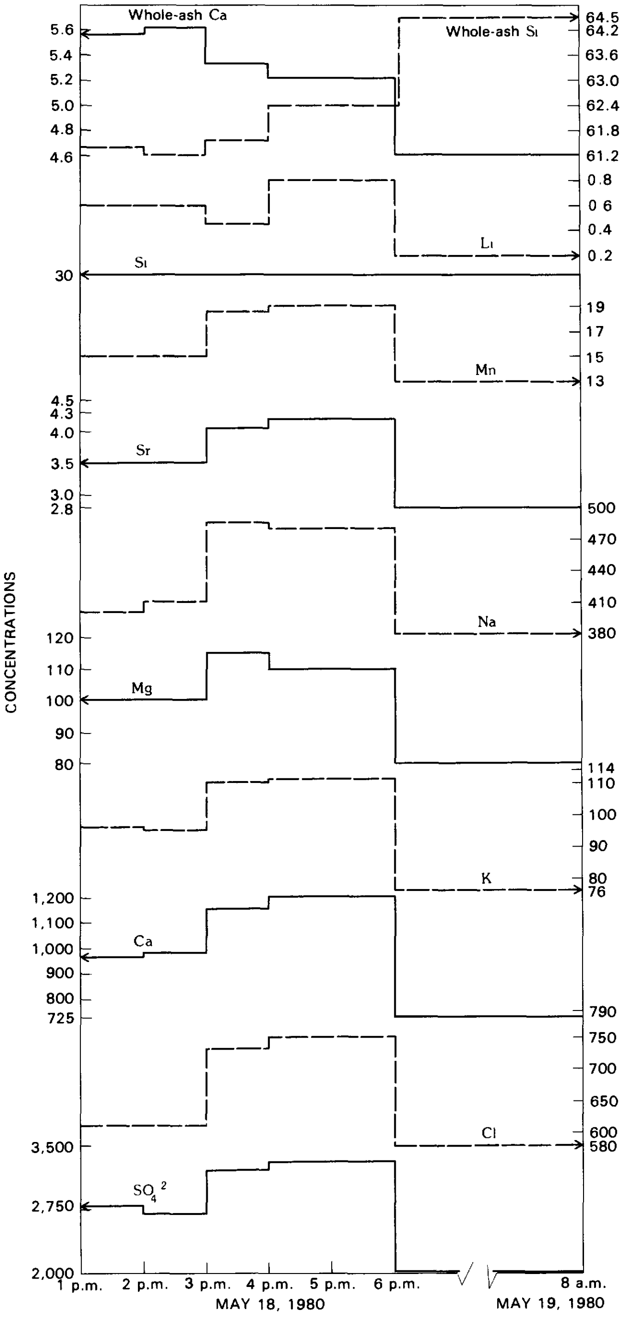

FIGURE 10.—Water leach concentrations (in ppm ash; whole-ash Ca and Si in weight percent) of solute species in samples collected through five abutting time increments at Almira, Wash. Arrows point to the appropriate concentration scale.

GRAIN SIZE OF THE ASH

Consideration of the varying average grain sizes of the ash samples in relation to amount and composition of leachates is complicated by the fact that the ash-fall

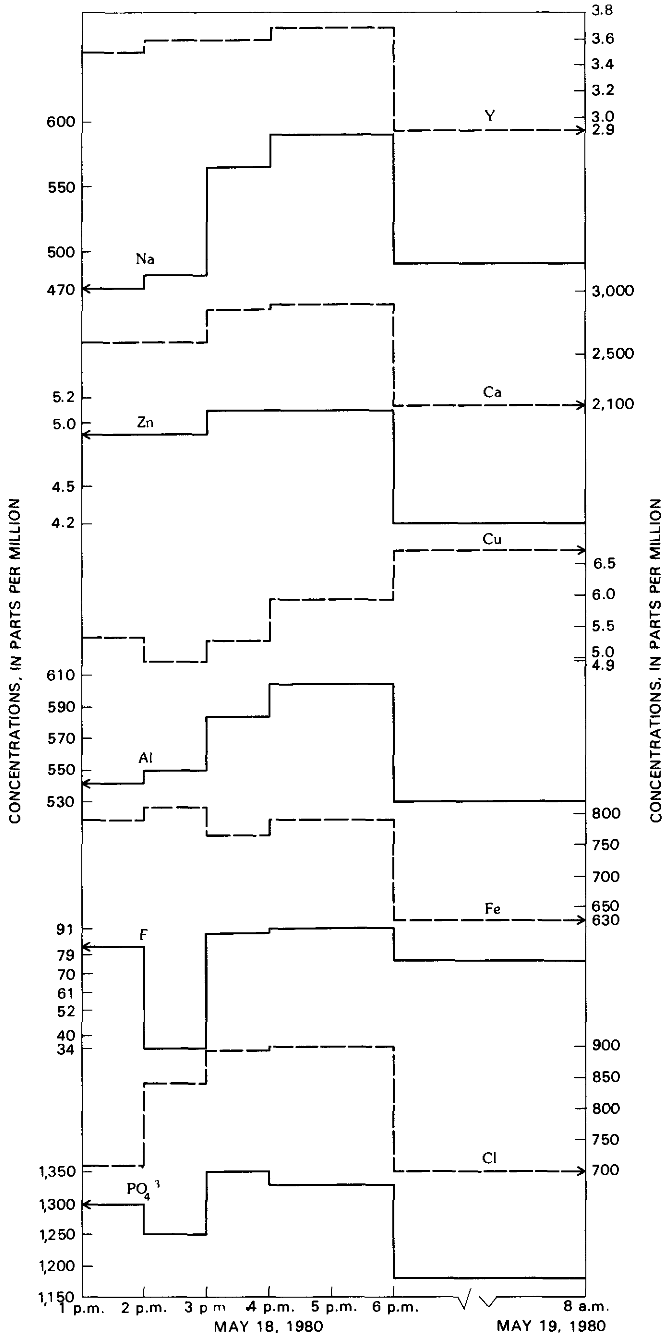

FIGURE 11.—Acid leach concentrations of solute species in samples collected through five abutting time increments at Almira, Wash. Arrows point to the appropriate concentration scale.

blanket is believed to be composed of discrete strata of variable relative thickness. The character and magnitudes of the component strata are discussed in detail by Sarna-Wojcicki, Shipley, and others (1981). Our ash samples represent vertical integrations of those strata, except for those from Almira and Missoula in which portions of the total thickness were sampled discretely. The basal "unit 1" of Sarna-Wojcicki, Shipley, and others (1981) is a thin, gray, silt-size ash; "unit 2," directly overlying unit 1, is also thin, and is a "salt and pepper," fine-sand-size ash composed of lithic and crystal fragments and fine pumice shards; "unit 3," directly overlying unit 2, is as much as 20 or more times thicker than units 1 or 2, and is a light-gray to tan, fine-sand- to silt-size ash composed of pumice and glass shards, crystals, and minor lithic fragments. Only at those geographic locations where the ash-fall blanket stratigraphy has been mapped could the relative amounts of the different strata represented in our samples be well determined and well interpreted; this would be most reliable in the thick central area of the ash-fall blanket, partly because of the ease of mapping the thick blanket in that region and partly because unit 3 increases its predominance over other units there. More detailed analysis of the data, and possibly more spatial grain size distribution information, would be required to determine whether there is any association between the larger observed yield of solute and the larger relative thickness of the finer grained unit 1 in ash close to the volcano. The same is true for the problem of determining the relationship between the relative amount of ferromagnesian constituents of the leachates and the relatively large amounts of dark units 1 and 2 from samples collected close to the volcano.

RELATIONSHIP OF LEACHATES OF MOUNT ST. HELENS ASH TO LEACHATES OF COMMON SOILS

COMPARISON OF AMOUNTS OF ELEMENTS REMOVED FROM ASH AND AMOUNTS REMOVED FROM COMMON SOILS, AND THE INTENSITY AND CAPACITY PROPERTIES OF THE TWO MATERIALS

Despite the higher solution extract values for ash than for soils (table 17), there is an important and fundamental difference between the intensity and capacity properties of ash and soils. This difference is that solute concentrations through a series of extractions on the ash decrease greatly, whereas it has been well established for decades (Adams, 1971) that solute concentrations from sequential extractions of typical soils, irrespective of the nature of the leach treatment, change only little. Table 26 presents measurements by Taylor and Lichte (1980) of concentrations of selected elements in three successive, 4-hour, single-pore-volume leaches of ash, and also compares these values to the average saturated-paste soil extract values of Bradford and others (1971). Ash leachate values obtained by the column method by Taylor and Lichte are presented in this table in spite of yielding, for many minor and trace elements, different values from those obtained by the 14:1 extraction method of the present study. It is interesting to note that among the elements listed in table 26 as having low concentrations in the ash leachates, there are some that are commonly thought of as being of "environmental concern" (Na, B, Ba, Mo); among those with high concentrations are some recognized as essential or beneficial to plant nutrition (K, Mg, Cu, Fe, Zn). A different impression is gotten from the data of table 17, in which leachate data from the present study and other ash leachate studies are compared to summarized leachate data for common soils. In table 17, in which the data are presented as whole-rock concentrations rather than as solution concentrations, the amounts of Na, Ba, and Mo released by ash are as large or larger than those released by soils. However, in evaluating the data on comparative amounts of metals released by ash and soils, the reader is cautioned to bear

TABLE 26.—*Successive pore-volume water leaches of ash compared to water extracts of common soils*

[Value in parentheses is semiquantitative. Successive pore-volume leaches are from data of Taylor and Lichte (1980) for ash from Spokane, Wash.; common soil extract values are from Bradford and others (1971)]

Element	Successive pore-volume leaches (mg/L) #1	#2	#3	Common soil extract mean (ppm)
	High concentrations in ash leachates			
Co	0.1	0.011	0.003	0.06
Cu	.3	.04	.02	.04
Fe	.1	.03	.2	.05
K	(70)			20
Li	.6	.14	.05	.11
Mg	109	20	6.7	38
Mn	22	3.8	1.2	.17
Zn	.6	.04	.008	.07
	Low concentrations in ash leachates			
B	0.8	0.4	0.08	3
Ba	.12	.1	.04	.26
Mo	.02	.01	.02	.7
Na	559	115	43	524
V	<.001	<.001	.003	.07

in mind the importance of the units in which the data are presented, and the different metal-releasing behaviors of ash and soils in successive leach treatments.

CONTRASTS IN LEACHABLE CHEMISTRY OF ASH AND TYPICAL SOILS

The correlations between compositions of whole-ash samples and their leachates in this study are stronger than those reported throughout the literature for whole soils and their leachates (Severson and others, 1978). There is better precision between leachate analyses of splits of ash samples in the present study than between those of splits of soil samples reported in the literature. Also, there is rather good correspondence between results on ash samples leached using somewhat different methods (namely, the deionized water leach method of the present study done at a 14:1 water:ash ratio and the single-pore-volume deionized water leach of Taylor and Lichte, 1980), whereas different methods used for availability analyses of soils commonly yield different results (Jenne and Luoma, 1977; Mitchell, 1972; Yagodin and Sobachkina, 1977). Most of these contrasts probably stem from the fact that the ash is a simpler material than most soils. The ash is largely composed of primary igneous materials (although 10 percent or more of distal and 25 percent or more of proximal ash samples may be altered material), whereas soils consist of primary minerals, secondary minerals, clays, organic matter, and grain coatings composed of sesquioxides of transition and other metals. In many soils, a major fraction of the reservoir of elements available to leaching treatments (or even whole-soil elements) could be contained in any of these phases. Recently, there has been discussion of the possibility of complex redistributions of chemical species (extractable ions) taking place among the many soil constituents during the laboratory extraction procedures themselves (Rendell and Batley, 1980). Such redistributions may be similar to processes operating in the system of plant roots, soil components, and solutions in nature. Such complications are much less likely to be important in the case of the ash and the complex redistribution of the chemical species it would release.

CONCLUSIONS

1. Elements yielded by the ash to the two leaching treatments used in this study come from two distinct types of source material in the ash. The first source material, which yielded the bulk of material removed by the near-neutral pH (water) leach treatment, is composed of salts or amorphous material and probably represents surficial coatings on the grains of the primary igneous species in the ash. Such material may be largely composed of alkali and alkaline earth metals, and Mn and Si, and the anions SO_4^{-2} and Cl^-, with lesser amounts of F^- and NO_3^-. The close electrical balance between cations and anions in the water leach solute implies congruent dissolution of ionic salt material. A PO_4^{-3} salt phase, susceptible to dissolution only by the harsher acid treatment, may also be present.

   The second source material is the primary igneous phases themselves, which largely through surficial cation–proton ion-exchange reactions yielded the bulk of the much larger amounts of material removed as solute by the low-pH (acid) leach treatment. In addition to the alkali and alkaline earth metals present in the water leach solute, large amounts of the mineral-forming species Fe, Al, and Si are present in the acid leach solute. In contrast to the water leach, no close electrical balance between cations and anions removed from the ash exists in the acid leach solute, confirming that surficial deposits of ionic salts are not the sole source of material removed by acid leach treatment. Cations in acid leach solute are present in different proportions from those in the grains themselves.
2. More generally, in both water and acid leach treatments, chemical species were removed from the ash in varying proportions of their whole-ash contents. Ni, Mn, and Co, and P, Cu, Y, La, and Mn were removed by water and acid leaches, respectively, to the greatest fractional extent. This is so in the water leach solute because the compositions of the surficial salt deposits are different from those of the grains of ash. In the acid leach it is so because some species were selectively removed during the cation–proton ion-exchange reactions that occurred on the surfaces of the various minerals. Larger absolute amounts of all elements were removed by acid leach than by water leach, but for some species the difference in removal by the two types of treatment was much greater than for others (50–500 times more Cu, Fe, and Zn were removed by acid leach than by water leach, but only 2–5 times more Mn, K, Mg, Ca, and Sr). This is due to (1) the partitioning of elements between grains and surface coatings, and (2) certain minerals, with their distinctive compositions, being more susceptible to acid attack than others.
3. Strong positive and negative statistical correlations between concentrations of an element in whole ash and amounts of the same element in water leach

solute show that of the two end-member compositional types of ash, the dark-colored type (rich in opaque and dark minerals and calcic plagioclase and partly altered material, and poor in glass and sodic plagioclase) released a greater amount of material to leach treatment than did the light-colored type. The contrast may be due to different eruption times and associated plume gas chemistries for the two types of ash, to different susceptibility to grain degradation while under attack by acid droplets shortly after eruption, or to other factors.

4. In nature, much of the material present as soluble surficial coatings was removed at the time of first contact of the ash-fall blanket with waters of near-neutral pH, such as rain. This was confirmed by laboratory measurements on samples from single sites, some collected before exposure to rain, some after. The excellent cation–anion electrical balance for material apparently removed by rain confirms the common-salt compositional nature of that material.
5. Single leach treatments of ash yielded larger solute concentrations of all species measured than would be yielded by soils. However, subsequent leaching of the ash yielded only much diminished solute concentrations, in contrast to natural soils that continue to release substantial quantities of solute to subsequent wettings.
6. There is a much better correspondence between whole-ash elemental concentrations and leachable concentrations, especially acid leach concentrations, than is ever the case for soils. This is probably a reflection of the absence from the ash of clays, organic matter, and oxide coatings.

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APPENDIXES C AND D

APPENDIX C.—COMPLETE TABULATION OF ANALYTICAL RESULTS FOR LEACHATES

[Leachate determinations were done by inductively coupled plasma optical emission spectroscopy for non-anionic species and by ion chromatography for anionic species, after 14:1 water:ash or 0.01 *M* H_2SO_4 acid:ash leach treatments of 4 hours, with gentle agitation. The leachate analyses are described in Chapter B of this volume]

Coding key for eight-character sample identifiers for ash samples analyzed is as follows:

Character 1.—0="original," collected by on-site colleagues immediately after deposition
L="later," collected by authors weeks after deposition.

Character 2.—D=not rained on before collection ("dry")
R=exposed to rain before collection ("rain")

Character 3.—Initial of State in which sample was collected: W=Washington, I=Idaho, C=Colorado, M=Montana, and K=Kentucky

Characters 4 and 5.—City or town or other name for locality:
AL=Almira
CA=Coeur d'Alene
CO=Connell
CR=Columbia River basin
DE=Denver
EL=Ellensburg
EM=Emida
GL=Glasgow
HA=Harrison
HE=Helena
LE=Lewistown
MC=Miles City
MI=Missoula
ML=Moses Lake
PL=Plummer
RA=Rest area, 18 miles east of Ellensburg
RI=Richland
RL=Ralston
RR=Randle Ranger District
RZ=Ritzville
SG=Sprague
SH=Mount St. Helens
SM=St. Maries
SP=Spokane
UC=Union City
YK=Yakima
YV=Yakima Valley

Character 6.—Collector of sample:
B=Mr. Burton
C=Russ Collett
E=Ellen Hall
H=Ed Heffern
K=Thor Kiilsgaard
L=Steve Luthy
M=Dan Mueller
P=Paul Hammond
Q=Air Qual. Bur.
R=Ken Cochran
S=Wyatt Silker
T=Anita Tarbert
V=Homer Evers
W=Willard Henning
X=Hansford Shacklette
Y=Donnie Rambo
Z=Kathleen Smith

Character 7.—Sample number of sub-location number, if more than one sample was collected by a single collector at the site identified by characters 4, 5, and 6.

Character 8.—An "x" indicates that sample is one member of a duplicate pair (analytical split). In each duplicate pair one sample is labelled "x", the other "o". All samples not split for duplicate analyses are labelled "o".

WATER LEACHATE ANIONS

[Values in ppm]

Sample	Cl	F	NO_3	PO_4	SO_4	Sample	Cl	F	NO_3	PO_4	SO_4
LRWSHP10	78	4	<50	<150	310	ODWALV30	790	12	<50	<150	3,500
LRWSHP20	980	7	50	<150	870	ODWALV3X	670	25	340	<150	2,900
LRWSHP30	320	6	<50	<150	340	ODWALV40	750	11	<50	<150	3,300
LRWSHP40	400	6	50	<150	390	ODWALV50	580	11	64	<150	2,000
LRWSHP50	350	6	69	<150	400	LRWCOZ10	8	5	60	<150	53
LRWSHP60	200	6	<50	<150	280	LRWCOZ1X	5	4	50	<150	36
LRWSHP70	170	6	<50	<150	220	LRWCOZ20	6	4	150	<150	34
LRWSHP80	21	2	<50	<150	63	LRWCOZ30	7	4	56	<150	48
LRWSHP90	5	4	50	<150	35	ODWRZY10	580	20	180	<150	870
LRWSHP00	12	3	<50	<150	7	ODWRZY1X	560	10	<50	<150	820
ODWRRR10	430	8	<50	<150	2,100	ODWRZW10	480	14	<50	<150	1,000
ODWRRR1X	520	13	60	<150	2,100	ODWRZW20	160	12	100	<150	220
ODWRRR20	720	9	63	<150	2,700	LRWRZZ10	15	10	160	<150	380
ODWRRR2X	730	9	53	<150	2,800	LRWRZZ20	16	7	<50	<150	87
ODWRRR30	430	11	56	<150	2,800	LRWRZZ2X	18	6	56	<150	110
ORWRRR40	5	4	63	<150	39	LRWRLZ10	40	13	<50	<150	160
ORWRRR50	41	4	<50	<150	91	LRWRLZ20	14	5	70	<150	59
LRWYVZ10	2	3	<50	<150	56	LRWSGZ10	36	5	<50	<150	73
LRWYVZ20	3	3	53	<150	100	LRWSGZ20	160	9	310	<150	405
LRWRAZ10	13	7	51	<150	120	ORWSPT10	86	7	<50	<150	730
LRWRAZ20	7	4	93	<150	50	ODWSPK10	620	13	140	<150	2,800
LRWELZ10	46	6	74	<150	550	ODWSPK20	460	10	<50	<150	990
LRWYKZ50	97	9	130	<150	160	ODWSPK30	450	11	120	<150	1,200
LRWCRZ10	12	5	<50	<150	74	ODIPLC20	470	20	220	<150	740
LRWCRZ20	13	5	<50	<150	97	LRIHAZ10	17	3	<50	<150	32
ODWRIS10	290	8	150	<150	980	ODICAE10	340	11	<50	<150	790
LRWMLZ10	36	6	<50	<150	120	ODIEMC30	490	13	84	<150	800
LRWMLZ1X	36	5	<50	<150	110	ODIEMC3X	460	11	<50	<150	760
LRWMLZ20	30	6	<50	<150	98	ODISMC10	490	10	<50	<150	770
LRWMLZ2X	43	6	68	<150	121	ODISMC1X	460	11	<50	<150	210
LRWMLZ30	24	7	77	<150	170	ODMMIL10	540	14	<50	<150	2,200
LRWMLZ40	8	5	76	<150	45	ODMMIL20	200	10	53	<150	720
ODWALV10	610	10	70	<150	2,800	ODMMIL30	410	11	69	<150	1,900
ODWALV20	610	10	<50	<150	2,700	ODMMIL40	150	18	<50	<150	1,440

WATER LEACHATE CATIONS

[Values in ppm]

Sample	Al	Ba	Ca	Co	Cu	Fe	K	La	Li	Mg	Mn	Na	Ni	P	Si	Sr	V	Y	Zn
ODWRRR10	<10	4.3	700	0.3	<0.1	<10	73	<0.1	0.5	70	10	420	0.2	<10	30	2.7	0.3	<0.1	<0.1
ODWRRR1X	<10	4.1	740	.3	<.1	<10	73	<.1	.3	80	11	420	.9	<10	20	2.7	.2	<.1	<.1
ODWRRR20	<10	6.6	890	.4	.1	<10	88	<.1	.6	90	14	520	1.0	<10	30	3.3	<.1	<.1	<.1
ODWRRR2X	<10	3.4	920	.3	<.1	<10	87	<.1	.6	90	14	520	.8	<10	20	3.3	.1	<.1	<.1
ODWRRR30	<10	4.8	900	.3	<.1	<10	98	<.1	<.5	100	18	340	.7	<10	20	3.4	.2	<.1	<.1
ORWRRR40	<10	5.1	40	.3	<.1	<10	<10	<.1	<.1	<10	1	50	.6	<10	<10	.2	.2	<.1	<.1
LRWRAZ10	<10	4.4	80	.3	<.1	<10	<10	<.1	<.1	<10	1	50	.8	<10	<10	.4	<.1	<.1	<.1
LRWRAZ20	<10	5.1	22	.3	<.1	<10	<10	<.1	<.1	<10	0	50	.6	<10	20	.2	.2	<.1	<.1
ODWRIS10	<10	3.2	430	.3	.3	<10	54	<.1	.1	50	8	200	3.9	<10	20	1.8	.2	<.1	.3
ODWALV10	<10	3.8	970	.3	<.1	<10	96	<.1	.6	100	15	400	.8	<10	30	3.5	.1	<.1	<.1
ODWALV20	<10	4.7	980	.4	<.1	<10	95	<.1	.6	100	15	410	.6	<10	30	3.5	.2	<.1	<.1
ODWALV30	<10	6.7	1,200	.3	<.1	<10	113	<.1	.6	120	19	510	.9	<10	30	4.3	.2	<.1	<.1
ODWALV3X	<10	4.8	1,100	.4	<.1	<10	107	<.1	.3	110	18	460	.6	<10	30	3.8	.2	<.1	<.1
ODWALV40	<10	3.3	1,200	.3	<.1	<10	111	<.1	.8	110	19	480	1.0	<10	30	4.2	.2	<.1	<.1
ODWALV50	<10	5.2	720	.3	<.1	<10	76	<.1	.2	80	13	380	.6	<10	30	2.8	.2	<.1	<.1
LRWCOZ10	<10	5.9	26	.3	<.1	<10	<10	<.1	.2	<10	0	30	.6	<10	<10	.2	.1	<.1	<.1
LRWCOZ1X	<10	3.5	30	.2	<.1	<10	<10	<.1	<.1	<10	0	30	.7	<10	20	.2	.1	<.1	<.1
LRWCOZ20	60	4.8	10	2.5	<.1	<10	<10	14.0	3.8	<10	0	40	.8	<10	20	<.1	<.1	5.7	<.1
LRWCOZ30	17	4.4	15	.3	<.1	<10	<10	<.1	<.1	<10	0	20	.9	<10	110	.1	.3	<.1	<.1
ODWRZY10	<10	3.2	380	.2	<.1	<10	54	<.1	.2	60	7	350	.7	<10	10	1.6	.2	<.1	<.1
ODWRZY1X	<10	5.4	360	.3	<.1	<10	51	<.1	.1	50	6	340	.5	<10	20	1.5	.2	<.1	<.1
ODWRZW10	<10	4.7	410	.2	<.1	<10	40	<.1	.2	40	6	280	.9	<10	20	1.7	.1	<.1	<.1
LRWRZZ10	<10	3.9	100	.2	<.1	<10	<10	<.1	<.1	<10	1	80	.6	<10	20	.4	.2	<.1	<.1
LRWRZZ20	<10	5.3	35	.3	<.1	<10	<10	<.1	<.1	<10	0	80	.8	<10	20	.2	.2	<.1	<.1
LRWRZZ2X	<10	4.0	70	.2	<.1	<10	<10	<.1	<.1	10	1	80	.6	<10	20	3.3	<.1	<.1	<.1
ORWSPT10	<10	4.2	280	.2	<.1	<10	35	<.1	.1	30	3	140	.9	<10	30	1.0	.2	<.1	<.1
ODWSPK10	<10	3.6	1,100	.3	<.1	<10	89	<.1	.4	90	16	400	.7	<10	30	3.8	.2	<.1	<.1
ODWSPK20	<10	4.4	410	.3	<.1	<10	48	<.1	.1	50	8	290	.8	<10	20	1.8	.2	<.1	<.1
ODWSPK30	<10	3.4	460	.2	<.1	<10	53	.1	.1	50	9	290	.6	<10	20	1.9	.2	<.1	<.1
ODIPLC20	<10	5.8	320	.3	<.1	<10	38	.2	<.1	40	7	300	.8	<10	20	1.5	.1	<.1	<.1
LRIHAZ10	<10	5.4	120	.3	.3	10	30	<.1	<.1	30	4	90	.7	<10	20	.8	.2	<.1	<.1
ODICAE10	<10	6.7	410	.4	<.1	<10	38	<.1	.3	40	3	230	.6	<10	30	1.6	.2	<.1	<.1
ODIEMC30	<10	3.2	330	.3	<.1	<10	36	<.1	<.1	40	6	270	.4	<10	<10	1.5	.2	<.1	<.1
ODIEMC3X	<10	2.2	330	.3	<.1	<10	37	<.1	<.1	40	6	260	.8	<10	10	1.6	.1	<.1	<.1
ODISMC10	<10	5.3	300	.2	<.1	<10	38	<.1	.3	40	6	260	.8	<10	<10	1.4	.2	<.1	<.1
ODISMC1X	<10	2.9	300	.3	<.1	<10	38	<.1	<.1	40	6	250	.7	<10	<10	1.4	<.1	<.1	<.1
ODMMIL20	<10	3.9	260	.3	<.1	<10	30	<.1	.1	30	3	200	.9	<10	10	1.3	.2	<.1	<.1
ODMMIL30	<10	4.8	700	.2	.2	<10	59	<.1	.3	60	9	310	.6	<10	20	2.6	.1	<.1	<.1
ODMMIL40	<10	4.9	540	.3	.3	<10	49	<.1	.1	50	8	230	.6	<10	20	2.0	.2	<.1	<.1

H_2SO_4 LEACHATE ANIONS

[Values in ppm]

Sample	Cl	F	NO_3	PO_4	Sample	Cl	F	NO_3	PO_4	Sample	Cl	F	NO_3	PO_4
LRWSHP10	130	55	<50	1,150	LRWYKZ50	79	45	200	780	ODWRZW20	200	40	71	730
LRWSHP20	1,100	62	<50	1,130	LRWCRZ10	35	44	150	900	LRWRZZ10	41	46	<50	850
LRWSHP30	550	54	<50	1,000	LRWCRZ20	36	43	78	880	LRWRZZ20	42	41	53	830
LRWSHP40	380	37	<50	700	ODWRIS10	370	60	210	980	LRWRZZ2X	46	42	<50	880
LRWSHP50	350	40	<50	750	LRWMLZ10	73	48	110	1,000	LRWRLZ10	80	42	59	1,000
LRWSHP60	260	52	<50	1,080	LRWMLZ1X	61	14	120	900	LRWRLZ20	53	42	<50	930
LRWSHP70	230	50	<50	1,150	LRWMLZ20	74	47	64	980	LRWSGZ10	80	46	<50	1,000
LRWSHP80	34	14	<50	430	LRWMLZ2X	73	43	69	900	LRWSGZ20	230	47	<50	1,000
LRWSHP90	29	34	67	800	LRWMLZ30	56	46	78	950	ORWSPT10	140	63	<50	1,030
LRWSHP00	29	17	<50	520	LRWMLZ40	31	45	<50	900	ODWSPK10	770	88	<50	1,250
ODWRRR10	580	69	110	1,100	ODWALV10	710	83	<50	1,300	ODWSPK20	510	55	<50	1,000
ODWRRR1X	330	67	95	1,020	ODWALV20	840	34	170	1,250	ODWSPK30	460	61	<50	1,050
ODWRRR20	860	66	56	930	ODWALV30	930	93	110	1,350	ODIPLC20	540	43	69	880
ODWRRR2X	840	67	<50	900	ODWALV3X	860	84	97	1,350	LRIHAZ10	6	36	<50	750
ODWRRR30	540	82	60	1,200	ODWALV40	900	90	<50	1,330	ODICAE10	440	56	60	1,000
ORWRRR40	24	23	50	520	ODWALV50	700	75	76	1,180	ODIEMC30	610	46	53	950
ORWRRR50	62	10	66	250	LRWCOZ10	20	36	<50	950	ODIEMC3X	570	49	<59	850
LRWYVZ10	24	32	70	800	LRWCOZ1X	32	48	77	1,230	ODISMC10	280	46	<50	800
LRWYVZ20	28	36	71	880	LRWCOZ20	34	41	70	1,050	ODISMCIX	570	46	59	980
LRWRAZ10	40	41	<50	1,180	LRWCOZ30	23	53	70	1,350	ODMMIL10	320	81	70	1,250
LRWRAZ20	28	38	<50	880	ODWRZY10	750	48	65	900	ODMMIL20	130	48	63	900
LRWELZ10	80	60	73	1,030	ODWRZY1X	680	48	<50	830	ODMMIL30	490	71	91	1,130
LRWYKZ40	130	59	110	930	ODWRZW10	290	52	78	900	ODMMIL40	200	29	<50	1,130

H_2SO_4 LEACHATE CATIONS

[Values in ppm]

Sample	Al	Ba	Ca	Co	Cu	Fe	K	La	Li	Mg	Mn	Na	Ni	P	Si	Sr	V	Y	Zn
ODWRRR10	530	1.8	2,100	0.5	5.0	820	540	2.7	1.0	500	63	510	0.7	390	280	6.6	1.7	2.9	4.3
ODWRRR1X	545	2.0	2,200	.5	5.3	820	520	3.2	.7	500	66	530	.8	400	290	6.9	1.7	3.1	4.4
ODWRRR20	540	2.2	2,300	.5	6.7	620	500	3.0	1.0	460	63	610	1.0	310	280	7.1	1.5	2.8	7.0
ODWRRR2X	516	2.1	2,200	.6	6.9	580	430	2.8	.8	420	60	600	1.1	300	250	6.8	1.4	2.7	7.1
ODWRRR30	582	2.5	2,500	.7	7.1	740	530	3.2	.9	490	72	460	.9	430	290	7.9	1.6	3.3	6.0
ORWRRR40	196	1.7	740	<.1	2.9	270	170	1.4	.2	150	16	100	<.1	230	120	1.8	.6	1.2	1.7
LRWRAZ10	207	1.8	1,100	.3	3.1	340	200	1.8	<.1	200	23	78	.4	400	120	2.5	.9	1.8	1.9
LRWRAZ20	358	2.0	1,000	.2	6.5	380	230	1.8	.1	230	24	150	.1	320	170	2.8	1.0	1.7	2.8
ODWRIS10	365	1.5	1,500	.3	8.7	360	290	2.7	.3	260	30	270	8.2	400	190	4.3	1.4	2.6	9.9
ODWALV10	543	2.1	2,600	.7	5.3	790	530	3.3	1.0	500	74	470	1.1	460	290	7.5	1.6	3.5	4.9
ODWALV20	549	2.5	2,600	.7	4.9	810	530	4.0	.9	510	75	480	1.4	470	300	7.6	1.7	3.6	4.9
ODWALV30	602	1.9	3,000	.4	5.6	780	530	4.1	.9	500	81	600	1.2	490	300	8.7	1.7	3.6	5.2
ODWALV3X	565	2.3	2,700	.7	4.9	750	500	3.9	1.2	480	77	530	.8	480	300	8.2	1.6	3.6	5.0
ODWALV40	604	2.2	2,900	.6	5.9	790	540	3.8	1.2	510	80	590	.8	480	310	8.6	1.8	3.7	5.1
ODWALV50	530	2.0	2,100	.4	6.7	630	440	3.0	.6	410	57	490	.3	430	260	6.4	1.4	2.9	4.2
LRWCOZ10	210	2.0	990	.3	3.3	260	170	1.8	<.1	170	20	58	.6	390	130	2.1	.8	1.9	1.6
LRWCOZ1X	240	2.2	1,100	.3	3.5	300	220	2.2	<.1	210	22	73	.3	420	160	2.4	.9	2.1	2.2
LRWCOZ20	328	1.9	960	.2	5.6	310	190	1.8	.3	190	20	120	.5	370	160	2.5	.9	1.8	1.9
LRWCOZ30	401	2.3	2,100	.4	.4	23	470	1.8	.1	460	36	20	.9	450	630	13.0	.3	2.6	1.3
ODWRZY10	395	2.1	1,300	.3	6.7	380	280	1.7	.7	270	32	480	.3	310	180	4.5	.9	1.8	2.7
ODWRZY1X	401	1.9	1,300	.4	6.6	380	290	2.0	.6	280	33	500	.4	320	180	4.3	1.0	1.9	2.5
ODWRZW10	387	2.1	1,400	.2	7.2	350	220	1.7	<.1	220	28	410	.3	340	170	4.2	.9	1.8	2.4
LRWRZZ10	399	2.2	1,100	.2	6.7	400	250	1.8	.3	240	21	220	<.1	310	190	3.3	.9	1.7	1.9
LRWRZZ20	411	1.8	1,000	<.1	7.0	400	250	1.7	.1	240	21	210	.2	310	200	3.0	.9	1.6	2.2
LRWRZZ2X	397	2.1	1,000	.2	6.4	410	230	1.5	.3	230	22	200	.6	320	180	3.0	1.0	1.8	2.3
ORWSPT10	464	2.1	1,500	.5	6.2	550	360	2.5	.2	340	39	230	.5	360	20	4.2	1.3	2.5	3.7
ODWSPK10	541	1.8	2,600	.3	7.0	670	470	3.4	.6	440	67	500	.7	450	280	7.5	1.5	3.5	5.2
ODWSPK20	412	2.5	1,500	.3	9.3	400	290	2.2	.3	270	37	420	<.1	390	200	4.7	1.1	2.3	2.9
ODWSPK30	397	1.5	1,500	.3	8.5	380	280	2.2	.4	260	37	410	.4	380	180	4.6	1.1	2.3	2.9
ODIPLC20	368	3.2	1,200	.2	9.2	280	210	1.7	.2	200	25	410	.3	330	170	4.0	.9	1.8	2.1
LRIHAZ10	354	2.6	910	.4	5.3	350	210	1.7	.2	200	17	160	<.1	330	160	3.0	.8	1.7	2.6
ODICAE10	422	2.1	1,800	.2	7.0	440	280	2.2	.2	270	40	380	<.1	360	240	5.7	1.0	2.2	12.0
ODIEMC30	360	2.0	1,200	.2	9.2	260	200	1.8	.2	200	23	390	.2	330	160	4.1	.8	1.8	2.5
ODIEMC3X	337	1.8	1,200	.2	8.7	250	190	1.6	.4	180	23	390	.8	330	150	3.9	.9	1.7	2.2
ODISMC10	358	2.1	1,200	.2	8.1	280	200	1.6	.1	190	25	380	<.1	330	160	3.9	.8	1.8	2.3
ODISMC1X	354	1.5	1,200	.2	7.5	270	190	1.6	.2	190	25	390	<.1	340	150	3.8	.8	1.8	2.3
ODMMIL20	346	2.0	1,200	.2	5.5	290	190	1.9	.2	190	21	330	<.1	350	160	3.8	.8	1.8	2.3
ODMMIL30	503	2.2	2,000	.3	8.4	380	310	3.2	.6	300	39	440	.8	420	230	6.1	1.5	3.0	3.4
ODMMIL40	453	2.0	1,700	.3	5.2	420	300	2.9	.5	280	31	320	.4	420	230	4.8	1.4	2.7	3.7

HNO_3 LEACHATE ANIONS

[Values in ppm]

Sample	F	Cl	PO_4	SO_4
ODWALV30	77	880	1,200	4,100
ODWALV3X	80	770	1,200	3,600
ODWRZY10	45	660	400	1,200
LRWRZZ2X	39	38	560	400
LRIHAZ10	32	30	470	500

OTHER MEASUREMENTS

Sample	Specific conductivity (micromhos/cm)	Cation exchange capacity (meq/100g)				Sample	Specific conductivity (micromhos/cm)	Cation exchange capacity (meq/100g)			
		Ca	K	Mg	Na			Ca	K	Mg	Na
ODWRRR10	0.47	6.2	0.2	0.8	1.8	ODWRZY1X	0.32	3.0	<0.1	0.6	1.5
ODWRRR1X	.50	6.4	.2	.8	1.8	ODWRZW10	.32	3.2	<.1	.4	1.2
ODWRRR20	.63	7.1	.1	1.0	2.2	LRWRZZ10	<.20	1.7	<.1	.2	.4
ODWRRR2X	.66	7.5	.6	1.0	2.5	LRWRZZ20	<.20	1.4	<.1	.2	.4
ODWRRR30	.55	7.5	.2	1.1	1.4	LRWRZZ2X	<.20	1.5	<.1	.2	.4
ORWRRR40	<.20	.5	<.1	<.1	<.1	ORWSPT10	<.20	3.2	<.1	.5	.5
LRWRAZ10	<.20	1.4	<.1	<.1	.2	ODWSPK10	.65	7.7	<.1	.9	1.7
LRWRAZ20	<.20	1.2	<.1	<.1	.2	ODWSPK20	.30	3.1	<.1	.5	1.2
ODWRIS10	.33	3.1	<.1	.5	.8	ODWSPK30	.35	3.6	<.1	.6	1.2
ODWALV10	.67	7.8	.1	1.0	1.7	ODIPLC20	.31	2.3	<.1	.4	1.1
ODWALV20	.63	7.8	.1	1.1	1.7	LRIHAZ10	<.20	1.0	<.1	.3	.2
ODWALV30	.80	10.3	.2	1.2	2.2	ODICAE10	.32	4.1	<.1	.5	1.0
ODWALV3X	.72	8.7	.2	1.2	2.0	ODIEMC30	.30	2.3	<.1	.4	1.1
ODWALV40	.69	8.1	.2	1.2	2.0	ODIEMC3X	.20	2.4	<.1	.4	1.1
ODWALV50	.38	5.6	.2	.8	1.6	ODISMC10	.30	2.3	<.1	.4	1.0
LRWCOZ10	<.20	.8	<.1	<.1	<.1	ODISMC1X	.28	1.9	<.1	.3	.9
LRWCOZ1X	<.20	.9	<.1	.1	<.1	ODMMIL20	.23	2.1	<.1	.3	.9
LRWCOZ20	<.20	.8	<.1	<.1	<.1	ODMMIL30	.39	5.0	<.1	.6	1.4
LRWCOZ30	<.20	6.9	.9	3.8	<.1	ODMMIL40	.33	3.5	.2	.4	.9
ODWRZY10	.35	2.9	<.1	.6	1.4						

APPENDIX D.—ESTIMATE OF ANALYTICAL ERROR IN CHEMICAL CONCENTRATION DATA FOR LEACHATES

Analytical precision is estimated by the geometric error for each chemical species determined. The geometric error is the antilog of the log standard error, and is calculated from the logarithms of the differences in measured concentrations between samples that are members of pairs of analytical replicates (splits). The use of logarithmic data minimizes the perturbing effect of uncommon, extreme-value data upon the final value of the error parameter. The number of sample pairs from whose data the error parameter calculation was made are also listed in the appendix.

For anions (Cl^-, F^-, PO_4^{-3}, and SO_4^{-2}), geometric error was calculated from concentration values of four pairs of samples. For samples with qualified values (below detection limit, where only an upper limit is given), a value of 0.7 times the detection limit was substituted and used in the calculation. The number of pairs free of qualified values is given in the table.

LEACHATE CHEMICAL ANALYSES AND CATION EXCHANGE CAPACITY

[Geometric error for specific conductivity, 1.10, determined on six pairs]

Chemical species	Geometric error	Number of pairs	Chemical species	Geometric error	Number of pairs	Chemical species	Geometric error	Number of pairs
Deionized water leach			H_2SO_4 leach			Cation exchange capacity		
Cl	1.16	10	Cl	1.27	10	Ca	1.07	8
F	1.30	10	F	1.33	10	K	1.49	3
NO_3	2.00	2	NO_3	1.36	4	Mg	1.11	7
SO_4	1.37	10	PO_4	1.09	10	Na	1.05	7
Ba	1.34	8	Al	1.04	8			
Ca	1.17	8	Ba	1.11	8			
Co	1.22	8	Ca	1.04	8			
K	1.02	6	Co	1.32	7			
Li	1.60	4	Cu	1.05	8			
Mg	1.10	6	Fe	1.04	8			
Mn	1.22	8	K	1.07	8			
Na	1.03	8	La	1.08	8			
Ni	1.49	8	Li	1.42	7			
Si	1.38	5	Mg	1.06	8			
Sr	1.87	8	Mn	1.03	8			
V	1.47	5	Na	1.06	8			
			Ni	1.54	7			
			P	1.02	8			
HNO_3 leach			Si	1.06	8			
Cl	1.85	1	Sr	1.04	8			
F	1.12	1	V	1.06	8			
PO_4	1.21	1	Y	1.04	8			
SO_4	1.52	1	Zn	1.08	8			

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