

AN ABSTRACT OF THE THESIS OF

GLENN ARNOLD BORCHARDT for the Ph. D.
(Name) (Degree)

in SOILS presented on August 15, 1969
(Major) (Date)

Title: NEUTRON ACTIVATION ANALYSIS FOR CORRELATING
VOLCANIC ASH SOILS

Abstract approved: Redacted for Privacy
M. E. Harward

The objectives of this study were: 1) To determine the trace element differences between sample sites and between deposits of Mazama, Newberry, Glacier Peak, and St. Helens volcanic ash in the Pacific Northwest, 2) To correlate volcanic ash in peat bogs with volcanic ash from upland sites, 3) To verify Mazama ash as parent material of soils occurring along a 450 km transect in Oregon, and 4) To determine the trace element composition of clays derived from volcanic ash.

Samples were irradiated in a TRIGA Reactor, followed by detection of elements with a high resolution 30cc Ge(Li) semiconductor detector and a 4096 multichannel analyzer. Gamma-ray spectra were analyzed with a computer program to determine the following average composition in Mazama volcanic glass:

Element	ppm	\pm s	Element	ppm	\pm s	Element	ppm	\pm s
Na	3.44 %	.16%	Sm	5.0	.4	Hf	6.4	.4
Rb	50.	8.	Eu	0.89	.08	Ta	0.23	.08
Cs	3.9	.7	Tb	0.83	.14	Co	2.6	.3
Ba	660.	70.	Yb	3.5	.7	Fe	1.48%	.09%
La	22.	2.	Lu	0.56	.07	Sc	6.4	.4
Ce	44.	3.	Th	6.5	.3	Cr	1.6	.6

Field variability of Mazama and Newberry ash deposits in Oregon was about 5%, whereas the variability of the crystal-rich Glacier Peak and St. Helens ash of Washington was greater. Low coefficients of variation of mean ratios (variation analysis) and discriminant function analysis of the concentrations of 19 elements classified unidentified volcanic ash samples with ash from known sources. The activation analysis data support previous identification of Mazama ash in the Pacific Ocean, and at Steptoe Canyon, Washington and Edmonton, Alberta.

At least 18 cm of Mazama ash (dated at 6500-7420 radio-carbon years) occurred in peat bogs up to 450 km from the source at Crater Lake, Oregon. An older ash layer from Glacier Peak (> 9650 years) occurs in northeastern Oregon. Soils in northeastern Oregon may contain about 5 cm of St. Helens Y, a 3000 year old ash, mixed into upper horizons.

The trace element compositions of volcanic glass from C horizons of soils along a 450 km transect in Oregon correlate with ejecta from Mt. Mazama. Enrichment and leaching effects in

weathered horizons interfere with correlations that use variation analysis. However, the discriminant function classified Al and AC as well as C horizon samples with the Mazama group. Enrichment of transition metals in upper horizons occurred in the following order: $Cr > Co > Fe = Sc$. Na/Fe and Na/Co ratios were measures of weathering intensity. The abundances of Hf, Th, and the rare earth elements remained relatively unchanged throughout 6600 years of weathering. Sc/Fe, Th/Hf, La/Sm, and Th/Sm ratios were not changed appreciably by weathering. These stable ratios were used with discriminant function analysis to aid in correlation of weathered soil horizons.

Weathering in soils developed on volcanic ash resulted in enrichment of trace elements in sand-size volcanic glass. This led to a study of the $<2\mu$ weathering products. The clay fractions of soils developed from Mazama ash contained phases other than glass. Rare earth element abundances were about three times the amounts found for unweathered volcanic glass. Sodium in the $<2\mu$ fraction was only 10% of the amount in glass while the transition metals were as much as nine times higher in clay than in glass. Such increases were remarkably similar for clays from five soils along the 450 km transect of Mazama volcanic ash derived soils. The abundances of Cr and Co, as well as Fe and Sc in clay fractions increased with weathering intensity in the Day Creek soil. The Sc/Fe ratio was about 4×10^{-4} for both clay and the Mazama volcanic glass from

which it was derived. Chemical treatments revealed the solubilities of rare earth elements in Day Creek clay to be greater than those in the more intensely weathered Parkdale clay. High Sc/Fe ratios indicated a possible detrital origin for the crystalline clay minerals comprising 20% of the clay fractions in both soils. Clays from non-ashy soils of western Oregon also contained high concentrations of transition metals and rare earth elements. An attempt to correlate clays from different volcanic ash layers revealed chemical similarities between soil clays from Glacier Peak and Mazama ash and lapilli, but the chemical composition was different for soil clays formed on Newberry lapilli.

Neutron Activation Analysis
For Correlating Volcanic Ash Soils

by

Glenn Arnold Borchardt

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

June 1970

APPROVED:

Redacted for Privacy

Professor of soils
in charge of major

Redacted for Privacy

Head of Department of Soils

Redacted for Privacy

Dean of Graduate School

Date thesis is presented August 15, 1969

Typed by Muriel Davis for Glenn Arnold Borchardt

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. M. E. Harward for his guidance and stimulating discussions. The suggestions and instructions in the technical aspects of activation analysis given by Dr. R. A. Schmitt were invaluable. Special thanks are extended to Drs. E. G. Knox, E. M. Taylor, and C. T. Youngberg for their interest in this study. The author is indebted to those individuals who contributed samples for analysis and to those members of the Department of Soils who helped collect samples. The assistance of J. A. Norgren in obtaining ash from peat bogs was extremely helpful. Special thanks go to Dr. A. A. Theisen who suggested this approach to the identification of volcanic ash deposits. I wish to thank my wife, Marilyn, for her encouragement and helpfulness during the investigation and throughout the preparation of this dissertation.

Partial support of the Atomic Energy Commission, contract AT(45-1)-2062, is gratefully acknowledged.

TABLE OF CONTENTS

		<u>Page</u>
	INTRODUCTION	1
	Statement of the Problem	2
	Objectives	3
I	TRACE ELEMENT CHARACTERIZATION AND CORRELATION OF CASCADE RANGE PYROCLASTICS	5
	Introduction	5
	Materials and Methods	9
	Standard Solutions	9
	Standard Rocks	9
	Standard Volcanic Ash Samples	9
	Unidentified Volcanic Ash	13
	Isolation of Volcanic Glass	15
	Analytical Methods	16
	Results and Discussion	18
	Standard Rocks	18
	Whole Samples Compared to Glassy Fractions	19
	Variability Within Deposits	21
	Differences Between Volcanic Ash Deposits	26
	Elemental Abundances	26
	Rare Earth Element Distributions	27
	Correlation of Samples	29
	Statistical Methods	29
	Correlation of Unidentified Samples	40
	Conclusions	49
II	CORRELATION OF VOLCANIC ASH LAYERS OF PEAT BOGS	51
	Introduction	51
	Materials and Methods	53
	Results and Discussion	57
	Radio- Carbon Dates	57
	INAAC	58
	Mazama Ash	62
	Glacier Peak Ash	67
	St. Helens Y Ash	67
	Elemental Ratios	70
	Conclusions	76

	<u>Page</u>	
III	CORRELATION OF VOLCANIC ASH SOILS	77
	Introduction	77
	Materials	79
	Methods	79
	Results and Discussion	83
	Vertical Homogeneity of Mazama Pumice	84
	Correlation of Soil Parent Materials with Mazama Volcanic Ash	86
	Weathering Effects	93
	Elemental Ratios for Correlating Soils	97
	Removal of Iron Oxide Coatings	106
	Conclusions	110
IV	TRACE ELEMENT CONCENTRATION IN AMORPHOUS CLAYS OF VOLCANIC ASH SOILS	111
	Introduction	111
	Materials	113
	Methods	116
	Results and Discussion	116
	Less than Two Micron Glass	116
	Trace Element Concentration as a Function of Depth	120
	Chemical Pretreatments	127
	Origin of 2:1 Layer Silicates	134
	Comparisons of Mazama Soil Clays to Weathering Products of Other Materials	135
	Clays from Other Volcanic Ash Deposits Comparison to Mazama Volcanic Glass	138
	Variation Analysis	141
	REE Distribution Patterns	143
	Conclusions	145
	BIBLIOGRAPHY	147
	APPENDICES	152

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
	I. TRACE ELEMENT CHARACTERIZATION AND CORRELATION OF CASCADE RANGE PYRO- CLASTICS	
1	Locations of volcanic ash sampling sites in the Pacific Northwest	6
2	Example of gamma-ray spectrum obtained with a Ge(Li) detector and a 4096 multichannel analyzer	17
3	Rare earth element (REE) distribution patterns for standard ash samples	28
	II. CORRELATION OF VOLCANIC ASH LAYERS OF PEAT BOGS	
1	Locations of peat bogs from which volcanic ash samples were obtained for activation analysis	52
	III. CORRELATION OF VOLCANIC ASH SOILS	
1	Locations of the five transect soils derived from Mazama ash, including Parkdale loam sampled near Mt. Hood	80
2	Elemental enrichment in Mazama volcanic glass in relation to soil depth	94
	IV. TRACE ELEMENT CONCENTRATION IN AMORPHOUS CLAYS OF VOLCANIC ASH SOILS	
1	Locations of soils and volcanic ash deposits from which clays were obtained for activation analysis	114
2	High angle X-ray diffraction patterns of residues from clays treated for removal of amorphous material	121
3	Low angle X-ray diffraction patterns of residues from clays treated for removal of amorphous material	122

<u>Figure</u>		<u>Page</u>
4	Effect of soil weathering on elemental enrichment in soil clays derived from Mazama ash	124
5	Scandium in clay and very fine sand-size glass of Day Creek soil horizons	126
6	La and Ce in relation to Sm for clays and glass from Mazama, Newberry, and Glacier Peak volcanic ash	144

LIST OF TABLES

<u>Table</u>	<u>Page</u>
I. TRACE ELEMENT CHARACTERIZATION AND CORRELATION OF CASCADE RANGE PYROCLASTICS	
1	Analyses of USGS rock standards and comparisons to INAA results of Gordon <u>et al.</u> (1968) 10
2	Volcanic ash samples used as standards 12
3	Unidentified volcanic ash samples 3
4	Comparison of whole samples of volcanic ash to glassy fractions 20
5	Analyses of volcanic glass isolated from standard ash layers 22
6	Ratios to Mazama volcanic glass composition (average of eight samples) for regional samples 31
7	Coefficients of variation (%) for standard ash samples normalized to average elemental abundances for Mazama; Newberry; Glacier Peak; St. Helens Y, W, and T layers 34
8	Multiple correlation coefficients for elemental abundances for nineteen standard ash samples (glassy isolates) from pyroclastics of the Pacific Northwest 38
9	Coefficients and constants of the discriminant functions for INAAC of five ash layers of the Pacific Northwest 39
10	Discriminant values for standard ash samples 41
11	Coefficients of variation (%) for regional ash samples 43
12	Discriminant values for regional ash samples 44

LIST OF TABLES (continued)

<u>Table</u>		<u>Page</u>
II. CORRELATION OF VOLCANIC ASH LAYERS OF PEAT BOGS		
1	Volcanic ash layers sampled in peat bogs of eastern Oregon and Washington	55
2	Activation analysis of volcanic ash from peat bogs (glassy separates 125-63 μ)	59
3	Coefficients of variation (%) for volcanic ash from peat bogs	63
4	Discriminant values for volcanic ash sampled in peat bogs	64
5	Elemental ratios and abundances used for correlating volcanic ash layers collected from peat bogs	72
6	Average elemental ratios and abundances of standard volcanic ash samples	74
7	Discriminant values for equations derived from elemental ratios least affected by weathering (Chapter III)	75
III. CORRELATION OF VOLCANIC ASH SOILS		
1	Volcanic ash soils sampled at intervals along the axis of the main lobe of the Mt. Mazama eruption (including Parkdale loam from near Mt. Hood)	81
2	Vertical trace element homogeneity of Mazama pumice at Huckleberry Spring (125-63 μ glassy fractions from ground lapilli)	85
3	Ratios to Mazama volcanic glass composition for transect soils developed in Mazama ash (125-63 μ glassy fraction)	87
4	Coefficients of variation (%) for analyses of glassy fine sand fractions of the Mazama transect soils	90
5	Discriminant values for soils developed in Mazama ash (125-63 μ glassy fractions)	92

LIST OF TABLES (continued)

<u>Table</u>		<u>Page</u>
6	Elemental ratios and elemental abundances used for correlating weathered volcanic ash	96
7	Multiple correlation coefficients for elemental abundances determined for seventeen soil horizon samples from the Mazama transect soils (125-63 μ glassy isolates)	98
8	Elemental ratios and statistics of standard volcanic ash samples	101
9	Coefficients and constants of the discriminant functions for INAAC with elemental ratios diminishing the effects of weathering upon classifications	103
10	Discriminant values for equations derived from elemental ratios least affected by weathering in volcanic ash soils	105
11	Effect of iron removal treatment upon 125-63 μ glassy fractions from soils	108
IV. TRACE ELEMENT CONCENTRATION IN AMORPHOUS CLAYS OF VOLCANIC ASH SOILS		
1	Clay samples and pretreatments used	115
2	Average analyses and coefficients of variation for volcanic glass and for clays separated from AC horizons of the Mazama transect soils	118
3	Ratios to Mazama volcanic glass composition for clay fractions from AC horizons of the transect soils	119
4	Ratios to Mazama volcanic glass composition for clays from a depth sequence for the Day Creek site	123
5	Ratios to Mazama volcanic glass composition for Day Creek AC horizon clay receiving various pretreatments	128
6	Ratios to Mazama volcanic glass composition for Parkdale AC horizon clay receiving various pretreatments	129

LIST OF TABLES (continued)

<u>Table</u>		<u>Page</u>
7	Ratios to Mazama volcanic glass composition for additional soil clays receiving the 0.05 <u>N</u> HNO ₃ treatment compared to untreated clays	130
8	Trace element allocation to the chemical phases present in Day Creek and Parkdale clay fractions	132
9	Ratios to Mazama volcanic glass composition for clays from western Oregon soils and for ferruginous bauxite	137
10	Ratios to Mazama volcanic glass composition for clays separated from Newberry, Glacier Peak, St. Helens Y, and Mazama volcanic ash samples	140
11	Coefficients of variation (%) for clays found in pyroclastics of the Pacific Northwest	142

LIST OF APPENDICES

	<u>Page</u>
I Neutron Activation for Distinguishing Cascade Range Pyroclastics	152
II Vesicular Pores of Pumice by Mercury Intrusion	155
III Separation of Glass from Volcanic Ash	157
IV Sample Site Descriptions	160
V Glass Percentages in Volcanic Ash	164
VI Concentrations of Monitors and Gamma-ray Peaks Used for Calculation of Abundances	167
VII Microscope Observations on Glass Separates Used for Activation Analysis	168
VIII Preparation of Volcanic Ash Samples	171
IX Dispersion of Clay with NH_4OH	173
X Clay Pretreatments Used in This Study	175
XI Detailed Instructions for SPECTRA: A Computer Program Developed for Analyzing Ge(Li) Gamma-ray Spectra	177
XII FORTRAN IV Programs Developed for Automated Data Processing of Activation Analysis Results	204
XIII Suggestions for Further Study	218

NEUTRON ACTIVATION ANALYSIS FOR CORRELATING VOLCANIC ASH SOILS

INTRODUCTION

Soils developed in volcanic ash layers present excellent opportunities for study of soil formation. Such a deposit was laid down by the cataclysmic eruption of Mt. Mazama 6600 years ago (Allison, 1966a; Williams, 1942). The eruption left a huge cavity now known as Crater Lake, Oregon in place of the once majestic Mt. Mazama. An extensive sheet of volcanic ash is evidenced by deposits over three meters thick at 90 kilometers from Crater Lake. Since the duration of weathering and the parent material can be determined, future soil studies of Mazama ash can limit the variables to climatic, biotic, and relief factors. However, other numerous volcanic vents exist in the Pacific Northwest. Some of these might have contributed pyroclastic material to soils formed from volcanic ash. Studies across a transect of soils from Mazama ash require recognition of the deposit and its distinction from other ash layers.

The importance of volcanic ash soils in Oregon has been generally underestimated. Intensively farmed soils in the Willamette River Valley of western Oregon have received much greater attention than the volcanic ash which exerts a major effect upon forested soils in eastern Oregon. The demand for increased supplies of lumber

products and more intensive management of these forests will likely promote interest in volcanic ash soils in the future. Agricultural soils containing volcanic ash usually occur in valley bottoms and other landscape positions where other parent materials have been mixed with them. Therefore, studies of volcanic ash soils were begun in upland areas containing "pure" systems obviously dominated by volcanic ash deposition. After the "pure" systems are better understood, studies on the more complex systems will be conducted.

Statement of the Problem

The problem of identification of ash deposits received the major emphasis throughout the course of this study. Primary emphasis was placed on the Mazama ash. Scientists investigating volcanic ash soils in Oregon should properly identify the parent material being studied and recognize the possible mixture of several ash layers. Identification of the volcanic ash parent material becomes complicated further by chemical weathering in soils. Therefore the effects of weathering and the formation of new phases in volcanic ash were also considered.

Volcanic ash layers have been correlated by using methods such as the determination of mineral composition (Wilcox, 1965) and the index of refraction of glass shards and minerals (Powers and Wilcox, 1964; Fryxell, 1965; Steen and Fryxell, 1965). Major

element analyses (Powers and Wilcox, 1964) and TiO_2 analyses (Czamanski and Porter, 1965) were used to distinguish between Mazama and Glacier Peak ash layers. Carbon dating and stratigraphic evidence have been useful in many volcanic ash correlations. Electron microprobe analysis of glass shards produced major element compositions distinctive for unweathered Mazama, Glacier Peak, and St. Helens pyroclastics (Smith and Westgate, 1969). However, major element compositions are likely to be affected by post-depositional changes produced by weathering. Some parameters such as index of refraction and mineral composition may show considerable overlap for different ash layers. Identifications are usually made on rather unweathered materials and with a combination of these methods.

Instrumental neutron activation analysis (INAA) enables one to determine a large number of trace elements in geologic materials much more rapidly than conventional wet chemical methods. It was hypothesized that the trace element compositions of pyroclastics would be dissimilar enough to distinguish the various layers in the Pacific Northwest.

Objectives

The major objectives of this study were:

1. To determine the trace element differences between

sample sites within the same deposit and between deposits of Mazama, Newberry, Glacier Peak, and St. Helens ash in the Pacific Northwestern United States;

2. To correlate the volcanic ash layers found in peat bogs with volcanic ash from upland sites;

3. To verify Mazama ash as the parent material of soils occurring along a 450 km transect in Oregon;

4. To determine the trace element composition of clay fractions from volcanic ash soils and their relationship to the glass from which they may be derived.

The text of this dissertation is organized in chapters pertaining to each of these objectives.

I. TRACE ELEMENT CHARACTERIZATION AND CORRELATION OF CASCADE RANGE PYROCLASTICS

Introduction

The extensive deposits of volcanic ash in the Pacific Northwest provide excellent stratigraphic markers for Quaternary research in archeology, oceanography, glacial geology, palynology, and soils. Studies of soil formation involving volcanic ash parent materials require a knowledge of the identity and characteristics of the particular deposit.

The most important deposit of volcanic ash in Oregon resulted from eruption of Mt. Mazama (now Crater Lake, Oregon) 6,600 years ago (Allison, 1966a). The fallout pattern for this ash deposit includes most of Oregon and Washington, and parts of Idaho, Montana, Nevada, Alberta, and British Columbia (Figure 1). An earlier eruption of Glacier Peak about 12,000 ybp (years before present) (Fryxell, 1965) distributed volcanic ash throughout Washington, Idaho, Montana, and the northeastern part of Oregon. Three eruptions of Mt. St. Helens in Washington have been designated as layers Y (3200 ybp), W (300 ybp), and T (160 ybp) (Crandell et al., 1962). Layer Y also has been identified in Alberta and British Columbia (Smith and Westgate, 1969). Less extensive deposits of Newberry (2000 ybp) (Higgins and Waters, 1968) and Devils Hill pumice occur in Oregon

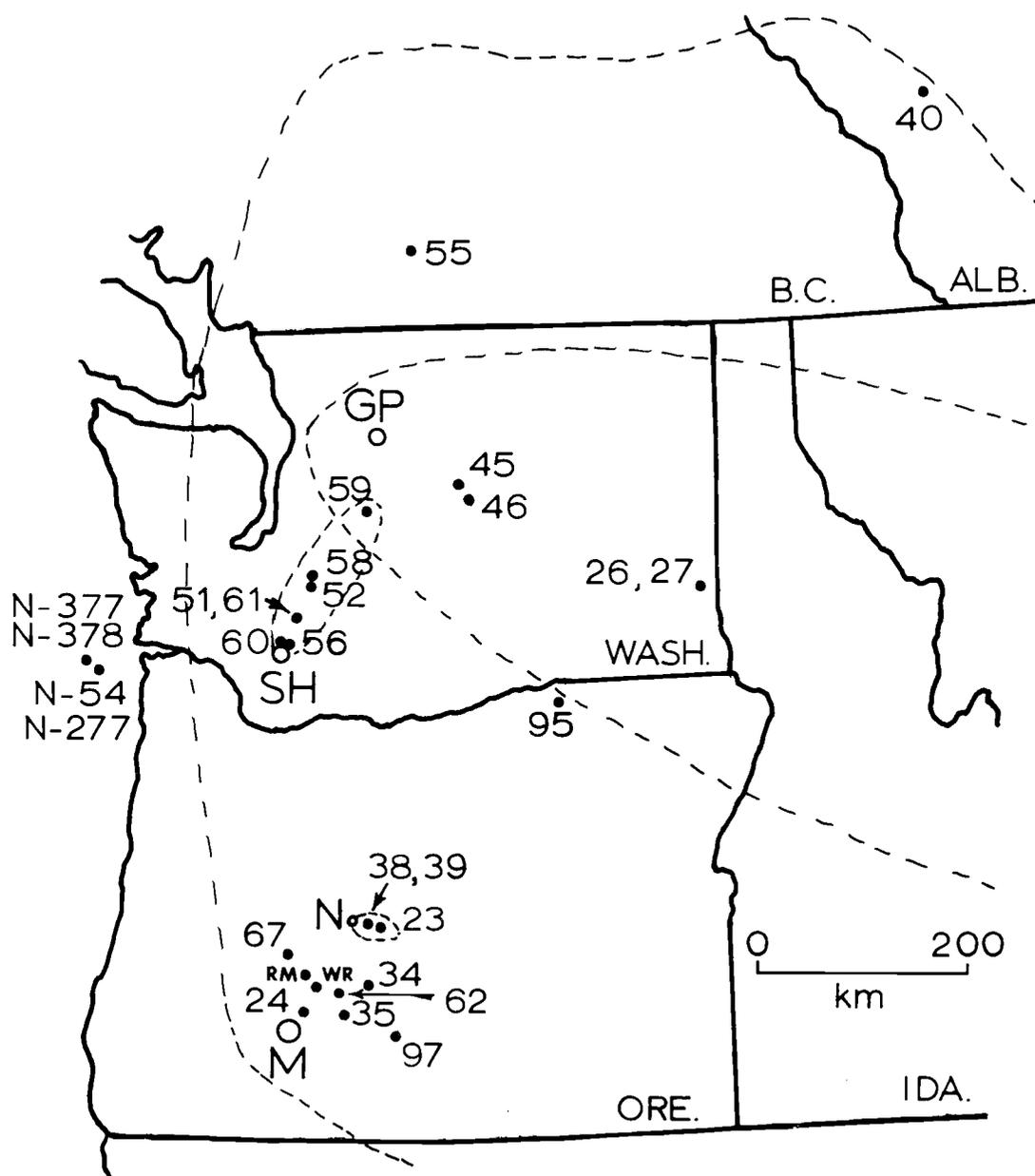


Figure 1. Locations of volcanic ash sampling sites in the Pacific Northwest. Numbers refer to sites given in Tables 2 and 3. Minimum extent of distribution taken from Fryxell (1965) and Crandell *et al.* (1962). M = Mazama, GP = Glacier Peak, SH = St. Helens Y, N = Newberry.

(Williams, 1942).

The petrographic and chemical methods of recognizing and correlating these pyroclastics have been reviewed by Wilcox (1965). Index of refraction of glass was used to distinguish between Mazama and Glacier Peak ashes (Powers and Wilcox, 1964; Fryxell, 1965; Steen and Fryxell, 1965). Distinctive mineral suites were found for certain ash layers (Wilcox, 1965). Analyses of Mazama, Glacier Peak and St. Helens ash layers resulted in considerable overlap in their contents of titanium dioxide (Czamanski and Porter, 1965). Powers and Wilcox (1964) found three times as much ytterbium and yttrium in Mazama as in Glacier Peak ash when comparing minor element analyses. Smith and Westgate (1969) distinguished between glass shards from the Mazama, Glacier Peak and St. Helens ash deposits by using an electron probe for major element analysis of unweathered samples. Combinations of these methods generally have been used to identify volcanic ash samples.

The feasibility of instrumental neutron activation analysis (INAA) for distinguishing volcanic ash was demonstrated by Theisen, Borchardt, Harward, and Schmitt (1968) (Appendix I). The method of INAA (Gordon et al., 1968) can be used to determine the abundances of Na, Rb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Th, Hf, Ta, Co, Fe, Sc, and Cr in most rocks. This method is non-destructive and rapid compared to traditional methods of analysis for these

elements. Calculations of concentrations from gamma-ray energy spectra can be done cheaply and easily with the aid of a computer (Appendix XI). Routine analyses of large numbers of geologic specimens could make INAA available to many geologists whose work involves stratigraphic correlation. Trace element abundances are also of interest to geochemists, as well as to soil scientists concerned with plant and animal nutrition on soils developed from volcanic ash.

Identification of or discrimination between volcanic ash deposits involves the question of what kind of differences in composition are required to classify an unknown ash sample into a certain category. This in turn requires information on accuracy of the method, variation within a deposit, and differences between deposits or sources. Accordingly, the objectives of this phase of the study were:

1. To determine the chemical differences between samples from different sites within the same deposit (deposit variability);
2. To determine the chemical differences between six volcanic ash layers within the region;
3. To develop a statistical method that compares unknown samples to characteristic compositions of ash deposits within the region.

Materials and Methods

Standard Solutions

Standard solutions (liquid monitors, Appendix VI) for each element were irradiated and analyzed at the same time as the volcanic ash and rock samples. Gamma-ray activities produced in these solutions were used to put the analyses of volcanic glass on a quantitative basis. Neutron self-shadowing is negligible for aqueous solutions and for rocks. Thus comparisons between the two are entirely valid.

Standard Rocks

USGS standard rocks (Table 1) were obtained by Dr. A. A. Theisen from Dr. G. K. Czamanske of the U. S. Geological Survey, Washington, D. C. These samples were used to check the analytical procedures and analyses. Subsamples of andesite (AGV-1) were used to determine the vertical neutron flux gradient within the reactor. This provided a basis for adjusting the data to reflect the lesser flux received by samples in TRIGA tube positions B, C, and D (Table 1).

Standard Volcanic Ash Samples

Samples of pumiceous lapilli were obtained from known deposits within the region (Table 2). These included the Mazama;

Table 1. Analyses of USGS rock standards and comparisons to INAA results of Gordon *et al.* (1968).

INAA	ppm*																		
No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
<u>Andesite AGV-1</u>																			
Reactor position A**																			
336	2.85	91	1.3	1190	42	65	8	6.2	1.68	.72	.77	.40	6.9	4.8	.62	14.4	4.86	13.7	5
±*	.05	18	.4	150	2	1	14	.1	.11	.20	.48	.07	.3	.2	.06	.3	.05	.3	2
Reactor position B																			
337	2.99	69	.8	1280	43	66	24	6.3	1.87	.73	.31	.21	7.5	4.9	.87	15.9	4.90	14.1	10
±	.06	14	.3	150	2	1	14	.1	.14	.32	.41	.07	.3	.2	.07	.3	.06	.3	2
Reactor position C																			
338	2.94	51	1.8	1130	43	64	41	6.0	1.81	.30	.29	.35	7.0	4.9	.83	15.3	4.84	13.5	9
±	.06	14	.5	110	1	1	21	.1	.11	.22	.43	.11	.2	.2	.07	.4	.06	.2	2
Reactor position D																			
339	3.10	80	1.2	1100	44	65	49	6.3	1.58	.58	.28	.33	6.6	4.9	.60	15.2	4.81	13.6	4
±	.06	16	.4	110	2	1	18	.1	.11	.23	.53	.09	.3	.2	.06	.3	.06	.2	2
Gordon <i>et al.</i> (1968)																			
±	3.15	61	1.3	1180	33	57	nd*	5.4	1.55	.77	1.60	.37	7.0	5.4	1.00	14.7	4.30	11.7	9
	.15	10	.3	100	3	3		.5	.06	.04	.30	.06	.5	.2	.20	.5	.20	.4	2
<u>Granite G-2</u>																			
204	3.18	149	1.8	1310	100	150	30	8.0	1.15	.77	0	.09	29.6	7.3	.98	4.4	1.89	3.7	4
±	.07	8	.3	50	2	1	3	.1	.04	.21	0	.03	.2	.1	.03	.1	.02	.1	1
Duplicate of G-2																			
334	2.92	176	1.3	1540	82	156	8	8.2	1.58	.59	0	.12	26.3	7.3	.97	3.8	1.83	3.7	3
±	.04	7	.3	40	2	1	9	.1	.10	.14	0	.02	.3	.1	.05	.2	.02	.1	1
Gordon <i>et al.</i> (1968)																			
±	2.95	129	1.4	1800	81	144	nd	8.7	1.37	.52	.8	.18	25.9	7.8	1.00	4.3	1.72	3.5	5
	.05	4	.3	70	1	4		.5	.05	.05	.2	.08	.5	.5	.10	.2	.05	.2	2

Table 1. (continued)

INAA		ppm*																		
No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr	
<u>Diabase W-1</u>																				
340	1.55	50	2.4	380	12	18	18	3.5	1.1	1.3	2.2	.81	1.4	2.3	.18	43	7.78	39.8	110	
±*	.03	20	1.0	170	1	2	14	.1	.1	.4	.9	.11	.3	.2	.06	1	.08	.7	7	
<u>Gordon et al. (1968)</u>																				
	1.68	<30	.8	<200	12	21	nd	2.8	1.1	.6	2.2	.44	2.6	3.0	.67	46	7.5	34.8	100	
±	.08		.2		2	2		.2	.1	.2	.4	.03	.2	.2	.06	2	.3	.8	5	
<u>Quartz Monzonite GSP-1</u>																				
341	1.87	260	1.5	1200	179	414	0	25.5	2.5	1.3	.1	.26	113	14.4	.71	6.2	2.87	6.4	4	
±	.05	20	.5	100	3	3	0	.2	.1	.2	.4	.07	1	.2	.08	.2	.04	.1	2	
<u>Gordon et al. (1968)</u>																				
	2.1	260	.8	1110	171	390	nd	23.2	2.0	1.3	2.0	.17	125	15	1.4	7.0	2.8	6.0	<18	
±	.2	10	.1	50	15	20		1.0	.1	.1	.5	.04	10	1	.3	.4	.1	.3		
<u>Basalt BCR-1</u>																				
335	2.22	50	.8	670	26	46	17	6.6	2.0	.9	3.3	1.00	6.3	4.6	.30	33.7	9.14	15.8	10	
±	.04	20	.4	200	1	2	13	.1	.1	.5	.7	.12	.3	.2	.06	.5	.09	.3	4	
<u>Gordon et al. (1968)</u>																				
	2.40	<105	1.5	650	23	46	nd	5.9	2.0	1.0	3.2	.60	6.7	4.7	.9	36.3	9.0	32.5	19	
±	.05		.2	30	2	5		.5	.1	.1	.4	.05	.3	.3	.2	.7	.2	.5		

* Na and Fe are in percent, ± = one standard deviation from counting statistics, nd = not determined.

** Samples in reactor positions B, C, and D were located 25, 50, and 75 mm above sample A where the neutron flux was greatest. Samples in reactor positions B, C, and D had 90, 80, and 70% of the flux occurring at position A. Count rates were therefore divided by the factors 0.9, 0.8, and 0.7 for comparison with liquid monitors activated in position A.

Table 2. Volcanic ash samples used as standards.

INAA No.	Sample Names and Numbers	Location	Reference **
<u>Mt. Mazama</u>			
274, 311	Huckleberry Spring (62-6, 62-16)	Sec. 36, T27S, R9E	Doak (1969)
216, 206	Antelope Unit (35-3, 35-4)	Sec. 1, T28S, R10E	Chichester (1967)
207, 208	Walker Rim (WRC1, WRC2)	Sec. 18, T26S, R9E	Chichester (1967)
209, 210*	Royce Mt. (RMC1, RMC2)	Sec. 3, T24S, R7E	Chichester (1967)
<u>Newberry</u>			
211	Weasel Butte (39-1)	Sec. 2, T22S, R13E	Doak (1969)
241	Pumice Butte (38-1)	Sec. 1, T22S, R13E	Doak (1969)
242	China Hat (23-1)	Sec. 9, T22S, R14E	Doak (1969)
<u>Glacier Peak</u>			
212	Phelps Creek (45-6)	Sec. 27, T30N, R16E	Doak (1969)
243*	North Sugarloaf (46-4)	Sec. 34, T27N, R18E	Doak (1969)
244*	Steptoe Canyon (27-1) ***	Steptoe Canyon, Washington	Appendix IV
<u>St. Helens Y</u>			
213	Randle (51-1)	Randle, Washington	Crandell <i>et al.</i> (1962)
240*	Longmire (52-1)	Longmire, Washington	Crandell <i>et al.</i> (1962)
<u>St. Helens W</u>			
214	Lower slopes Mt. St. Helens (56-1)	Mt. St. Helens, Washington	Crandell <i>et al.</i> (1962)
238	Lake Keechelus (59-1) ***	L. Keechelus, Washington	Crandell <i>et al.</i> (1962)
239	Crystal Mountain (58-1)	Crystal Mt., Washington	Crandell <i>et al.</i> (1962)
<u>St. Helens T</u>			
236*	Randle (61-1)	Randle, Washington	Crandell <i>et al.</i> (1962)
237	Lower slopes Mt. St. Helens (60-1)	Mt. St. Helens, Washington	Crandell <i>et al.</i> (1962)

* Glassy isolates from these samples had five or more percent crystal content.

** Samples listed under Crandell *et al.* (1962) were kindly furnished by D. R. Crandell, University of Washington, Seattle.

*** Glass was obtained from pumiceous ash (<4mm). All other samples consisted of pumiceous lapilli (>4mm).

Glacier Peak; and St. Helens Y, W, and T layers. The samples were obtained from two, three, or four sites within each deposit. The average analytical values for samples of each of the different deposits were used as reference to which all unknown samples were compared. The Mazama deposit is characterized by a layer of coarse pumice (C1 horizon of Chichester, 1967) overlying finer material (C2 horizon) at each site. Separate samples of the C1 and C2 horizons were taken at each of the four Mazama sites.

Unidentified Volcanic Ash

Various unweathered volcanic ash samples (Table 3) were chosen to test the method of INAA for correlating volcanic ash from Mt. Mazama, the volcano suspected of having been the primary contributor to volcanic ash soils in Oregon. Many of these samples were not strictly "unidentified". Other workers (Table 3) have considered the marine sediments and the samples from Steptoe Canyon and Alberta to be from the eruption of Mt. Mazama even though the samples were found at considerable distances from Crater Lake (Figure 1). Other samples occurred within the known distribution area of Mazama ash, but in the field they appeared to be unlike Mazama ash. Samples from Squaw Creek and Devils Hill were known to be unrelated to any of the standard ash samples, and thus were not expected to correlate with any of these standards.

Table 3. Unidentified volcanic ash samples.

INAA No.	Sample Names and Numbers	Location	Reference**
301*	Marine sediment (N-377)	Astoria fan, Pacific Ocean	Nelson <i>et al.</i> (1968)
302*	Marine sediment (N-378)	Astoria fan, Pacific Ocean	Nelson <i>et al.</i> (1968)
346	Marine sediment (N-54) (50-20 μ)	Astoria fan, Pacific Ocean	Nelson <i>et al.</i> (1968)
347	Marine sediment (N-277) (50-20 μ)	Astoria fan, Pacific Ocean	Nelson <i>et al.</i> (1968)
254	Steptoe Canyon (26-1)	Site No. 65-S-36	Czamanski and Porter (1965)
253	Edmonton, Alberta (40-1), JW 13866(i)	N. Saskatchewan River	Westgate and Dreimanis (1967)
247	Pumice Flat (34-1)	Sec. 16, T26S, R10E	Appendix IV
321	Stage Gulch (95-1)	Sec. 6, T3N, R31E	Appendix IV
245	Mazama glowing avalanche (24-2)	Sec. 16, T28S, R8E	Appendix IV
255	Huckleberry Spr. grey pumice (62-10)	(See # 274)	Doak (1969)
235	Kamloops, B. C. (55-1)	Kamloops, B. C.	Crandell <i>et al.</i> (1962)
329	Squaw Creek I (97-1)	Sec. 4, T31S, R14E	Appendix IV
330	Squaw Creek II (97-2)	Sec. 4, T31S, R14E	Appendix IV
305	Devils Hill (67-1)	Century Drive, Trail #20	Appendix IV

* Glassy isolates from these samples had five or more percent crystal content.

** Samples from the Pacific Ocean were kindly furnished by L. D. Kulm, Dept. of Oceanography, Oregon State University, Corvallis. The sample from Edmonton, Alberta was furnished by J.A. Westgate, Dept. of Geology, University of Alberta, Edmonton. Sample listed under Crandell *et al.* (1962) was furnished by D. R. Crandell, University of Washington, Seattle.

Isolation of Volcanic Glass

Information concerning the large variability in the proportion of crystals in pumiceous ash from Mt. Mazama (Williams, 1942) led to the hypothesis that trace element compositions of whole ash samples might be too variable for correlation work. It also was desirable to compare pumiceous lapilli sampled near the source with much finer textured material occurring farther away. In addition, the proportion of dense particles (feldspar, amphibole, and pyroxene) was expected to decrease with distance from the volcano (Knox and Short, 1963). Thus, chemical compositions of whole samples taken from different parts of the ash sheet could not be compared directly. For these reasons only volcanic glass was analyzed. The chemical composition of glass fractions occurring in the fine ash deposits was expected to be identical with that of glassy fractions from ground pumiceous lapilli sampled near the source. The very fine sand fraction was chosen because it was amenable to heavy liquid density separations and because this fraction could be obtained from samples from nearly all locations.

Special care was taken to minimize possibilities of trace element contamination throughout the handling and treatment of the samples. Very fine sand fractions (125-63 μ) were prepared by grinding pumiceous lapilli with a hard surfaced diamonite mortar and pestle

and by sieving in stainless steel sieves. Fine ash samples obtained at some distance from the eruptive vent were sieved directly. High purity heavy liquids, bromoform and bromobenzene, were mixed to form a solution with a density of 2.4 g/cc. Ultrasonic scrubbing, centrifuging, and freezing were used to isolate the less than 2.4 g/cc separates from whole samples (Powers and Malde, 1961).

Analytical Methods

The method of instrumental neutron activation analysis used was essentially that described by Gordon et al. (1968). One milliliter volumes (one-half to one gram) of volcanic glass, standard rock powder, and standard solutions were irradiated in the Oregon State University TRIGA reactor for six hours at a flux of 7×10^{11} n/sec/cm². Samples were counted with a 30 cc Ge(Li) semiconductor detector in conjunction with a 4096 Nuclear Data multichannel analyzer.

The isotopes ²⁴Na, ¹⁴⁰La, and ¹⁵³Sm were counted for ten minutes after the samples had decayed for six days. The isotopes ⁸⁶Rb, ¹³⁴Cs, ¹³¹Ba, ¹⁴¹Ce, ¹⁴⁷Nd, ¹⁵²Eu, ¹⁶⁰Tb, ¹⁶⁹Yb, ¹⁷⁷Lu, ²³³Pa(Th), ¹⁸¹Hf, ¹⁸²Ta, ⁶⁰Co, ⁵⁹Fe, ⁴⁶Sc, and ⁵¹Cr were counted for 100 minutes after 14 days of decay (Figure 2). The contributions of γ -ray peaks of Fe, Eu, and Yb were subtracted from peaks of Ce, Tb, and Pa(Th), respectively (Appendix VI). A possible contribution of ¹⁹²Ir-317 (74 day half life) to the ⁵¹Cr-320 kev peak (28

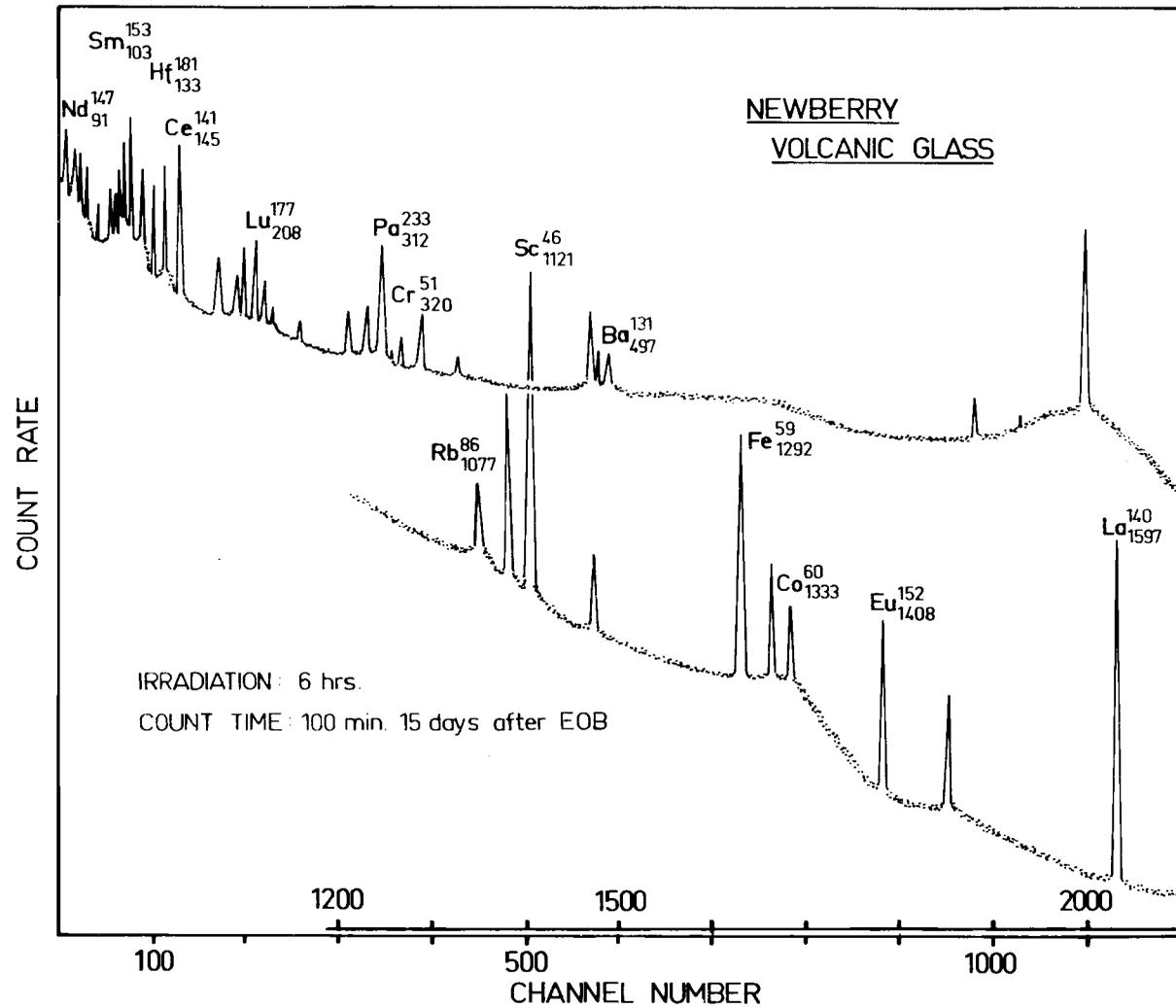


Figure 2. Example of gamma-ray spectrum obtained with a Ge(Li) detector and a 4096 multichannel analyzer.

day half life) exists. Since the Ir abundance could not be determined, its contribution could not be subtracted from the Cr peak. Thus the values for Cr may be slightly high.

Each spectrum was obtained in two forms of output, punch tape used for computer analysis of the spectra, and printer paper to check the computer calculations. The punch tape was transferred to high speed magnetic tape, corrected for punching errors, and analyzed with a FORTRAN IV program (Appendix XI).

Results and Discussion

Standard Rocks

Results obtained for USGS standard rocks were compared to those obtained by Gordon et al. (1968) (Table 1). In general the data agree within the error due to counting statistics. Since the gamma-ray energy peaks were quite small for chromium and neodymium, reproducibility was poor for these elements. The statistical error could have been reduced by counting the samples for longer periods of time. INAA samples 336, 337, 338, and 339 were used to determine the vertical neutron flux gradient (about 3.7%/cm) in the reactor. The data in Table 1 and in all subsequent tables have been multiplied by factors corresponding to the differences in flux received by samples in position A and samples 25, 50, and 75 mm above

position A (designated by B, C, or D). The correction factors were calculated from the average activities of the short lived nuclides ^{24}Na , ^{140}La , ^{153}Sm in standard rock AGV-1. The liquid monitors used as standards were irradiated in position A and therefore needed no flux correction.

Whole Samples Compared to Glassy Fractions

The assumption regarding differences in chemical composition between whole volcanic ash samples and glassy fractions was proven to be correct (Table 4). Whole samples that contain amphiboles and pyroxenes have higher amounts of the transition metals than glassy isolates. Whole ground lump pumice (pumiceous lapilli) had lower amounts of transition metals than the $<63\mu$ fractions in which the pyroxenes and amphiboles apparently were concentrated as a result of grinding. Newberry, an ash with very few crystals, had no significant differences between whole samples and glassy separates. Whole samples of ash from Glacier Peak and Mt. St. Helens had more than three times the concentration of transition metals and about twice the concentration of alkali metals found in their respective glassy fractions. Since crystal content varies with source and distance (Knox and Short, 1963; Appendix V), glassy separates were used throughout the remainder of this study. It was assumed that glass isolated from easily identified lump pumice was not originally different

Table 4. Comparison of whole samples of volcanic ash to glassy fractions.

INAA No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	ppm*									
										Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
<u>Mazama pumice (35-3)</u>																			
Whole sample, ground lump																			
219	3.18	57	3.1	450	26	45	33	5.8	.86	.85	4.0	.56	6.1	6.6	.21	2.4	2.13	7.8	2.8
Ground lump, <63μ																			
306	2.73	55	1.8	510	36	69	96	7.6	1.32	.34	5.6	.81	4.4	5.7	.38	11.4	3.75	12.0	24.0
Glassy fraction, 125-63μ																			
216	3.23	53	3.5	630	22	48	24	5.5	.97	.79	4.4	.65	7.1	7.0	.30	3.1	1.49	6.8	1.0
<u>Newberry pumice (39-1)</u>																			
Whole sample, ground lump, <63μ																			
344	3.66	122	5.2	670	32	66	12	8.1	.90	1.24	4.8	1.36	13.5	10.0	.82	1.0	1.62	6.9	2.0
Glassy fraction, 125-63μ																			
211	3.60	97	5.2	530	33	57	28	6.9	.79	1.45	6.8	.99	12.2	8.5	.99	1.2	1.51	6.1	2.7
<u>Glacier Peak (45-6)</u>																			
Whole sample, ground lump, <63μ																			
343	2.32	58	1.6	530	21	40	5	3.5	.69	.48	.8	.33	8.5	3.9	.24	5.9	1.85	6.1	7.0
Glassy fraction, 125-63μ																			
212	1.47	23	1.4	220	11	18	2	1.6	.34	0	.4	.12	4.5	1.7	.12	1.4	.52	1.8	0.8
<u>St. Helens Y (51-1)</u>																			
Whole sample, ground lump, <63μ																			
345	2.86	41	1.7	330	18	38	18	4.1	.98	.35	.4	.26	3.7	3.5	.35	7.2	2.12	4.9	5.6
Glassy fraction, 125-63μ																			
213	1.54	16	1.2	140	12	19	14	1.8	.14	.73	.6	.18	2.3	1.4	.19	2.3	.74	1.6	1.6

* Na and Fe are in percent.

from glass isolated from fine ash at a considerable distance from the source. The correctness of this assumption was demonstrated for Mazama ash on transect samples obtained from bogs (Chapter II) and from soils (Chapter III). Microscopic observations indicated the presence of less than five percent crystal content in most isolates (Tables 2 and 3). Subsequent tests on 50-20 μ fractions of Mazama ash samples (346 and 347) resulted in excellent separations for these unweathered marine sediments. Glacier Peak and St. Helens ashes contained many small crystal inclusions in the glass which were impossible to remove. It was assumed that the amounts of these crystals would not decrease with distance from the source.

Variability Within Deposits

The agreement of analytical data for Mazama ash indicates that sample selection has been uniform (Table 5). The average analytical values for eight samples of glass from Mazama pumiceous lapilli had coefficients of variation that were generally no higher than the coefficients of variation for counting statistics (Table 5). For elements detected with an instrumental error of 2 or 3%, the sample to sample variability was 5 to 8%. This would be the lower limit of agreement to be expected with the methods of sample preparation and analysis used.

Two layers of Mazama pumiceous lapilli differing in particle

Table 5. Analyses of volcanic glass isolated from standard ash layers.

INAA No.	ppm**																		
	Na	Pb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
MAZAMA																			
Huckleberry Spring C1																			
274	3.46	35	3.1	690	19.6	40	20	5.2	.89	.65	2.5	.40	6.3	6.0	.30	2.4	1.37	5.9	2.3
Antelope Unit C1																			
216	3.23	53	3.6	630	22.4	48	25	5.5	.97	.79	4.4	.65	7.1	7.0	.30	3.1	1.49	6.8	1.0
Walker Rim C1																			
207	3.32	57	4.6	760	21.0	46	34	4.5	.92	.76	4.2	.54	6.7	6.4	.29	3.0	1.56	6.7	1.8
Royce Mountain C1																			
209	3.34	64	3.8	580	25.1	44	35	5.2	.99	.97	3.3	.59	6.5	6.9	.30	2.8	1.62	7.1	1.4
Avg*	3.34	52	3.7	670	22.0	45	28	5.1	.94	.79	3.6	.54	6.7	6.6	.30	2.8	1.51	6.6	1.6
± *	.10	10	.6	70	.2	3	6	.4	.04	.12	.7	.09	.3	.4	.01	.3	.09	.4	.5
Huckleberry Spring C2																			
311	3.61	53	3.5	670	23.4	43	26	5.2	.76	.94	3.4	.55	5.9	6.2	.15	2.1	1.42	6.1	1.6
Antelope Unit C2																			
206	3.50	42	3.8	610	18.6	43	28	4.5	.85	1.03	3.3	.50	6.6	6.3	.24	2.3	1.53	6.6	.5
Walker Rim C2																			
208	3.32	51	3.3	590	19.9	40	32	4.7	.95	.61	2.8	.63	6.2	5.9	.07	2.5	1.35	5.8	2.1
Royce Mountain C2																			
210	3.73	47	5.4	780	22.0	44	34	5.6	.78	.87	4.5	.58	6.7	6.6	.21	3.0	1.52	6.5	1.7
Avg	3.54	48	4.0	660	21.1	42	30	5.0	.84	.86	3.5	.57	6.3	6.3	.17	2.5	1.46	6.2	1.5
±	.15	4	.8	80	1.9	2	3	.5	.08	.15	.6	.04	.3	.3	.06	.3	.07	.3	.6
GA*	3.44	50	3.9	660	21.5	44	29	5.0	.89	.83	3.5	.56	6.5	6.4	.23	2.6	1.48	6.4	1.6
±	.16	8	.7	70	2.0	3	5	.4	.08	.14	.7	.07	.3	.4	.08	.3	.09	.4	.6
CV%*	5	17	19	11	9	6	17	8	9	17	19	13	5	6	34	13	6	7	35
CV%+*	2	22	15	16	8	3	29	2	11	34	14	17	5	4	28	10	3	2	87

Table 5. (continued)

INAA No.	ppm**																		
	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
NEWBERRY																			
Weasel Butte 39-1																			
211	3.60	97	5.2	530	33	57	28	6.9	.79	1.45	6.8	.99	12.2	8.5	.99	1.2	1.51	6.1	2.7
Pumice Butte 38-1																			
241	3.82	99	4.7	570	38	60	10	7.4	.66	1.44	6.5	.90	13.1	9.2	.92	1.4	1.52	6.3	3.5
China Hat 23-1																			
242	3.74	93	5.0	680	36	60	30	7.0	.72	1.05	6.6	.92	13.5	9.1	1.16	1.0	1.55	6.3	1.4
Avg*	3.72	96	5.0	630	36	59	23	7.1	.72	1.31	6.6	.94	12.9	8.9	1.02	1.2	1.53	6.2	2.5
±	.09	2	.2	70	2	1	9	.2	.05	.18	.2	.04	.5	.3	.10	.2	.02	.1	.9
GLACIER PEAK																			
Phelps Creek 45-6																			
212	1.47	23	1.4	220	11	18	24	1.6	.34	0	.4	.12	4.5	1.7	.12	1.4	.52	1.8	.8
N. Sugarloaf 46-4																			
243	2.39	51	3.0	540	21	34	15	3.5	.64	.35	1.6	.41	10.1	4.0	.38	3.6	1.52	5.0	4.4
Steptoe Canyon 27-1																			
244	2.54	49	3.3	380	14	26	6	2.5	.48	.34	.4	.19	4.6	2.0	.35	3.5	1.03	2.8	.8
Avg	2.13	41	2.6	380	15	26	8	2.5	.49	.23	.8	.24	6.4	2.5	.28	2.9	1.02	3.2	2.0
±	.47	13	.9	140	4	7	5	.8	.12	.16	.5	.12	2.6	1.0	.12	1.0	.41	1.3	1.7
ST. HELENS Y																			
Randle 51-1																			
213	1.54	16	1.2	140	12	19	14	1.8	.14	.73	.6	.18	2.3	1.4	.19	2.3	.74	1.6	1.6
Longmire 52-1																			
240	3.03	51	2.6	300	21	26	19	3.5	.75	.32	.9	.21	4.9	2.8	.46	3.4	1.61	3.5	2.8
Avg	2.29	34	1.9	220	17	23	16	2.7	.45	.53	.7	.20	3.6	2.1	.33	2.8	1.18	2.5	2.2
±	.75	13	.7	80	5	3	3	.9	.30	.21	.2	.02	1.3	.7	.14	.6	.44	.9	.6

Table 5. (continued)

INAA No.	ppm**																		
	Na	Kb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
ST. HELENS W																			
Lower slopes 56-1																			
214	3.47	78	3.2	380	17	32	20	3.5	.75	.60	1.9	.31	4.5	4.5	.43	2.9	1.29	3.6	1.5
Lake Keechelus 59-1																			
238	2.72	68	4.2	410	21	34	24	3.7	.52	.51	2.2	.49	6.9	5.2	.69	3.0	1.32	4.6	1.8
Crystal Mt. 58-1																			
239	3.57	63	2.9	540	20	31	14	3.7	.71	.43	1.8	.32	4.9	5.2	.46	3.1	1.51	4.3	3.1
Avg*	3.25	70	3.4	440	19	32	19	3.6	.66	.51	2.0	.37	5.4	4.9	.53	3.0	1.37	4.2	2.1
±*	.38	6	.6	70	2	1	4	.1	.10	.07	.2	.08	1.0	.3	.12	.1	.10	.4	.7
ST. HELENS T																			
Randle 61-1																			
236	3.04	40	1.9	370	14	33	14	3.4	.63	.80	.7	.25	4.7	3.5	.37	5.1	1.48	3.5	2.1
Lower slopes 60-1																			
237	3.80	60	2.2	370	18	33	21	4.0	.65	.85	1.8	.50	4.9	5.2	.28	5.3	2.35	9.4	1.6
Avg	3.42	50	2.1	370	16	33	18	3.7	.64	.83	1.3	.38	4.8	4.3	.33	5.2	1.92	6.5	1.9
±	.38	10	.2	0	2	0	9	.3	.02	.03	.5	.13	.1	.9	.05	.1	.44	2.9	.3

* Avg = average for group; ± = one standard deviation for group average; GA = grand average for all eight Mazama samples; CV% = coefficient of variation for grand average; CV%± = coefficient of variation for counting statistics.

** Na and Fe are in percent.

size (Chichester, 1967) and pore size distribution (Doak, 1969) have been observed. Major element analyses of pumiceous lapilli from a vertical section at Huckleberry Spring appear to show no abrupt chemical changes at the boundary between the two layers (Borchardt and Theisen, 1968). The trace element data determined here also agree with the conclusion that chemical differences between the C1 and C2 horizons are not detectable (Table 5). This might support the conclusion of Wilcoxson (1967) that both eruptive sequences must have occurred during a period of days or weeks rather than months or years.

Site to site variability for trace element analyses of Newberry volcanic glass was low (Table 5). Such excellent reproducibility is probably the result of two factors: 1) Newberry pumiceous lapilli contained very few crystals (< 2%, Appendix VII) and 2) the young age (2000 ybp) of Newberry pumice allowed less leaching than observed for other samples.

Glacier Peak ash from different locations had wide ranges in elemental composition. The sample from North Sugarloaf was slightly oxidized and weathered, although it was classified as a "C1" soil horizon. Considerable variability also was indicated for volcanic glass from the St. Helens Y samples (Table 5). The Na and Fe concentrations for the Glacier Peak sample from Steptoe Canyon and for the St. Helens Y sample from Longmire were quite similar to data of Smith and Westgate (1969). Varying amounts of crystal

inclusions (Appendix VII) may have contributed to analytical variability for the ash samples from Washington. Recent work suggests more than one eruption of the 12,000 year old Glacier Peak ash (Wilcox, 1969). The possibility for misidentification exists particularly for the extremely complex St. Helens and Glacier Peak sequences. Larger numbers of samples are needed for a more accurate measurement of the chemical compositions for future correlation work.

Differences Between Volcanic Ash Deposits

Elemental Abundances

Comparisons between elemental abundances of each of the samples must consider the relative accuracy of determination. For Mazama volcanic glass, the most accurately determined elements were Na, Sm, Sc, Fe, Ce, Hf, and Th (coefficients of variation were less than 5% for counting statistics, Table 5). La, Co, Eu, Yb, Cs, Ba, and Lu were intermediate (CV = 8-17%) while Rb, Ta, Nd, Tb, and Cr had large errors due to counting statistics (CV = 22-87%). In a later section, statistical comparisons between analyses will consider these differences in analytical error.

Despite the variable chemical compositions of the standard ash samples from Washington, they were consistently lower in trace elements than the Newberry and Mazama ash samples from Oregon

(Table 5). This may be related to the numerous feldspar inclusions in the glass shards from Mt. St. Helens and Glacier Peak. One of the few trace element analyses in the literature concerning Mazama and Glacier Peak pumice reported 3ppm and 1ppm Yb, respectively, for glassy fractions (Powers and Wilcox, 1964). This agrees with the values of 3.6 ± 0.7 and 0.8 ± 0.4 ppm Yb determined with activation analysis (Table 5). The major elements Na and Fe had higher concentrations in Mazama ash than in Glacier Peak ash as reported by Powers and Wilcox (1964). Yb, Lu, Th, Rb, and Ta contents in Newberry volcanic glass were more than twice those in Mazama glass while the concentrations of Na, Cs, Ba, and the transition metals were quite similar for both deposits. Differences in elemental abundances occurring among the St. Helens ash layers were less striking, no doubt because they originate from the same vent.

Rare Earth Element Distributions

Rare earth element distribution patterns (Figure 3) are characteristic of a particular geologic material. The abundances of the rare earth elements (REE) are divided by the average abundances found for 20 chondritic meteorites, the best available specimens for the study of original nebular abundances (Haskin et al., 1966). These values are then divided by the value for Yb resulting in a straight line when chondritic meteorites are plotted against ionic

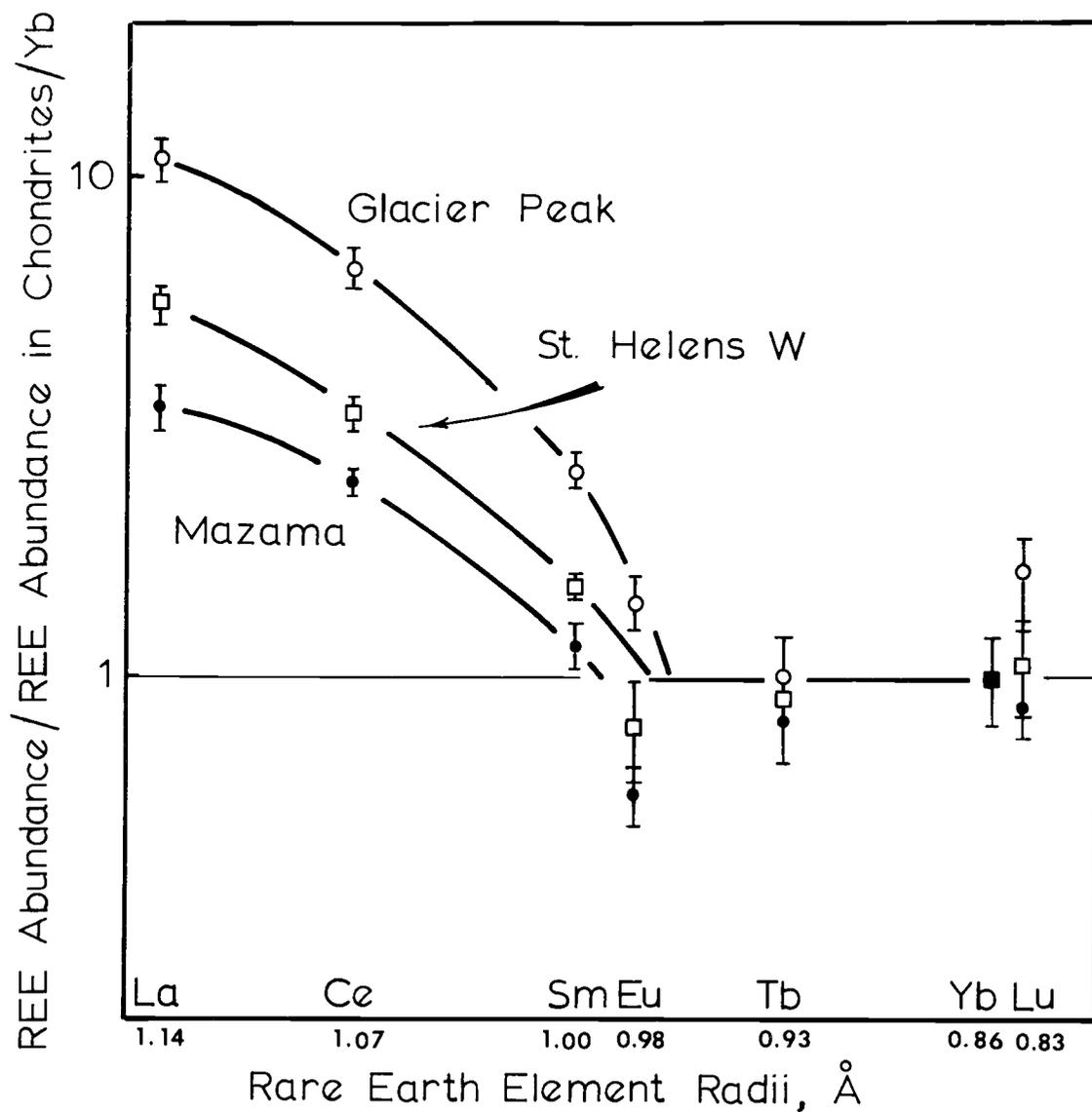


Figure 3. Rare earth element (REE) distribution patterns for standard ash samples. REE abundances were divided first by abundances in chondritic meteorites, and then by the resulting value for Yb as described by Haskin *et al.* (1966).

radii of the REE. Varying degrees of enrichment in the light rare earths La, Ce, and Sm were exhibited by the standard ash samples (Figure 3). Similar enrichment patterns have been observed for most sediments and for siliceous rocks (Haskin et al., 1966). Enrichment of the light REE (La, Ce, and Sm) in the standard ashes appears to be in the order Glacier Peak = St. Helens Y > St. Helens T > St. Helens W > Mazama > Newberry. This was also the approximate order of decreasing crystal inclusions observed in the glass shards. Different results might be expected for analyses of the glassy areas of the shards that have large amounts of crystal inclusions. REE analyses of the heavy mineral species occurring in whole samples would be needed in order to infer differing geochemical conditions prior to eruption of the pyroclastics.

Correlation of Samples

Statistical Methods

Variation Analysis. A method of comparing samples whose analyses contain large numbers of elements was developed for correlation work. One or two numbers were needed to represent all 19 elements in a sample. This could be obtained by using a discriminant function described in the next section. A simpler method not involving large matrix inversion can be easily applied to chemical

compositions. For example, a 19 element vector consisting of elemental concentrations for a sample

$$A = [3.4\%, 7 \text{ ppm}, \dots 4\text{ppm}]$$

is compared to the analyses for another

$$B = [3.4\%, 6 \text{ ppm}, \dots 4 \text{ ppm}].$$

Divide vector A by vector B:

$$C = \frac{A}{B} = [1.00, 1.16, \dots 1.00].$$

Each element of the new vector is nearly 1.00 if the vectors A and B are similar. The variation about the average of all elements of the new vector, C, is a measure of the dissimilarity of the two analyses. This is given by the coefficient of variation (CV) calculated from the standard deviation (s) about the average (\bar{x}):

$$\%CV = \frac{s}{\bar{x}} \times (100)$$

where
$$\bar{x} = \frac{1.00 + 1.16 + \dots + 1.00}{19}$$

$$s = \sqrt{\frac{(\bar{x} - x)^2}{19}}$$

In essence, the extent to which compositions differed was expressed in terms of relative concentrations. For example, comparisons in Table 6 could be made easily from one sample to another and from one element to another. The abundances for each element were divided by the average abundances (Table 5) for eight Mazama

Table 9. Ratios to Mazama volcanic glass composition (average of eight samples) for regional samples.

INAA No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Ratios X 100																			
Marine sediment N-377																			
301	100	110	111	88	92	96	150	96	109	90	120	111	88	100	55	90	101	97	70
±	2	20	15	10	6	2	40	2	13	30	20	7	5	3	30	10	2	2	80
Marine sediment N-378																			
302	95	100	85	96	108	102	110	99	88	120	110	104	92	96	61	140	101	101	140
±	2	20	14	11	8	3	40	2	12	30	20	7	4	3	30	10	3	2	60
Marine sediment N-54 (50-20 μ)																			
346	105	130	79	114	106	98	40	103	94	130	82	100	94	101	65	90	101	98	130
±	2	20	10	12	6	2	40	2	7	20	15	9	3	2	9	5	1	2	90
Marine sediment N-277 (50-20 μ)																			
347	100	90	118	114	96	93	50	95	102	80	79	100	88	99	22	85	96	94	80
±	2	10	12	15	6	2	30	2	8	10	14	9	3	2	13	5	2	2	70
Steptoe Canyon																			
234	107	110	106	93	107	95	160	92	80	180	96	82	99	94	100	115	101	97	50
±	2	20	19	13	7	3	30	1	8	40	11	23	6	3	17	10	3	2	50
Edmonton, Alberta																			
233	83	130	114	95	79	94	100	87	101	80	105	120	82	94	152	130	118	103	140
±	1	40	26	13	5	3	30	1	11	30	12	27	6	4	17	10	3	2	80
Pumice Flat																			
247	96	120	123	85	104	94	90	98	82	110	105	100	77	99	148	120	109	99	60
±	2	30	19	20	9	3	30	2	10	40	14	20	5	4	26	10	3	2	40
Stage Gulch																			
321	98	110	66	99	108	100	110	102	119	50	90	104	89	98	109	140	113	106	340
±	2	20	13	11	6	3	50	2	12	30	20	7	4	20	26	10	3	2	140

Table 6. (continued)

INAA No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Ratios X 100																			
Glowing avalanche, Mazama																			
245	98	100	90	100	89	93	120	94	81	180	90	110	86	94	74	116	89	92	60
±	2	30	20	30	7	4	30	2	11	50	20	20	7	5	26	14	3	2	100
Huckleberry Spring, dark grey pumice																			
235	91	100	80	110	77	74	60	75	79	60	70	80	78	72	100	91	82	76	80
±	2	20	10	20	7	2	20	2	6	20	10	20	4	2	13	5	1	1	30
Kamloops, B. C.																			
235	54	90	70	70	50	49	40	44	44	80	50	50	39	46	43	64	53	51	30
±	1	20	20	20	5	2	20	1	7	20	10	16	5	3	13	8	2	1	40
Squaw Creek I																			
329	70	280	160	120	179	160	40	175	115	170	180	245	207	148	135	16	91	152	120
±	1	30	20	20	7	3	60	2	12	20	20	20	5	3	26	3	2	3	70
Squaw Creek II																			
330	67	220	110	110	187	198	60	177	99	140	170	229	196	148	135	14	89	147	100
±	1	30	10	30	7	3	60	2	10	30	20	20	6	3	26	4	2	3	100
Devils Hill																			
305	86	190	70	120	99	82	40	69	83	0	50	86	130	71	278	72	78	57	40
±	2	20	10	10	6	2	40	1	12	10	20	7	40	3	30	12	3	1	100

* ± = one standard deviation for counting statistics.

volcanic glass samples. Values varying widely from 1.00 (and thus from Mazama glass composition) are easily seen in this way. The average ratio for all elements in the sample should be 1.00 and the relative deviation (coefficient of variation) about this mean value should be low. The deviation in mean ratio from a value of 1.00 and large values for the coefficient of variation would reflect the lack of agreement with Mazama composition.

The %CV obtained for division of two analyses of the same ash sample would be a measure of the experimental variation of the data and the minimum value to be expected for correlation of unknowns. The analysis for an unknown sample can be divided by the analyses for any number of samples representing known ash layers. This has been done by dividing the analyses of each standard ash sample by the average analysis for each of the seven ash layers investigated (Table 7). The lowest CV in the first row is 10% and sample 274 would be classified as most similar to the Mazama layer which it is known to be. The average ratio for this analysis was 0.92, near the expected value of 1.00. The remaining coefficients of variation in the first row of Table 7 illustrate the range in values calculated for comparison of sample 274 to the average compositions of other standard ashes. The remaining standard ash samples were compared to their averages and to the averages of the standard ashes from other sources. Generally the standard ash samples from

Table 7 Coefficients of variation (%) for standard ash samples normalized to average elemental abundances for Mazama; Newberry; Glacier Peak; St. Helens Y, W, and T layers.

INAA No.	Ash layer	Av. ratio for lowest CV	Mazama	Mazama	Newberry	Glacier Peak	St. Helens		
			C1	C2			Y	W	T
274	Mazama C1	0.92	10*	21	49	33	39	23	31
216	"	1.05	7*	15	53	49	53	26	44
207	"	1.02	8*	15	55	49	52	25	45
209	"	1.03	7*	16	50	43	41	23	33
211	Mazama C2	0.99	13	7*	40	46	44	26	37
206	"	0.94	10*	12	45	50	45	27	37
208	"	0.92	8*	8	46	38	39	18	32
210	"	1.09	14	9*	48	51	53	26	48
211	Newberry	0.99	43	72	6*	64	65	38	57
241	"	1.02	40	65	6*	61	61	37	54
242	"	1.01	50	83	9*	58	62	36	56
212	Glacier Peak	0.61	29	33	67	14*	31	30	40
243	"	1.43	44	53	79	16*	31	31	38
244	"	1.01	42	59	103	19*	24	25	37
213	St. Helens Y	0.69	38	49	107	21	11*	26	29
240	"	1.34	38	58	81	21	9*	20	29
214	St. Helens W	0.94	32	51	68	25	27	10*	29
238	"	1.05	44	77	59	28	30	13*	40
239	"	1.01	27	49	69	22	24	8*	24
236	St. Helens T	0.89	44	56	119	22	17	29	17*
237	"	1.12	38	41	96	37	40	36	13*

* Lowest CV classifies the sample with this group.

Washington volcanoes have higher correlating CV's than those for Mazama and Newberry. However it is not difficult to distinguish between Oregon and Washington ash deposits.

An advantage of variation analysis is that the analyst can weight the data to utilize more fully those values with small errors of determination. The following formula was used to calculate a weighting factor for each element:

$$F = 1 - \frac{s_i/x_i}{0.33}$$

where s_i = one standard deviation for counting statistics on element i and x_i = abundance of element i . The factor 0.33 was selected because the limit of detectability was approached when the standard deviation (s_i) was more than 33% of the abundance (x_i). Minus values for F were set equal to zero. The factor for an elemental abundance of 10ppm and standard error of ± 0.6 ppm would be 0.82. This value is then multiplied by the corresponding ratio for that element. For example, if we had two elements each determined with the accuracy mentioned above, and if both ratios to Mazama volcanic glass composition were 1.00, the average of the two would be:

$$\frac{(0.82 \times 1.00) + (0.82 \times 1.00)}{0.82 + 0.82} = 1.00$$

In this case the weighting factor did not affect the result, but more accurately determined ratios would influence the resulting average and coefficient of variation (Appendix XII) more than ratios

determined with less accuracy. For elements with greater than 33% error of determination, the value for F would be 0 and these elements would not be included in the average ratio and CV determination. This was often the case for neodymium and chromium. Weighting factors were used to calculate average ratios and coefficients of variation in all tables concerning variation analysis.

Discriminant Function Analysis. The discriminant function can be used to classify analyses with several parameters (Krumbein and Graybill, 1965). Discriminant values (Y_i) are calculated for comparisons of compositions of unknown samples with compositions representing each group (i) of previously identified standard ash samples. A sample having a composition similar to one of the standard ash layers will be indicated by the discriminant value.

Generally discriminant function analysis would be sufficient for correlation problems of this type. However, the method of calculating the discriminating equations was confronted with a special problem. Discriminant function analysis is based upon the assumption of independence of variables (Griffiths, 1966). Interdependent variables produce a redundant matrix that will not invert. In the analysis performed here, 8 of the 19 elements were rare earths which are interrelated (Haskin et al., 1966). The concentrations of some of the elements were highly related to each other, resulting in redundancy in the 19 sample x 19 element matrix that must be

inverted to calculate the functions. Redundancy was overcome by first calculating a correlation matrix involving all 19 elements¹ (Table 8). A correlation diagram was then drawn for pairs of elements with correlation coefficients greater than 0.85. This illustrated the great dependence between the rare earth elements and between these elements and hafnium. Thus 19 independent parameters have not been obtained. If Ce has been utilized in calculating the discriminant function, there is no need to include Hf because both elements appear to measure similar properties for these particular samples. Another set of ash samples or a different geologic material will not produce exactly the same relationships. Multiple correlation matrices should be determined for each set of data for discriminant function analysis.

Elimination of the elements Ce, Sm, Eu, Yb, and Hf from the discriminant analysis removed the highest correlations and the matrix could be inverted. Calculations using the remaining elements resulted in the discriminant functions for five groups of ash samples (Table 9). A chi-square value of 73,900 (d. f. = 56) led to rejection of the hypothesis that the mean values are the same in all five ash layers for these 14 variables. Each discriminant coefficient (C_{ij})

¹ Appreciation is expressed to R. G. Petersen, Professor, Dept. of Statistics, Oregon State University, for suggestions regarding the elimination of redundancy.

Table 8. Multiple correlation coefficients for elemental abundances determined for nineteen standard ash samples (glassy isolates) from pyroclastics of the Pacific Northwest.

	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Na	1	.66	.77	.79	.68	.79	.59	.83	.78	.64	.71	.68	.48	.83	.37	-.13	.83	.79	.14
Nb		1	.73	.38	.85	.73	.25	.72	.34	.61	.73	.76	.77	.74	.84	-.33	.58	.46	.32
Cs			1	.76	.75	.85	.62	.82	.53	.70	.84	.82	.70	.84	.56	-.20	.70	.77	.10
Ba				1	.57	.80	.62	.77	.75	.54	.71	.67	.52	.81	.14	-.07	.73	.92	.13
La					1	.89	.35	.92	.41	.78	.89	.90	.90	.88	.79	-.50	.66	.66	.40
Ce						1	.57	.97	.61	.86	.97	.96	.83	.98	.58	-.46	.69	.87	.14
Nd							1	.54	.70	.49	.53	.55	.21	.60	.03	-.00	.64	.76	-.17
Sm								1	.62	.84	.94	.94	.80	.97	.58	-.45	.71	.84	.22
Eu									1	.37	.50	.50	.27	.65	-.01	.13	.79	.84	.04
Tb										1	.88	.85	.64	.83	.51	-.54	.50	.67	.07
Yb											1	.97	.82	.95	.63	-.57	.58	.78	.11
Lu												1	.86	.94	.64	-.53	.60	.78	.18
Ta													1	.78	.79	-.52	.51	.57	.41
Hf														1	.56	-.45	.71	.88	.15
Ta															1	-.47	.35	.20	.32
Co																1	.18	-.13	.12
Fe																	1	.80	.39
Sc																		1	.08
Cr																			1

Table 9. Coefficients and constants of the discriminant functions for INAAC of five ash layers of the Pacific Northwest.

Coefficient No.	Element	Coefficients				
		Mazama	Newberry	Glacier Peak	St. Helens	
					Y	W
1	Na	6348.	5075.	779.	-1090.	3115.
2	Rb	60.6	53.1	5.94	-14.5	30.2
3	Cs	-192.4	-154.	-30.3	12.6	-98.8
4	Ba	-0.179	.304	-0.152	-0.197	-0.064
5	La	-465.	-382.	-47.8	100.	-227.
6	Nd	101.	62.6	18.0	-3.46	48.7
7	Tb	-2293.	-1686.	-250.3	473.	-1078.
8	Lu	2738.	2912.	152.0	-691.	1428.
9	Th	-738.	-583.	-67.1	145.	-355.
10	Ta	3747.	3593.	358.	-750.	1977.
11	Co	-1112.	-1038.	-80.9	282.	-553.
12	Fe	-23683.	-18693.	-2879.	4183.	-11544.
13	Sc	7330.	5705.	847.	-1353.	3535.
14	Cr	877.	720.	94.7	-168.	434.
	Constant	-10586.	-7245.	-211.	-485.	-2552.

was multiplied by the respective elemental abundances (X_j) for each sample being compared. These were added together with the discriminant constant to get a single value Y_i for each ash layer where

$$Y_i = K_i + \sum_{ij} C_{ij} X_j$$

i = ith group

j = jth element

K_i = discriminant constant.

The equation for each ash layer maximizes the discriminant values (Y_i) for samples having analyses similar to the average for that layer. Thus the highest value among the five calculated for a particular sample corresponded to the ash layer to which it was most similar (Table 10). Discriminant function analysis of the standard ash samples supports the conclusions reached by using the simpler variation analysis. Agreement between these methods should produce the desired correlations for unknown ash samples.

Correlation of Unidentified Samples

The utilization of activation analysis data along with the statistical methods found useful for classifying the standard ash samples constitutes the method of INAAC (instrumental neutron activation analysis correlation). The method was tested on 14 "unidentified" volcanic ash samples from very near Crater Lake, Oregon to as

Table 10. Discriminant values for standard ash samples.

INAA No.	Sample names and numbers	Mazama	Newberry	Glacier Peak	St. Helens	
					Y	W
<u>Mazama</u>						
274	Huckleberry Spring (62-6)	10610*	9560	2350	-4160	7770
216	Antelope Unit (35-3)	10830*	9720	2370	-4220	7860
207	Walker Rim (WRC1)	10540*	9480	2320	-4200	7720
209	Royce Mt. (RMC1)	10570*	9470	2340	-4130	7730
311	Huckleberry Spring (62-16)	10600*	9630	2330	-4170	7770
206	Antelope Unit (35-4)	10440*	9400	2320	-4150	7670
208	Walker Rim (WRC2)	10340*	9310	2310	-4120	7630
210	Royce Mt. (RMC2)	10770*	9640	2370	-4180	7830
<u>Newberry</u>						
211	Weasel Butte (39-1)	6340	7380*	1780	-3530	5950
241	Pumice Butte (38-1)	6070	7140*	1780	-3470	5810
242	China Hat (23-1)	6150	7220*	1780	-3470	5850
<u>Glacier Peak</u>						
212	Phelps Creek (45-6)	-7950	-5210	210*	-820	-1250
243	North Sugarloaf (46-4)	-7980	-5190	230*	-780	-1250
244	Steptoe Canyon (27-1)	-8170	-5350	200*	-750	-1330
<u>St. Helens Y</u>						
213	Randle (51-1)	-14290	-10280	-510	490*	-4310
240	Longmire (52-1)	-14240	-10220	-500	480*	-4270
<u>St. Helens W</u>						
214	Mt. St. Helens (56-1)	-120	1310	1090	-2250	2640*
238	Lake Keechelus (59-1)	-430	1110	1040	-2210	2490*
239	Crystal Mountain (58-1)	-310	1110	1050	-2220	2530*

* Highest discriminant value classifies the sample with this group.

far away as Edmonton, Alberta. In addition, the data were expected to answer the question of whether or not the trace element composition of Mazama glass separated from fine pumiceous ash was similar to the glass from pumiceous lapilli sampled near Crater Lake.

Coefficients of variation and average ratios (Table 11) were calculated as previously described. Nelson et al. (1968) tentatively identified the first four samples as Mazama ash on the basis of refractive index of glass and carbon dates. Variation analysis, as well as discriminant function analysis classified these marine samples as Mazama ash (Tables 11 and 12). Ash from the Astoria fan (sample 347) had a CV of only 8% for comparison to the unweathered Mazama C2 layer. The lowest CV observed for Mazama ash from pumice near Crater Lake was 7%. The average ratio to Mazama C2 for sample 347 was 0.98, very near the theoretical value of 1.00 for a perfect correlation. Similarly, the analysis of sample 347 was divided by the average analysis for Newberry, Glacier Peak, St. Helens Y, W, and T layers, respectively, resulting in differing average ratios (not shown). The coefficient of variation (Table 11) for each ratio would reflect any similarities or dissimilarities between sample 347 and the other ash layers, whereas an average ratio of 1.00 might be accidental. These additional coefficients of variation were important for eliminating the other ash layers as possibilities. High CV's such as those above 40%

Table 11. Coefficients of variation (%) for regional ash samples.

INAA No.	Description	Av. ratio for lowest CV	Mazama C1	Mazama		Glacier Peak	St. Helens		
				C2	Newberry		Y	W	T
301	Marine sed. vfs	1.02	11	10*	40	50	50	25	43
302	Marine sed. vfs	1.00	10*	12	63	43	42	21	35
346	Marine sed. silt	1.02	17	12*	46	47	42	29	34
347	Marine sed. silt	0.98	11	8*	43	35	40	21	37
234	Steptoe Canyon	1.07	21	18*	58	64	44	33	42
233	Edmonton, Alberta	0.98	15*	28	66	47	51	25	41
247	Pumice Flat	0.99	13*	23	57	44	48	22	41
321	Stage Gulch	1.02	13*	17	68	32	37	22	28
245	Glowing avalanche	0.98	18	15*	56	54	41	28	34
285	Mazama grey pumice	0.79	11*	18	59	36	43	22	36
235	Kamloops, B. C.	0.53	20	19*	58	39	43	22	41
329	Squaw Creek I	1.11	38	37	29	59	59	42	52
330	Squaw Creek II	1.07	34	33	28	56	59	42	51
305	Devils Hill	1.07	45	72	39	29	43	26	43

* Lowest CV classifies the sample with this group.

Table 12. Discriminant values for regional ash samples.

INAA No.	Sample names and numbers	Mazama	Newberry	Glacier Peak	St. Helens	
					Y	W
301	Marine sediment (N-377)	11260*	10020	2400	-4300	8060
302	Marine sediment (N-378)	8420*	7590	2140	-3650	6670
346	Marine sediment (N-54)	10580*	9800	2280	-4290	7780
347	Marine sediment (N-277)	9270*	8550	2130	-4050	7080
234	Steptoe Canyon (26-1)	7880*	7240	2120	-3480	6440
233	Edmonton, Alberta (40-1)	6570*	6450	1760	-3620	5790
247	Pumice Flat (34-1)	6210*	6060	1800	-3410	5620
321	Stage Gulch (95-1)	12110*	10600	2510	-4410	8490
245	Glowing avalanche (24-2)	9890*	9020	2290	-3950	7430
285	Mazama dark grey pumice (62)	7190*	6990	1900	-3650	6120
235	Kamloops, B. C. (55-1)	400	1580	1070	-2490	2800*
329	Squaw Creek (97-1)	27190*	23790	4050	-7770	15920
330	Squaw Creek (97-2)	23680*	20680	3720	-6900	14180
305	Devils Hill (67-1)	-880	1270	920	-2360	2340*

* Highest discriminant value classifies the sample with this group.

demonstrate the dissimilarity of the Newberry, Glacier Peak and St. Helens Y and T layers. The possibility of correlating samples like 347 with these layers would be remote. After very large numbers of comparisons have been made for any one material, the statistical distribution of the coefficient of variation could be studied. A definite probability of correct classification could then be stated.

The Steptoe Canyon ash sampled in an alluvial fan in a thin layer above Glacier Peak ash correlates well with Mazama ash. The data for Edmonton ash supports other evidence for the presence of Mazama ash in Canada (Powers and Wilcox, 1964; Wilcox, 1965; Westgate and Dreimanis, 1967; Smith and Westgate, 1969). The glassy fraction from the Edmonton ash sample (number 233) had 17% less sodium and 18% more iron than unweathered Mazama glass to which it was compared (Table 5). The comparison to Mazama C1 resulted in a CV of 15% and the comparison to Mazama C2 resulted in a CV of 28% (Table 11). The better agreement of the Edmonton ash sample with the Mazama C1 layer probably reflects slight leaching effects in both materials.

The Pumice Flat sample occurred in a strangely non-vegetated area north of the Antelope Unit site near Crater Lake. Soil horizonation was not apparent at the site and the pumice lumps were somewhat elongated as if the deposit had been abraded by water or wind. The appearance of this pumice in the field led to the hypothesis that

it was not from Mt. Mazama. INAAAC resulted in rejection of this hypothesis since the sample correlated with the ash from Mt. Mazama (Tables 11 and 12).

The Stage Gulch sample, collected in northeastern Oregon, was expected to be St. Helens ash layer Y by virtue of its particle size and location above a very thick (> 20 ft.) alluvial deposit of Mazama ash (Norgren and Harward, 1968). However, a low CV of 12%, an average ratio of 1.03, and microscopic observations (Appendix VII) correlate this sample with Mazama ash. Post-depositional movement probably accounts for its accumulation as a distinct layer.

The glowing avalanche sample was from the culminating eruption of Mt. Mazama. This deposit is not as extensive as the air fall materials preceeding it, but a chemical analysis was desired for comparison to the air fall pumice. The sample had slightly less Fe and Sc (Table 6), but its trace element composition was otherwise very similar to the Mazama average. Correlations could be made with the Mazama ash layer without difficulty (Tables 11 and 12).

Dark gray fragments of pumice were found intermixed with buff colored pumice in the upper part of the Mazama C2 layer. A sample of glass isolated from dark gray fragments correlated with Mazama ash (CV = 11%), although the average ratio to Mazama composition was 0.79 instead of 1.00. This resulted from the depletion

of rare earth elements consistent with the high amounts of feldspar microlites that tend to occur in dark colored pumice (Ewart, 1963). Feldspar tends to exclude the rare earth elements from its structure (Haskin et al., 1966).

The Kamloops, B. C. sample was analyzed initially as an example of St. Helens layer Y. There were several reasons for suspecting the sample was not from the layer represented by St. Helens Y samples from Randle and Longmire, Washington (Table 5). Although the average ratio relative to St. Helens Y was 1.03, (data not shown) the CV of 43% was much too high for correlation to St. Helens Y. The lowest CV corresponded to Mazama ash but the average ratio for this comparison was 0.53. The glass shards of the Kamloops sample have the tubular appearance more like those of Mazama ash than those from St. Helens Y which has numerous crystal inclusions (Appendix VII). The discriminant function classifies the sample with the St. Helens W group (Table 12). The discriminant function alone would not be sufficient for correct classification of the sample. The average ratio corresponding to the CV of 22% (Table 11) for the comparison to St. Helens layer W was 0.64 (data not shown). The Kamloops sample was not definitely correlated with any of the layers tested and its identity remains in doubt.

The Squaw Creek and Devils Hill samples were included to test the method with ash samples known to be unrelated to any of

the deposits studied. Consequently, none of the CV's for these samples were less than 25%, suggesting that this should be an upper limit for correlations done with the INAAC method. Values higher than about 20% may indicate chemical dissimilarity produced by: 1) greater experimental error than found for these data, 2) different formulas for weighting the results, 3) weathering or alteration of samples through leaching of alkali elements and accumulation of transition elements, or 4) actual differences in chemical compositions of the two samples being compared. For the Squaw Creek and Devils Hill samples, the average ratios for comparisons having the lowest CV's were nearly 1.00 (Table 11). This illustrates that this parameter should not be used as positive evidence in correlation.

Rather, the coefficient of variation should be considered first. Average ratio deviation from 1.00 should be considered only as evidence against a correlation with a particular group. The appearance of the Squaw Creek pumice was very much like that of Newberry pumice although it was sampled at a great distance from the known fallout area for Newberry ash. This is probably the crystal free ash layer initially correlated with Newberry ash (Allison, 1945) and later recognized as pumice older than Newberry (Allison, 1966b).

The Devils Hill pumice layer in the Cascade Mountains of Oregon overlies a small part of the Mazama pumice sheet. There should be no problem distinguishing between Devils Hill and Mazama

pumice because comparisons to Mazama have CV's greater than 45%. Comparisons of this sample to other Devils Hill samples should produce low CV's. The discriminant function classified the Devils Hill sample with the St. Helens W ash layer (Table 12). The use of the discriminant function alone would have resulted in an incorrect classification in this instance. The CV of 26% for the comparison between Devils Hill pumice and the St. Helens W layer was too high for a correlation. This emphasizes that both statistical methods should agree before a correlation is made.

Conclusions

1. Instrumental neutron activation analysis was capable of detecting significant differences in contents of alkali, rare earth, and transition elements in glassy isolates from several volcanic ash layers of the Pacific Northwest.
2. The trace element contents were considerably lower for the Glacier Peak and St. Helens ash layers in Washington than for the Mazama and Newberry ash layers in Oregon.
3. Na, Sm, Sc, Fe, Ce, Hf, and Th could be determined most accurately (one standard deviation of less than 5%); La, Co, Eu, Yb, Cs, Ba, and Lu were intermediate (relative deviation less than 17%); while Rb, Ta, Nd, Tb, and Cr had large errors due to counting statistics (greater than 22%).

4. Site to site variability of the Mazama and Newberry ash deposits was about 5% (one standard deviation), whereas variability for the crystal-rich Glacier Peak and St. Helens ashes was greater.

5. Ratios of "unidentified" regional samples to averages of previously identified standard ash samples produced low coefficients of variation (5-15%) indicating the proper classifications. Coefficients greater than 20-25% for all groups indicated samples unrelated to any of the six standard ashes.

6. Discriminant function analysis for 14 elements produced classifications generally agreeing with those of the simpler variation analysis method. Both statistical methods should be used to increase the chances of obtaining a correct correlation.

7. Data support previous identification of Mazama ash in the Pacific Ocean, at Steptoe Canyon, Washington, and at Edmonton, Alberta.

II. CORRELATION OF VOLCANIC ASH LAYERS OF PEAT BOGS

Introduction

Peat bogs were sampled in northeastern Oregon in conjunction with studies of soil formation in Mazama ash. Hansen (1947) utilized volcanic ash layers as stratigraphic horizon markers while studying pollen grains deposited in peat bogs of northwestern United States. Ash samples collected from peat bogs provided additional thickness measurements, unweathered samples, peat for carbon dating, and stratigraphic correlations to supplement information obtained from volcanic ash soils. With the deposition of peat between ash layers, intermixing, which proved to be a problem in some upland deposits, was minimized.

The eruption of Mt. Mazama 6,660 ybp (years before present) at Crater Lake, Oregon was expected to have contributed most of the volcanic ash found in peat bogs of eastern Oregon. The fallout area for Glacier Peak ash (12,000 ybp) has been predicted for the northeastern corner of Oregon (Fryxell, 1965). The distribution patterns indicated for pyroclastics from Mt. St. Helens (Crandell et al., 1962) did not include Oregon although Mt. St. Helens is closer to some of the Oregon sample sites than either Glacier Peak or Crater Lake (Figure 1).

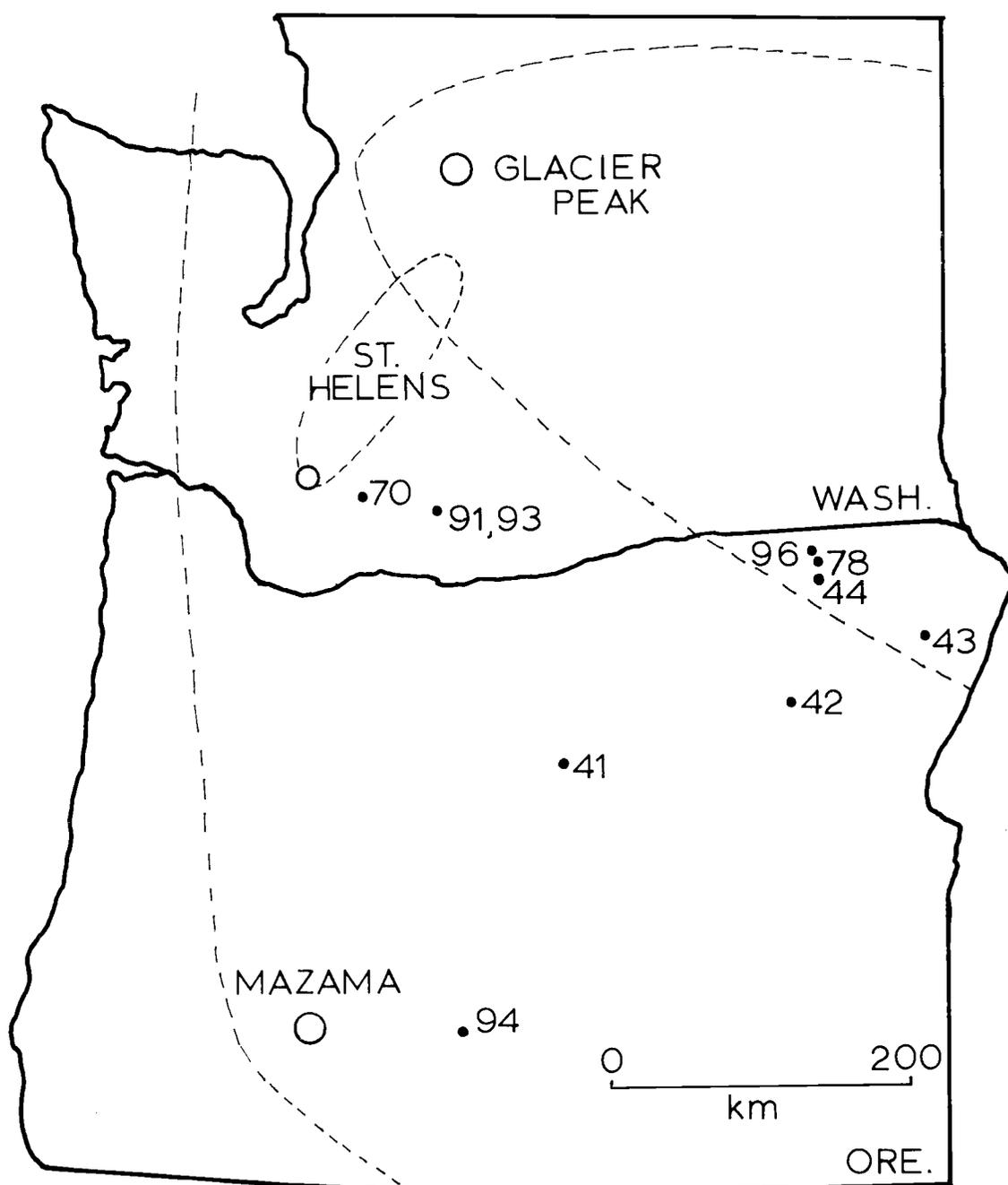


Figure 1. Locations of peat bogs from which volcanic ash samples were obtained for activation analysis.

The objective of this study was to correlate volcanic ash deposits of peat bogs with known ash layers of the Pacific Northwest by means of instrumental neutron activation analysis correlation (INAAC).

Materials and Methods

Samples from peat bogs have been obtained during the past few years by personnel working on volcanic ash projects in the Department of Soils at Oregon State University. These samples were taken to determine stratigraphy of deposits, and as reference materials to upland sites. They were utilized in this study by application of INAA techniques. The peat bogs were sampled at increasing distances northeast of Crater Lake, Oregon along the main lobe of Mazama ash deposition (Figure 1). Many of the volcanic ash layers were sampled in bogs adjacent to volcanic ash soils of interest (Chapter III). Other peat bogs were sampled at increasing distances from Mt. St. Helens.

Most samples of volcanic ash were collected in bogs that met the following criteria: 1) small watershed size, 2) minimal adjacent relief, and 3) sampling location at a suitable distance from any drainage inlet. Samples were obtained with a tiling spade when possible. The depth of peat sometimes made it necessary to use

specially constructed tubes to extract a core.² The great variation in the types of peat, depths encountered, and moisture conditions allows no existing sampler to be used under all conditions. Samples were described (Table 1 and Appendix IV) and photographed. After discarding a layer one cm thick around each core, samples were obtained for INAAC. The 125-63 μ very fine sand fraction was obtained from the finer ash samples by sieving with stainless steel sieves. Pumice lumps present in some ash layers were ground to 125-63 μ with a hard surfaced diamonite mortar and pestle. Pumice from Sycan Marsh was scrubbed initially with ultrasonic vibration (Biosonic III) to remove brown coatings along with the exterior portions of the pumice lapilli. A five minute treatment at 100 kilocycles per second provided a less weathered inner core for analysis. It was necessary to treat some of the samples with hydrogen peroxide to remove organic matter (Table 1). All samples were centrifuged in bromoform-bromobenzene ($\rho = 2.4$ g/cc) to obtain the glassy fraction. Microscopic observations were used to check the effectiveness of the H₂O₂ and heavy liquid separation treatments (Appendix VII).

Instrumental neutron activation analysis of volcanic ash was

² Reconnaissance sampling was done with a peat sampler furnished by Dean H. P. Hansen, Oregon State University, Corvallis. Other sampling equipment was devised by J. A. Norgren, Dept. of Soils, Oregon State University, Corvallis.

Table 1. Volcanic ash layers sampled in peat bogs of eastern Oregon and Washington.***

INAA No.	Depth (cm)	Description	Site and sample No.	Age (ybp)*
<u>Sycan Marsh (Sec. 4, T32S, R14E)</u>				
	0-33	Dark mucky soil		
	33-87	Alternating light and dark layers		
326	87-99	Coarse pumice	94-1	
327	99-120	Fine pumice	94-2	
328	120-130	Coarse and fine pumice	94-3	
	130+	Muck		
<u>Simpson Place (Sec. 32, T12S, R21E)</u>				
	0-51	Mucky peat		
	51-118	Fibrous peat		
223	118-150	Stratified ash and fine pumice	(top) 41-1 41-2 41-3 41-4	
224			(bottom) 41-5	← 6500±130
	150+	Peat		
<u>Anthony Lakes Meadow (Sec. 7, T7S, R37E)</u>				
	0-51	Peat		
225	51-69	Upper ash	(top) 42-1	
226			(bottom) 42-2	← 6910±140
	69-196	Peat		
227	196-206	Lower ash	42-3	← 9460±130
	206+	Unoxidized clay		
<u>Tollgate Summit (Sec. 34, T3N, R38E)</u>				
	0-69	Peat		
231	69-104	Ash	(top) 44-1	
232			(bottom) 44-2	
	104-168	Unoxidized clay		
<u>Olinger Meadow (Sec. 36, T4N, R37E)</u>				
	0-73	Fibrous mucky peat		
	73-74	Fine charcoal		
323**	74-77	Sandy loam	78-1	
	77-81	Silty clay loam, olive gray		
	81-82	Silt loam, buff		
	82-92	Dark silty clay with charcoal		
	92-100	Silty clay loam, olive gray		
324	100-120	Coarse silt loam		
	120-130	Sandy loam	78-2	
	130-137	Very fine sandy loam		
	137-140	Coarse sandy loam		
	140-144	Sandy loam		
	144-147	Laminated coarse silt		
	147-157	Silty clay loam		
325	157-176	Fine loam to silt loam	78-3	
	176-198	Silty clay loam		

Table 1. (continued)

INAA No.	Depth (cm)	Description	Site and sample No.	Age (ybp)*
<u>Bald Mt. Saddle (Sec. 34, T4N, R38E)</u>				
	0-10	Mucky soil		
	10-12	Grey silt		
	12-17	Loamy ash (stratified)		
322	17-20	White silt and grey loamy fine sand	96-1	
	20-150	Laminated silts and loams		
	150+	Basalt		
<u>Hurricane Creek (Sec. 13, T2S, R44E)</u>				
	0-122	Peat		
228	122-127	Upper ash	43-1	← 2430±100
	127-208	Peat and mineral matter		← 3120±105
229	208-226	Lower ash	(top 12cm) 43-2	
			(bottom 4cm) 43-3	← 7420±160
	226-241	Peat and mineral matter		
	241-254	Gravel		
<u>South Camp (Sec. 11, T7N, R8E)</u>				
	0-13	Fibrous peat		
	13-15	Fine sand, dark grey		
	15-17	Very fine sand		
	17-19	V. coarse sand size pumice		
	19-20	Fine sand, grey		
	20-58	Peat		
303	58-90	Coarse sand grading to coarse gravel	70-2	
	90-115	Fine silty grey ash grading to coarse sandy buff pumice		
<u>Lakebeds Meadow (Sec. 17, R16E, T6N) South end</u>				
	0-12	Peat		
	12-13	Medium to fine sand, grey		
	13-14	Organic matter		
319**	14-17	Silty ash, buff	91-1	
	17-25	Muck and mineral matter		
320**	25-33	Coarse sand	91-2	
	33-40	Silt loam and muck and charcoal		
<u>Lakebeds Meadow (Sec. 17, R16E, T6N) SE side</u>				
	0-21	Dark mucky peat		
317**	21-31	Buff medium to coarse sand	93-1	
	31-36	Muck and mineral matter		
318	36-68	Cream colored silt	93-2	

* Years before present. Personal communication, Dr. M. E. Harward, Oregon State University.

**Samples treated with HNO₃ acidified hydrogen peroxide for removal of organic matter.

***Appreciation is expressed to Dean H. P. Hansen, Dr. K. F. Oles, and Dr. W. H. Taubeneck for suggesting locations of some of the peat bogs sampled.

performed according to the method described in Chapter I and by Gordon et al. (1968). The results were compared to analyses of standard ash samples by calculating the average ratios, coefficients of variation, and discriminant values as previously described (Chapter I).

Samples of peat for carbon dating were obtained by sampling a layer one cm thick above and/or below certain ash layers (Table 1). Fibrous roots and humic acids that contributed modern carbon were removed prior to the radio-carbon analysis by Isotopes, Inc.

Results and Discussion

Radio-Carbon Dates³

The commonly accepted age for Mazama ash is 6600 ybp (years before present) (Allison, 1966a). The date obtained for peat below the ash layer at Simpson Place was 6500 ± 130 ybp (Table 1). The upper ash at Anthony Lake was 6910 ± 140 ybp, while peat below the lower ash at Hurricane Creek was slightly older (7420 ± 160 ybp). This older date probably resulted from sampling a 10 cm vertical section of peat at Hurricane Creek, while other peat samples were

³ Appreciation is expressed to J. A. Norgren, M. E. Harward, A. A. Theisen, C. T. Youngberg, W. H. Doak, and M. J. Dudas who helped obtain the peat samples for age dating and ash samples for INAA.

only about one cm thick. The radio-carbon dates for ash at Simpson Place, the upper ash at Anthony Lakes Meadow and the lower ash at Hurricane Creek all correlate with Mazama ash and verify Mazama as the most dominant Recent ash deposit across the transect.

The dates for the upper ash at Hurricane Creek (2430-3120 ybp) suggest that this layer may be St. Helens Y, dated at 3200 ybp (Crandell et al., 1962).

The date for the lower ash layer at Anthony Lakes Meadow (> 9460 ybp) was obtained by sampling peat above the ash layer at a site where no peat occurred beneath the ash. It was assumed at the time of sampling that this ash was from Glacier Peak. The accepted age of 12,000 years for Glacier Peak ash has been determined by dating coincident freshwater mollusc shells (Fryxell, 1965). It would be desirable to obtain organic matter from beneath the lower ash layer at Anthony Lakes Meadow so that the maximum age could be determined.

INAAC

In general, it was possible to obtain clean, unweathered volcanic ash from peat bogs. However, when the ash layers were thin and where peat accumulation was slow, the effects of mixing and weathering were apparent. Visual comparison of analytical data (Table 2) is difficult at best. The method of INAAC (described in

Table 2. Activation analysis of volcanic ash from peat bogs (glassy separates 125-63 μ).

INAA No.	ppm**																		
	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
<u>Sycan Marsh, top layer (94-1)</u>																			
326	3.35	79	3.2	730	22	43	16	5.0	.62	1.2	3.6	.65	6.3	6.1	.25	2.9	1.53	6.9	4.2
±**	.07	16	.6	90	2	2	20	.1	.12	.3	.9	.05	.3	.2	.07	.3	.05	.2	2.2
<u>Sycan Marsh, middle layer (94-2)</u>																			
327	3.33	51	3.9	690	22	40	26	4.7	.96	.6	3.2	.49	5.4	6.2	.11	2.4	1.44	6.2	4.0
±	.07	13	.5	90	1	1	15	.1	.10	.2	.8	.11	.3	.2	.05	.2	.03	.1	1.8
<u>Sycan Marsh, bottom layer (94-3)</u>																			
328	3.31	71	4.5	790	25	41	38	5.1	1.12	.5	2.4	.58	5.2	6.6	.14	3.3	1.66	7.0	4.9
±	.07	15	.7	120	2	1	20	.1	.11	.2	1.3	.11	.3	.2	.05	.3	.04	.1	2.1
<u>Simpson Place, top of layer (41-1)</u>																			
223	3.32	71	4.8	690	24	40	18	4.8	.76	1.0	3.1	.45	5.6	6.1	.20	4.1	1.57	7.2	5.4
±	.07	15	.8	180	2	2	8	.1	.09	.3	.5	.17	.4	.3	.05	.3	.05	.1	1.4
<u>Simpson Place, bottom of layer (41-5)</u>																			
224	1.84	32	2.5	360	12	23	8	2.3	.44	.2	2.3	.29	2.6	2.4	.12	1.2	.69	3.3	.9
±	.04	8	.5	90	1	1	6	.1	.07	.2	.4	.08	.2	.1	.04	.2	.02	.1	.8
<u>Anthony Lake, top of upper layer (42-1)</u>																			
225	3.39	65	3.4	830	21	44	30	5.2	.89	1.3	3.0	.50	7.6	6.8	.27	2.9	1.58	7.0	.7
±	.07	12	.4	120	2	2	8	.1	.08	.3	.5	.12	.5	.2	.05	.2	.04	.1	1.0
<u>Anthony Lake, bottom of upper layer (42-2)</u>																			
226	1.77	27	2.4	370	11	25	14	2.9	.54	.1	2.5	.28	2.7	3.4	.16	2.1	.90	4.4	1.1
±	.03	10	.7	100	1	2	7	.1	.08	.2	.4	.08	.3	.2	.04	.3	.03	.1	1.5
<u>Anthony Lake, lower layer (42-3)</u>																			
227	2.71	70	2.7	410	22	34	3	3.0	.54	.9	1.0	.32	8.6	3.4	.31	2.6	.94	3.2	1.3
±	.05	12	.6	100	2	2	6	.1	.09	.3	.4	.10	.4	.2	.04	.4	.03	.1	.7

Table 2. (continued)

No.	ppm**																		
	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
<u>Tollgate Summit, top of layer (44-1)</u>																			
231	3.40	55	4.4	620	20	43	34	5.3	1.00	.5	3.6	.58	6.8	6.2	.30	3.2	1.47	7.1	2.2
±**	.07	11	.7	130	1	1	8	.1	.09	.3	.5	.13	.4	.2	.05	.3	.04	.1	1.1
<u>Tollgate Summit, bottom of layer (44-2)</u>																			
232	3.76	47	3.1	580	20	43	26	4.9	.90	.6	3.5	.50	6.1	6.6	.30	2.5	1.40	6.2	1.1
±	.07	13	.4	120	1	1	7	.1	.09	.3	.4	.09	.3	.2	.04	.2	.03	.1	1.1
<u>Olinger Meadow, upper layer (78-1)</u>																			
323*	1.75	36	3.6	300	10	24	14	2.4	.79	.2	.1	.14	4.6	3.6	.64	2.6	1.14	6.9	8.3
±	.04	13	.9	80	1	1	15	.1	.12	.2	.5	.05	.3	.2	.09	.2	.04	.2	2.4
<u>Olinger Meadow, middle layer (78-2)</u>																			
324*	2.28	46	3.0	620	22	51	63	4.7	1.35	0	3.0	.62	5.8	6.3	.24	5.1	2.38	11.5	7.4
±	.05	13	.8	100	2	2	23	.1	.15	.3	2.2	.07	.4	.3	.08	.4	.05	.2	2.6
<u>Olinger Meadow, bottom layer (78-3)</u>																			
325*	1.52	84	2.6	680	24	52	6	4.4	1.20	.6	2.1	.53	9.7	5.0	.49	8.4	2.75	16.3	15.8
±	.04	18	.6	110	1	2	14	.1	.15	.3	.7	.07	.3	.2	.08	.5	.06	.3	3.3
<u>Bald Mountain Saddle, upper layer (96-1)</u>																			
322*	2.72	45	2.6	580	20	35	26	4.1	.88	.8	1.2	.33	4.6	3.9	.38	3.0	1.24	5.7	4.3
±	.05	12	.5	80	1	1	5	.1	.10	.3	.5	.04	.2	.2	.07	.2	.03	.1	2.1
<u>Hurricane Creek, upper layer (43-1)</u>																			
228*	3.39	65	3.7	480	17	36	20	4.5	.66	1.0	.9	.26	4.7	4.0	.42	4.8	1.53	4.4	4.3
±	.07	13	.7	130	1	1	7	.1	.11	.4	.4	.11	.3	.2	.08	.3	.05	.1	1.2
<u>Hurricane Creek, top of lower layer (43-2)</u>																			
229	3.44	83	3.5	770	22	41	26	5.2	.91	.7	3.6	.48	6.5	4.1	.26	3.4	1.55	6.2	2.0
±	.07	15	.5	130	2	1	8	.1	.10	.3	.5	.11	.4	.2	.05	.2	.03	.1	.8
<u>Hurricane Creek, bottom of lower layer (43-3)</u>																			
230	3.63	60	3.5	580	20	41	24	5.2	.91	.9	3.1	.56	5.0	6.4	.25	3.0	1.53	6.3	1.2
±	.07	17	.6	80	2	1	8	.1	.11	.3	.5	.10	.3	.2	.05	.3	.04	.1	1.5

Table 2. (continued)

INAA		ppm**																	
No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
<u>South Camp, second layer (70-2)</u>																			
303	3.07	54	2.3	420	19	32	41	3.3	.74	.3	.2	.16	3.8	2.7	.68	1.9	1.00	2.4	3.9
±**	.06	12	.4	70	2	1	26	.1	.12	.2	.6	.04	.3	.2	.09	.3	.03	.1	1.9
<u>Lakebeds Meadow, upper layer (91-1)</u>																			
319*	3.05	55	2.8	440	13	28	18	2.8	.74	.2	.5	.16	3.9	3.5	.38	1.5	.99	3.2	1.4
±	.06	10	.5	50	1	1	11	.1	.09	.1	.4	.04	.2	.1	.05	.2	.03	.1	1.2
<u>Lakebeds Meadow, second layer (91-2)</u>																			
320*	3.22	40	1.9	340	13	22	20	2.2	.86	.4	.7	.16	2.8	2.5	.34	2.4	1.01	2.8	2.1
±	.06	12	.4	60	1	1	10	.1	.09	.2	.4	.04	.2	.1	.05	.2	.03	.1	1.0
<u>Lakebeds Meadow, upper layer (93-1)</u>																			
317*	3.06	51	1.6	450	15	30	11	3.1	.82	.1	.8	.19	4.1	3.2	.55	2.3	1.01	2.7	3.1
±	.06	11	.5	70	1	1	13	.1	.10	.2	.4	.04	.2	.2	.06	.2	.03	.1	1.6
<u>Lakebeds Meadow, second layer (93-2)</u>																			
318*	1.92	46	1.4	370	28	63	50	6.7	1.23	.4	5.4	.81	6.4	6.5	.35	4.2	1.25	12.2	16.2
±	.04	12	.5	90	2	2	21	.1	.20	.2	1.3	.07	.4	.3	.09	.4	.05	.2	3.5

*Samples having more than 5% crystal content.

**Na and Fe are in percent. ± = one standard deviation for counting statistics.

Chapter I) utilizes the coefficient of variation of normalized data (Table 3), as well as the discriminant function (Table 4) to correlate geologic specimens. The methods developed in Chapter III for reducing weathering effects upon correlations were applied to the data as well.

Mazama Ash

The pumice samples from Sycan Marsh were of interest for two reasons. First, they represent easily identified coarse lapilli near Mt. Mazama, occurring in a wet environment. Second, Sycan Marsh had a large quantity of extremely coarse material at the bottom of the deposit. Compositional differences between this layer and the two above it might indicate an earlier eruption of Mt. Mazama. However, the activation analysis data indicated no significant differences between the three layers (Table 2). Each layer correlates with Mazama ash when classified by the coefficient of variation (Table 3) and by the discriminant function (Table 4).

Volcanic ash occurred at Simpson Place in one of the few peat bogs in the Ochoco Mountains. The upper part of this ash deposit was considerably darkened by organic matter and iron oxides. Microscopic observations also revealed devitrified glass shards and iron oxide coatings. Apparently the sample was considerably weathered. Comparison of the analysis of the upper part of the layer

Table 3. Coefficients of variation (%) for volcanic ash from peat bogs.

INAA No.	Description	Av. ratio	Mazama			Glacier	St. Helens		
		for lowest CV	C1	C2	Newberry	Peak	Y	W	T
326	Sycan Marsh T**	1.02	16*	16	50	45	41	26	32
327	Sycan Marsh M	0.98	7	7*	46	33	39	19	34
328	Sycan Marsh B	1.06	13*	15	55	26	35	19	32
223	Simpson Pl. T	1.28	35	38	75	36	40	24	38
224	Simpson Pl. B	0.53	14	12*	35	53	57	26	50
225	Anthony L. I T	1.03	12*	15	50	44	41	26	33
226	Anthony L. I B	0.57	14*	19	66	51	56	28	47
227	Anthony L. II	1.22	33	43	61	25	33	29	41
231	Tollgate S. T	1.02	7*	16	58	45	45	23	37
232	Tollgate S. B	0.95	7*	19	48	45	47	23	37
323	Olinger Md. I	1.38	79	98	80	50	49	52	63
324	Olinger Md. II	1.37	31	35	82	38	42	36	26
325	Olinger Md. III	2.65	99	102	117	62	59	73	76
322	Bald Mt. Sd. I	0.82	19*	36	67	25	29	21	26
228	Hurricane Ck. I	1.58	39	49	99	20	18*	22	27
229	Hurricane Ck. II T	0.99	17*	21	64	40	45	23	39
230	Hurricane Ck. II B	0.95	10*	14	57	39	42	21	34
303	South Camp II	0.83	57	93	51	37	29	26	46
319	Lakebeds Md. I	0.78	31	52	47	27	30	19*	34
320	Lakebeds Md. II	0.72	38	56	80	33	30	29	36
317	Lakebeds Md. II	0.83	45	77	65	30	27	21	39
318	Lakebeds Md. III	2.68	108	112	95	66	63	72	84

* Lowest CV classifies the sample with this group. ** T = top of layer, M = middle of layer, B = bottom of layer; I = upper layer, II = second layer, and III = third layer, each separated by a layer of peat.

Table 4. Discriminant values for volcanic ash sampled in peat bogs.

INAA No.	Description		Mazama	Newberry	Glacier Peak	St. Helens	
						Y	W
326	Sycan Marsh	T**	15110*	13470	2770	- 5180	10000
327	Sycan Marsh	M	12290*	10860	2500	- 4540	8560
328	Sycan Marsh	B	13290*	11590	2600	- 4730	9040
223	Simpson Place	T	14620*	12500	2800	- 4950	9690
224	Simpson Place	B	3080	3650	1390	- 2960	4100*
225	Anthony Lakes Md.	I T	9910*	9080	2260	- 4080	7430
226	Anthony Lakes Md.	I B	5420*	5240	1670	- 3350	5180
227	Anthony Lakes Md.	II	-6700	-3890	430*	- 980	- 550
231	Tollgate Summit	T	17130*	14580	3100	- 5380	10910
232	Tollgate Summit	B	13920*	12160	2750	- 4740	9380
323	Olinger Meadow	I	24190*	20210	3800	- 6890	14350
324	Olinger Meadow	II	24790*	19730	3940	- 6730	14430
325	Olinger Meadow	III	46310*	36690	6360	-10970	24860
322	Bald Mt. Saddle	I	10500*	9410	2330	- 4120	7730
228	Hurricane Creek	I	-1910	- 410	940	- 1810	1740*
229	Hurricane Creek	II T	8580*	8040	2090	- 3880	6800
230	Hurricane Creek	II B	10830*	9770	2350	- 4240	7880
303	South Camp	II	-1330	420	980	- 1880	2110*
319	Lakebeds Meadow	I	4430	4920*	1580	- 3170	4830
320	Lakebeds Meadow	II	1050	2030	1260	- 2360	3180*
317	Lakebeds Meadow	II	460	1850	1140	- 2370	2940*
318	Lakebeds Meadow	III	59870*	47890	8070	-13050	31630

* Highest discriminant value classifies the sample with this group. ** T = top of layer, M = middle of layer, B = bottom of layer; I = upper layer, II = second layer, and III = third layer, each separated by a layer of peat.

relative to the standard Mazama ash gave a CV of 35% (Table 3). The comparison to the St. Helens W layer produced the lowest CV, 24%. Since the Simpson Place ash layer was dated at 6500 ± 130 ybp (Table 1), it would not be expected to contain ash from the St. Helens W eruption 300 years ago. The discrepancy is probably due to weathering effects. Coefficients of variation over 20%, therefore should not be used in making classifications.

A particularly unusual result occurred for ash in Simpson Place bog and Anthony Lakes Meadow (Table 3). The analyses for the bottom part of each layer (samples 224 and 226) were similar to each other and they had CV's correlating with Mazama glass, but the average ratios to Mazama glass composition were too low. These low ratios could not be explained by differences in sample weights and volumes, which were similar to other ash samples from Simpson Place and Anthony Lakes Meadow. The top part of the upper ash layer at Anthony Lakes Meadow correlated with Mazama ash (Tables 3 and 4). Also, dilution by organic matter was not great. More recent field work has revealed a thin layer at the base of the Mazama ash in the Ochoco Mts. which is grey when dry and pinkish when wet. Perhaps further work on this layer would help explain the anomalous results.

Some of the best specimens of Mazama ash were obtained at the Tollgate Summit bog, 450 km from the source at Crater Lake.

Very low coefficients of variation and average ratios near 1.00, along with favorable discriminant results, produced excellent correlations with Mazama ash (Tables 3 and 4). However, this was not the case for samples from nearby Olinger Meadow. Loess may have been mixed with these samples since only 20% of the very fine sand fraction was glass shards ($\rho < 2.4\text{g/cc}$). Ten percent of the glassy fraction was crystals (Table 2) and much devitrification was also noted (Appendix VII). About 20% of sample 323 from Olinger Meadow consisted of diatoms that were probably concentrated as a result of the heavy liquid separation used to obtain the glassy fractions (Appendix VII). The amounts of trace elements contributed by diatoms are not known. Procedures for their removal would be needed if materials containing them are to be analyzed correctly. Devitrification and iron oxidation of the glass also indicated the sample may have been weathered.

The sample from Bald Mt. Saddle was similarly devitrified, oxidized, and contaminated by foreign materials. The CV of 19% was somewhat high and the average ratio (0.82) was too low for good correlation with Mazama ash, although the discriminant classification placed it with the Mazama group.

The lower ash layer (18 cm thick) at Hurricane Creek correlates with Mazama ash. Sample 229 represents the top 12 cm of this layer and sample 230 represents 4 cm taken from the lower part.

No significant chemical differences between the two samples could be detected for these glassy fractions. This confirms the conclusions drawn from chemical analysis of the two coarse pumice layers (C1 and C2) nearer the source (Chapter I).

Glacier Peak Ash

A distinct ash layer (10 cm thick) was found at Anthony Lakes Meadow a considerable distance beneath the Mazama ash layer (Table 1). This older ash layer was thought to be Glacier Peak ash, since it was sampled near the limits of the area indicated by Fryxell (1965) for the minimum extent of Glacier Peak fallout (Figure 1). Although the CV for the comparison to Glacier Peak ash was over 20%, the discriminant function classified the lower ash layer with the Glacier Peak group (Table 4). This agrees with the carbon date of > 9460 ybp, indicating the possibility of 12,000 year old Glacier Peak ash at this site.

St. Helens Y Ash

Peat sampled above (2430 ybp) and below (3120 ybp) the upper ash layer at Hurricane Creek gave radio-carbon dates (Table 1) similar to the "Y" layer from Mt. St. Helens. However, the previously indicated minimum extent of the St. Helens Y deposit (Crandell et al., 1962) does not include Oregon. In fact, the main

distribution of St. Helens Y ash occurred in a northeasterly direction from Mt. St. Helens rather than in a southeasterly direction (Figure 1). Identification of St. Helens Y ash in Oregon would suggest the possibility of a southeastern lobe.

Field Observations. The upper ash layer at Hurricane Creek, suspected of being layer Y from Mt. St. Helens, received additional attention during subsequent field work. An attempt was made to identify this layer near the vicinity of Mt. St. Helens, Washington (sample 303), and then trace it easterly and southeasterly into northeastern Oregon (samples 320, 317, and 228). In Washington the layer of coarse pumiceous lapilli (30 cm thick) occurred between greyish bands of finer ash. The layer decreases in thickness to less than 5 cm and in particle size (< 1 mm) with distance from the presumed source. Although the layer is thin in Oregon, it has significance for certain studies involving soil formation. Norgren (1962) observed the presence of an additional ash layer in northeastern Oregon soils. His petrographic studies of the Tolo soil developed from Mazama ash revealed a mineralogic discontinuity in upper horizons. Mineralogical differences between ash layers could be much greater than changes due to weathering. The additional ash layer has further importance as a stratigraphic marker.

Laboratory Results. It was difficult to confirm the identification of the upper ash layer at Hurricane Creek with the INAAC

data. Comparison of the sample to the average for St. Helens Y resulted in a CV of 18% and a ratio of 1.58 (Table 3). The discriminant function classified it with the 300 year old St. Helens W layer, in obvious disagreement with ^{14}C data. The Mazama and Newberry ash deposits were eliminated as possibilities by both classifications. Cumingtonite, a mineral reported to be unique to the St. Helens Y layer (Westgate and Dreimanis, 1967), has been identified in the Hurricane Creek sample by Wilcox (1969).

The St. Helens Y ash near Mt. St. Helens has a layer of buff colored lapilli between two greyish layers of finer material. Only the buff pumice was analyzed from the sample taken at the South Camp bog. Perhaps the sample from Hurricane Creek contains both types of material, making classification difficult. The sample to sample analytical variability was considerable for standard samples of St. Helens Y volcanic ash (Chapter I). The analyses of samples from South Camp bog (sample 303) and Lakebeds Meadow (samples 320 and 317) did not agree with the analysis of St. Helens since the CV's were greater than 27% (Tables 3 and 4). A comparison of ash from South Camp bog (sample 303) with ash from Lakebeds Meadow (sample 317) produced a CV of 13% and an average ratio of 1.03 (data not shown), indicating that these samples are from the same source (Figure 1). All of the Lakebeds Meadow samples had more than 5% crystal content and the analyses produced

no definitive correlations with the standard ash layers. Sample 318 from Lakebeds Meadow, thought to be Mazama ash since it was located beneath the St. Helens Y layer, appeared devitrified and slightly weathered (Appendix VII).

Elemental Ratios

In the correlation of weathered samples from volcanic ash soils, it was found advantageous to consider elemental ratios in addition to absolute abundances (Chapter III). Dividing the concentration of one element by that of an element similarly affected by weathering resulted in relatively constant ratios for the soil samples. An attempt was made to classify the ash samples from peat bogs by using the ratios found useful for soil samples (Chapter III, Tables 6 and 8).

Low Na/Fe and Na/Co ratios indicate leaching of sodium and accumulation of iron and cobalt. These ratios were particularly sensitive indicators of weathering. Sc/Fe, Th/Hf, La/Sm, and Th/Sm ratios were found to remain constant throughout moderate weathering (Chapter III). Sc/Fe ratios for the Glacier Peak and St. Helens pyroclastics were about 3×10^{-4} , whereas those from Mazama and Newberry were 4×10^{-4} . The selection of elemental ratios, their values for the standard ash samples, and the application of the discriminant function are explained in Chapter III.

In general, the bog samples correlated with Mazama ash by other methods also appear similar to Mazama ash in trace element ratios. The lower ash at Anthony Lakes Meadow had the low Sc/Fe ratio and high Th/Hf and Th/Sm ratios expected for Glacier Peak ash (Tables 5 and 6). The low Sc/Fe ratio for the Hurricane Creek upper ash layer appears to be the most important indicator for classifying the sample with the St. Helens Y samples 303, 320 and 317 which are also distinguished by low Sc/Fe ratios.

The low Na/Fe and high Sc/Fe ratios for the samples from Olinger Meadow further establish the unpredictable effects of contaminating materials. Trace element ratios are not expected to aid in correlation of such samples. In future studies, attention should be given to chemical and physical methods to obtain purer samples containing unweathered volcanic glass.

Application of the discriminant functions (Chapter III, Table 9) to the trace element ratios in Table 5, (except for Na/Fe and Na/Co which indicate weathering) resulted in classifications (Table 7) generally agreeing with those calculated from the abundance data (Table 4). The discriminant function classified the lower part of the ash layer at Simpson Place with Mazama ash instead of St. Helens W. The sample from South Camp, the peat bog nearest Mt. St. Helens, classified with the St. Helens Y ash (Table 7). However, some of the samples initially thought to be from St. Helens Y

Table 5. Elemental ratios and abundances used for correlating volcanic ash layers collected from peat bogs.

INAA No.	Layer	Elemental ratios								ppm	
		Na/Fe	Na/Co ($\times 10^4$)	Sc/Fe ($\times 10^4$)	Sc/Co	Th/Hf	La/Sm	Sm/Eu	Th/Sm	Ce	Hf
<u>Sycan Marsh</u>											
326	T*	2.19	1.16	4.5	2.4	1.04	4.3	8.1	1.25	43	6.1
327	M	2.31	1.37	4.3	2.6	0.87	4.7	4.9	1.15	40	6.2
328	B	1.99	1.01	4.2	2.2	0.79	4.9	4.6	1.01	41	6.6
<u>Simpson Place</u>											
223	T	2.11	0.80	4.6	1.7	0.92	4.9	6.3	1.16	40	6.1
224	B	2.67	1.60	4.7	2.8	0.79	5.4	5.2	1.14	23	3.3
<u>Anthony Lakes Meadow</u>											
225	I T	2.13	1.18	4.4	2.4	1.12	4.1	5.8	1.47	44	6.8
226	I B	1.97	0.86	4.8	2.1	0.80	3.8	5.3	0.95	25	3.4
227	II	2.83	1.03	3.4	1.2	2.51	7.4	5.5	2.89	34	3.4
<u>Tollgate Summit</u>											
231	T	2.31	1.07	4.8	2.2	1.09	3.8	5.3	1.28	43	6.2
232	B	2.69	1.52	4.4	2.5	0.93	4.2	5.4	1.26	43	6.6
<u>Olinger Meadow</u>											
323	I	1.54	0.67	6.0	2.6	1.27	4.3	3.0	1.96	24	3.6
324	II	0.96	0.45	4.8	2.3	0.92	4.8	3.4	1.24	51	6.3
325	III	0.55	0.18	5.9	1.9	1.95	5.5	3.6	2.23	52	5.0
<u>Bald Mt. Saddle</u>											
322	I	2.19	0.92	4.6	1.9	1.20	4.8	4.7	1.11	35	3.9
<u>Hurricane Creek</u>											
228	I	2.22	0.71	2.9	0.9	1.15	3.7	6.9	1.03	36	4.0
229	II T	2.22	1.01	4.0	1.8	1.58	4.2	5.7	1.27	41	4.1
230	II B	2.37	1.22	4.1	2.1	0.79	3.9	5.7	0.97	41	6.4

Table 5. (continued)

INAA No.	Layer	Elemental ratios								ppm		
		Na/Fe	Na/Co ₋₄ (X10 ⁻⁴)	Sc/Fe ₄ (X10 ⁻⁴)	Sc/Co	Th/Hf	La/Sm	Sm/Eu	Th/Sm	Ce	Hf	
				<u>South Camp</u>								
303	II	3.07	1.61	2.4	1.2	1.43	5.7	4.5	1.15	32	2.7	
				<u>Lakebeds Meadow</u>								
319	I	3.08	1.98	3.3	2.1	1.11	4.6	3.7	1.41	28	3.5	
320	II	3.19	1.36	2.8	1.2	1.13	6.2	2.5	1.28	22	2.5	
317	II	3.03	1.31	2.7	1.2	1.29	4.8	3.7	1.35	31	3.2	
318	III	1.54	0.46	9.8	2.9	0.99	4.2	5.4	0.96	63	6.5	

* T = top of layer, M = middle of layer, B = bottom of layer; I = upper layer, II = second layer, and III = third layer, each separated by a layer of peat.

Table 6. Average elemental ratios and abundances of standard volcanic ash samples.

Standard ash	Elemental ratios							ppm		
	Na/Fe	Na/Co ($\times 10^{-4}$)	Sc/Fe ($\times 10^4$)	Sc/Co	Th/Hf	La/Sm	Sm/Eu	Th/Sm	Ce	Hf
Mazama	2.33	1.33	4.3	2.5	1.01	4.3	5.7	1.29	44	6.4
Newberry	2.43	3.21	4.1	5.4	1.45	5.0	9.9	1.83	59	8.9
Glacier Peak	2.29	.81	3.1	1.1	2.52	6.2	5.1	2.55	26	2.6
St. Helens Y	1.98	.79	2.2	0.9	1.65	6.3	8.8	1.31	23	2.1
St. Helens W	2.37	1.08	3.1	1.4	1.09	5.3	5.7	1.49	32	4.9
St. Helens T	1.84	.66	3.2	1.2	1.15	4.3	5.8	1.30	33	4.3

Table 7. Discriminant values for equations derived from elemental ratios least affected by weathering (Chapter III).

INAA No.	Layer	Mazama	Newberry	Glacier Peak	St. Helens	
					Y	W
<u>Sycan Marsh</u>						
326	T**	654*	404	-624	-384	423
327	M	624*	327	-772	-504	375
328	B	621*	341	-734	-461	394
<u>Simpson Place</u>						
223	T	674*	360	-737	-473	410
224	B	729*	193	-1183	-861	284
<u>Anthony Lakes Meadow</u>						
225	I T	574*	376	-581	-354	404
226	I B	743*	131	-1330	-1010	223
227	II	149	814	1324*	1284	831
<u>Tollgate Summit</u>						
231	T	718*	372	-786	-540	393
232	B	618*	322	-780	-520	363
<u>Olinger Meadow</u>						
323	I	886*	153	-1457	-1151	233
324	II	850*	433	-820	-551	456
325	III	1034*	785	-155	-19	724
<u>Bald Mt. Saddle</u>						
322	I	744*	444	-576	-350	474
<u>Hurricane Creek</u>						
228	I	229	320	-76	82	405*
229	II T	565	616*	103	223	601
230	II B	561*	275	-801	-533	333
<u>South Camp</u>						
303	II	163	535	584	674*	603
<u>Lakebeds Meadow</u>						
319	I	278	210	-412	-208	323*
320	II	198	281	-52	129	424*
317	II	159	330	104	243	439*
318	III	2330*	747	-2340	-1910	583

* Highest discriminant value classifies the sample with this group.

**T = top of layer, M = middle of layer, B = bottom of layer; I = upper layer, II = second layer, and III = third layer, each separated by a layer of peat.

layer (samples 228, 320, and 317) were classified with St. Helens W. The discriminant function calculated from elemental ratios generally substantiated the results calculated from elemental abundances, but was unable to improve classifications of mixed materials from Olinger Meadow.

Conclusions

1. Instrumental neutron activation analysis correlation (INAAC) and radiocarbon dating provided definitive evidence for at least 18 cm of Mazama ash occurring in peat bogs up to 450 km from the source at Crater Lake, Oregon.
2. Volcanic ash from Mt. St. Helens (layer Y) dated about 3000 ybp and from Glacier Peak (> 9650 ybp) may occur in northeastern Oregon. Soils derived from Mazama ash in northeastern Oregon are likely to contain volcanic ash from Mt. St. Helens mixed into upper horizons.
3. Elemental ratios may improve classifications of slightly weathered volcanic ash, but greater emphasis should be placed upon obtaining pure volcanic glass for analysis.

III. CORRELATION OF VOLCANIC ASH SOILS

Introduction

Interest in volcanic ash soils in the United States has increased in recent years (Tidball, 1965; Borchardt, Theisen, and Harward, 1968 (Appendix II); Chichester, Youngberg, and Harward, 1969). Huge acreages of pumice and ash deposits exist on forested lands of the Pacific Northwest. As the demand for wood products increases, more intensive management and more knowledge of soils derived from volcanic ash will be desired. Although the soils in this study were located almost exclusively on broad forested ridge tops, most soils in Oregon have been influenced by volcanic ash to some degree. The properties of soils from volcanic ash are quite different from those of other soils. There is a need to understand volcanic ash type parent materials, weathering products, and the relationship of volcanic ash to soil properties. Volcanic ash deposits provide interesting materials for studies of soil formation because they can often be dated. They generally have deposits of unweathered materials for characterizing parent material and they fall in diverse areas in which climate and relief are variable.

The eruption of Mt. Mazama at Crater Lake, Oregon occurred 6600 years ago (Allison, 1966a) distributing large amounts of

pumiceous lapilli and ash for great distances. Most of this material was blown in a northeasterly direction from Crater Lake. More than 18 cm of airfall Mazama ash has been identified at Hurricane Creek bog (Chapter II) over 400 km from the source. Other bogs and soils in northeastern Oregon have even thicker deposits.

Current research projects at Oregon State University are considering the weathering, clay mineral formation, and physical-chemical properties of soils developed from Mazama ash. A transect of soils corresponding to the axis of the main lobe of the deposit have been tentatively selected for investigation. A sound basis for these studies requires the ability to recognize the Mazama deposit and distinguish it from other pyroclastic layers in the region.

Therefore, the objectives of this study were:

1. To test the method of instrumental neutron activation analysis for correlation of volcanic ash soils with ash erupted from volcanoes in Oregon and Washington;
2. To verify the samples at the transect sites as soils derived from Mazama ash;
3. To determine depths and effects of weathering upon abundances of trace elements in volcanic glass from soil horizons.

Materials

Volcanic ash soils were sampled along a transect extending 450 km northeast of Crater Lake (Figure 1, Table 1). Care was taken to select sampling sites on forested ridge tops with less than 5% slope to avoid the confounding effects of erosion and redeposition. Detailed descriptions (Doak, 1969) indicate that most of the soils have not been intensely weathered. Soil horizonation normally consisted of an Al-AC-C1-C2 sequence in which the soil was developed in a coarser material (C1) overlying a finer textured, lighter colored layer (C2). Glassy separates were compared to similarly activated standard samples of Mazama, Glacier Peak, Newberry, St. Helens Y, W, and T ash layers of the Pacific Northwest (Chapter I).

Methods

Soil samples received minimal treatment to avoid possible trace element contamination. The very fine sand fraction (125-63 μ) was selected for analysis since suitable amounts of this fraction could be obtained from most soils across the transect. The separates were obtained by sieving of air dried soil samples with stainless steel sieves. Where large pumice lumps predominated, this material was selected to represent the deposit, and ground with a

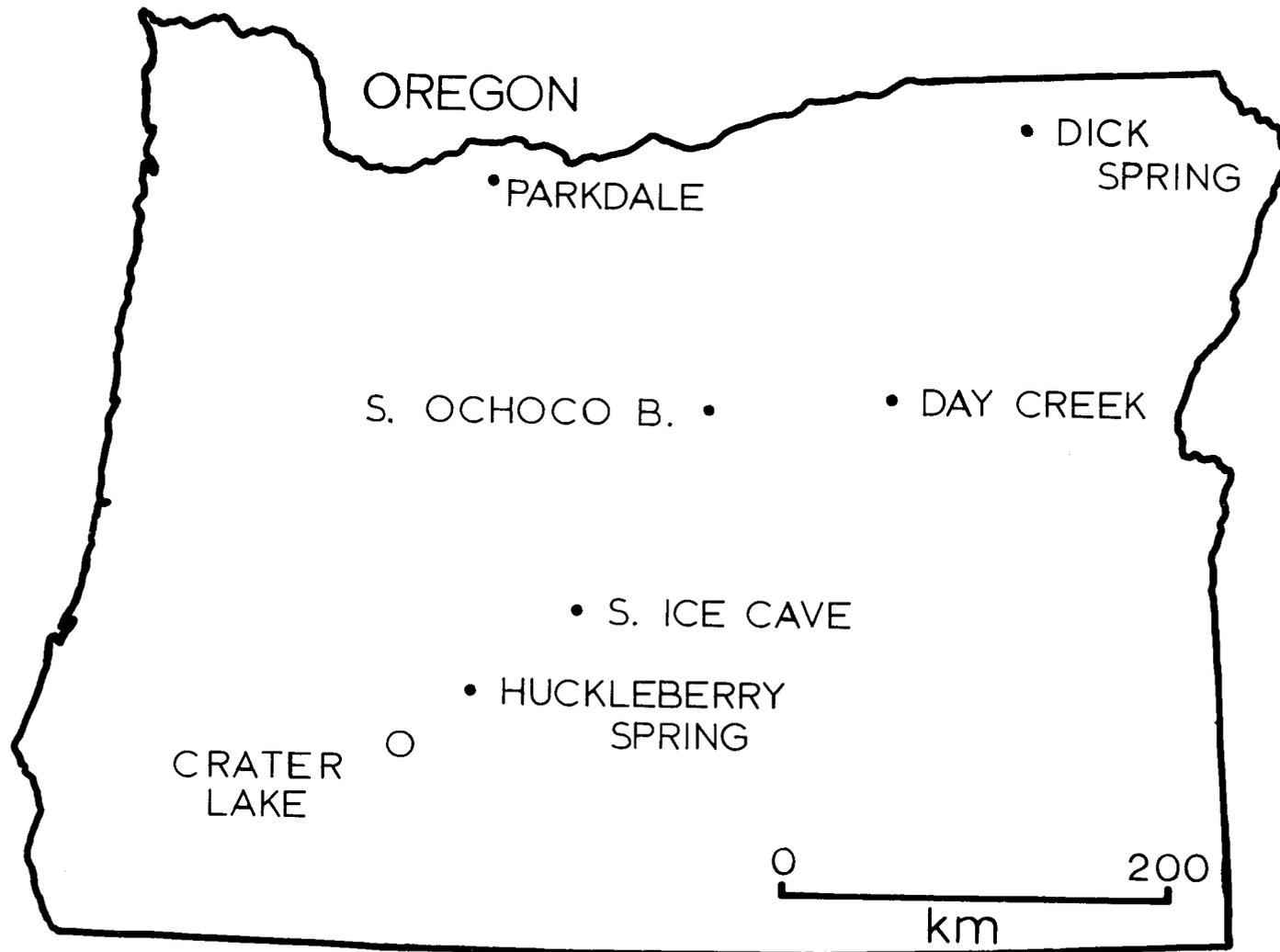


Figure 1. Locations of the five transect soils derived from Mazama ash, including Parkdale loam sampled near Mt. Hood.

Table 1. Volcanic ash soils sampled at intervals along the axis of the main lobe of the Mt. Mazama eruption (including Parkdale loam from near Mt. Hood).

Site No.	Site Name and Soil Texture	Location	Distance from Crater Lake (km)
62	Huckleberry Spring (sl)	NE $\frac{1}{4}$ sec. 36, T27S, R9E	50
37	South Ice Cave (lcos)	NE $\frac{1}{4}$, SE $\frac{1}{4}$, sec. 13, T23S, R13E	107
50	South Ochoco Butte (fsl)	NE $\frac{1}{4}$, SE $\frac{1}{4}$, sec. 11, T13S, R20E	222
49	Day Creek (l)	SE $\frac{1}{4}$, NE $\frac{1}{4}$, sec. 24, T11S, R30E	304
47	Dick Spring (sil)	SE $\frac{1}{4}$, NW $\frac{1}{4}$, sec. 11, T3N, R37E	445
11	Parkdale (l)	S $\frac{1}{2}$, NE $\frac{1}{4}$, sec. 29, T1N, R10E	290

glazed diamonite mortar and pestle. The glassy fractions of each ash deposit were obtained by centrifuge separation in high purity bromoform-bromobenzene ($\rho = 2.4 \text{ g/cc}$). An additional separation was made for A horizons at a density of 2.2 g/cc to remove dark fragments of plant residues. Ultrasonic vibration was used to break up aggregates of particles finer than 63μ . The separations were checked with a polarizing light microscope and the amount of organic matter and crystals remaining with the glass were estimated (Appendix VII).

Varying amounts of crystals of feldspar, pyroxene, and amphibole could have given much variation in the trace element results if allowed to remain in the sample. The percentage of glass in the very fine sand fraction of the fine Mazama ash increases with distance from 40% at 222 km to 72% at 445 km (Appendix V).

Sodium dithionite-citrate-bicarbonate free iron removal treatment (Jackson, 1956) was performed to determine its usefulness for correlation work on weathered samples. The method was tested on a considerably devitrified and iron oxide coated sample from Parkdale loam, which was hypothesized to have weathered from Mazama ash in the Hood River Valley. After the iron removal treatment, the fine sand fractions were washed several times with dilute nitric acid to remove adsorbed sodium.

The method of instrumental neutron activation analysis

utilized was described in Chapter I and by Gordon et al. (1968).

One gram samples of volcanic glass were irradiated for six hours at a flux of 7×10^{11} n/cm²/sec. They were counted for 10 minutes after six days radioactive decay and for 100 minutes after 14 days of decay. Counting equipment consisted of a 30cc Ge(Li) semiconductor detector and a 4096 multichannel analyzer.

Gamma-ray spectra were obtained on computer compatible punch tape, transferred to high speed magnetic tape, and analyzed with a computer program developed for the purpose (Appendix XI). The statistical methods involving discriminant function analysis and variation analysis of normalized data were described previously (Chapter I).

Results and Discussion

Transect samples were compared to the compositions of standard samples of Mazama, Glacier Peak, Newberry, and St. Helens Y, W, and T volcanic ash, all analyzed under the same conditions. Since there was major interest in soils derived from Mazama ash, analytical data have been normalized by dividing the compositions of the soil samples by the average for known Mazama ash samples (Chapter I, Table 5). This allowed for easy observation of percentage differences between soils and between horizons.

Vertical Homogeneity of Mazama Pumice

In the thick deposits of pumiceous lapilli near Crater Lake, a coarse layer (C1) overlies a fine layer (C2) separated by a distinct textural boundary (Chichester, 1967). This distinctive boundary remains evident in the fine ash deposits beyond South Ochoco Butte, 220 km from Crater Lake. This might indicate the possibility of two distinct eruptions of Mt. Mazama.

The hypothesis that there is a difference in trace element composition between the C1 and C2 layers of Mazama pumice was tested by sampling the Huckleberry Spring pumice at various depths. For comparison, the elemental abundances in the soil samples were divided by the average abundances determined from eight Mazama volcanic glass samples. Data obtained for glassy fractions of very fine sand from crushed lapilli of Huckleberry Spring indicated no detectable differences in chemical composition between the C1 and C2 horizons (Table 2). The abundances for C horizon samples from increasing depths fluctuated no more than was expected from analytical error. No chemical changes existed across the C1-C2 boundary that could not be accounted for by weathering. The concentrations of the major elements, Si, Al, Fe, Ti, Ca, and K, determined by X-ray fluorescent spectroscopy also did not change abruptly at the C1-C2 boundary (Borchardt and Theisen, 1968).

Table 2. Vertical trace element homogeneity of Mazama pumice at Huckleberry Spring (125-63 μ glassy fractions from ground lapilli).

INAA No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Ratio to average analysis of 8 Mazama samples (X100)																			
AC 20 - 30 cm																			
256	95	60	88	120	103	108	100	105	90	110	110	107	74	110	100	119	107	108	120
C1 40 - 50 cm																			
257	94	150	88	80	93	91	110	94	90	80	100	84	71	93	83	100	96	91	170
C1 50 - 60 cm																			
274	101	70	80	100	91	93	70	104	100	80	70	71	98	93	130	91	93	92	140
C1 60 - 70 cm																			
275	101	90	109	130	104	96	60	100	80	120	110	95	75	95	139	92	95	96	120
C2 90 - 100 cm																			
275	101	130	98	100	114	99	80	104	100	130	120	111	78	102	117	96	101	96	160
C2 120 - 130 cm																			
277	104	130	104	90	97	101	60	108	90	90	100	155	101	100	126	114	97	96	70
C2 150 - 160 cm																			
278	106	120	88	90	94	90	40	93	80	80	90	98	89	93	117	81	91	90	80
C2 150 - 160 cm (duplicate)																			
311	105	110	91	100	109	99	90	103	90	110	100	98	90	97	65	80	96	95	100
C2 180 - 190 cm																			
279	101	80	90	110	98	93	90	86	80	120	90	91	101	98	109	90	95	94	70
C2 210 - 220 cm																			
280	104	130	93	100	114	96	70	98	100	110	90	105	100	100	104	88	97	96	80
\pm^*	2	20	15	16	8	3	30	2	11	30	14	17	5	4	30	10	3	2	90

* \pm = one standard deviation for counting statistics calculated for eight Mazama volcanic glass samples (Chapter I, Table 5).

Chemical differences between the two ash layers might be considered evidence for two eruptions separated by a significant period of quiescence. The reason for the abrupt boundary remains unexplained. A wind velocity increase, an abrupt increase in eruptive violence or showers within a short period of time have been suggested, along with the possibility of two separate eruptions. The significant point is that both layers of ash have the same composition for purposes of correlation.

Correlation of Soil Parent Materials with Mazama Volcanic Ash

Unweathered volcanic ash deposits found in alluvial fans, in the Pacific Ocean, and in peat bogs of northeastern Oregon have been correlated successfully with the Mazama ash deposit (Chapters I and II). The correlation of volcanic ash soils is more difficult because the initial elemental abundances change through weathering by leaching and enrichment. Kline and Brar (1969) found that distinctions between whole soil samples from different parent materials were difficult to obtain with the low resolution NaI detector and 400 multichannel analyzer.

Normalized data for C horizons of five transect soils show less variability than the upper soil horizons (Tables 2 and 3). The coefficient of variation for the mean ratio measures this variability

Table 3. Ratios to Mazama volcanic glass composition for transect soils developed in Mazama ash (125-63 μ glassy fraction).

INAA No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hi	Ta	Co	Fe	Sc	Cr
Ratios X 100																			
<u>South Ice Cave</u>																			
AC 5-31 cm																			
258	77	140	109	83	136	125	70	111	100	175	119	141	151	109	243	188	130	132	260
C1 31-41 cm																			
248	78	100	143	130	136	124	130	133	153	143	154	112	97	110	187	233	151	153	390
C2 41-69 cm																			
249	81	120	135	107	131	109	110	130	111	176	128	139	111	107	143	176	132	135	320
<u>South Ochoco Butte</u>																			
A1 0-18 cm																			
259	71	100	102	95	99	106	90	88	87	94	102	98	105	92	135	276	156	135	330
AC 18-45 cm																			
260	74	90	131	105	106	106	120	85	88	88	91	118	102	95	135	258	149	135	320
C1 45-68 cm																			
250	80	100	115	94	90	110	120	99	133	46	112	130	82	100	130	234	140	140	350
C2 68-85 cm																			
251	84	80	110	82	108	99	70	84	109	87	105	104	84	95	100	165	122	119	140

Table 3. (continued)

INAA No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
<u>Day Creek</u>																			
A1 0-25 cm																			
261	75	100	109	121	104	107	90	86	79	57	96	102	90	96	122	342	170	150	440
AC 25-45 cm																			
262	80	100	110	110	100	109	70	88	108	154	109	104	109	98	148	245	151	144	380
C1 45-60 cm																			
252	83	130	117	105	90	112	90	80	104	101	133	84	90	76	126	183	140	129	150
C2 60-72 cm																			
253	88	100	86	78	97	88	70	79	88	88	84	86	77	93	65	110	104	102	100
<u>Dick Spring</u>																			
A1 0-22 cm																			
263	67	150	98	168	123	126	110	105	100	73	94	98	128	103	174	332	192	146	460
AC 22-50 cm																			
254	73	70	92	103	114	119	100	91	117	142	103	88	128	106	152	247	163	139	260
C 50-68 cm																			
255	94	100	79	91	106	94	100	85	96	105	94	91	108	71	109	119	105	109	130

(Table 4). The average of all 19 ratios to Mazama volcanic glass should be near 1.00 if the chemical composition of a sample is similar to the composition of Mazama volcanic glass. The chemical compositions of the soil samples also were divided by the chemical compositions of Newberry, Glacier Peak, and St. Helens Y, W and T standard ash samples. Low coefficients of variation for average ratios calculated from these comparisons would indicate similarities to ash deposits other than Mazama. The coefficients of variation calculated from ratios to Mazama ash were 9 to 19% for samples from Huckleberry Spring near Crater Lake. The CV's for comparisons of this site to the other standard ash layers ranged from 23 to 57%, showing that they were less similar to the Huckleberry Spring samples. The lowest coefficients of variation for the other soils were 12% for unweathered C horizons of Day Creek and Dick Spring soils. In addition, the average ratios were reasonably close to the expected value of 1.00.

Coefficients of variation and average ratios to Mazama ash were highest for upper horizons indicating the effects of weathering. Apparently weathering processes have also penetrated the C horizons of soils at South Ochoco Butte and South Ice Cave. Some of the AC and Al horizon samples compared more favorably with some of the ash layers from Washington (Table 4). However, previous work indicated that no genetic implications should be drawn from

Table 4. Coefficients of variation (%) for analyses of glassy fine sand fractions of the Mazama transect soils.

INAA No.	Depth	Horizon	Av. ratio for lowest CV	Mazama	Mazama	Newberry	Glacier Peak	St. Helens		
				C1	C2			Y	W	T
<u>Huckleberry Spring</u>										
256	20-30 cm	AC	1.01	12*	13	57	49	54	28	45
257	40-50 cm	C1	0.93	19*	19	52	49	47	23	40
274	50-60 cm	C1	0.92	10*	21	49	33	39	23	31
275	60-70 cm	C1	0.97	14*	23	48	53	56	30	48
276	90-100 cm	C2	1.00	11*	15	45	52	54	28	45
277	120-130 cm	C2	1.01	14*	19	55	43	48	26	39
278	150-160 cm	C2	0.90	10*	18	44	42	46	23	37
311	150-160 cm	C2	0.99	13	7*	40	46	44	26	37
279	180-190 cm	C2	0.92	11*	14	46	49	48	26	39
280	210-220 cm	C2	0.98	9*	11	43	41	43	23	36
<u>South Ice Cave</u>										
258	5-31 cm	AC	1.31	28	42	73	49	44	28	35
248	31-41 cm	C1	1.39	33	39	86	52	54	33	47
249	41-69 cm	C2	1.23	23*	26	71	51	49	30	42
<u>South Ochoco Butte</u>										
259	0-18 cm	A1	1.41	47	51	116	42	44	36	36
260	18-45 cm	AC	1.43	45	49	106	40	41	33	36
250	45-68 cm	C1	1.49	45	49	94	45	46	33	40
251	68-85 cm	C2	1.03	20*	22	81	44	49	26	40
<u>Day Creek</u>										
261	0-25 cm	A1	2.11	66	70	128	43	45	47	44
262	25-45 cm	AC	1.48	45	49	102	46	45	35	38
252	45-60 cm	C1	1.07	25*	29	85	54	57	33	49
253	60-72 cm	C2	0.92	13	12*	61	42	45	23	35
<u>Dick Spring</u>										
263	0-22 cm	A1	2.32	58	61	116	36	40	41	39
254	22-50 cm	AC	1.51	35	40	99	43	41	30	31
255	50-68 cm	C	0.95	12*	17	62	44	44	25	36

* Lowest CV classifies the sample with this group.

comparisons using CV's much greater than 20-25%.

The discriminant function (Krumbein and Graybill, 1965) also provides a single value for comparisons to each ash layer. The five equations produced for Mazama, Newberry, Glacier Peak and St. Helens Y and Wash layers (Chapter I) were used to classify each soil sample into the group corresponding to the highest discriminant value (Table 5). All samples from the Huckleberry Spring site were classified correctly with the Mazama group. The discriminant function agreed with the classifications produced by coefficients of variation that were less than 25% (Table 4). All C horizon samples from the Mazama transect soils correlated with the Mazama ash layer when the discriminant function was used. Glass samples isolated from the Dick Spring and South Ochoco Butte AC and A1 and Day Creek A1 horizons were classified with ash layers other than Mazama. The upper horizons at Dick Spring may have about 5 cm of St. Helens Y ash mixed with them (Chapter II). The large negative discriminant values for the Mazama group indicated that this was the least likely classification for these samples. The low coefficients of variation (< 15%), average ratios near 1.00, and agreement with the discriminant function should be considered substantial evidence for correlating the Day Creek C2 and Dick Spring C horizons with the Mazama ash layer. At least portions of volcanic ash soils located in northeastern Oregon were developed from

Table 5. Discriminant values for soils developed in Mazama ash (125-63 μ glassy fractions).

INAA No.	Description		Mazama	Newberry	Glacier Peak	St. Helens	
	Depth	Horizon				Y	W
<u>Huckleberry Spring</u>							
256	20-30 cm	AC	10350*	9220	2280	-4090	7600
257	40-50 cm	C1	11540*	10310	2420	-4410	8220
274	50-60 cm	C1	10610*	9560	2350	-4160	7770
275	60-70 cm	C1	11030*	10120	2320	-4340	7990
276	90-100 cm	C2	9670*	9050	2170	-4070	7340
277	120-130 cm	C2	11980*	10970	2440	-4550	8480
278	150-160 cm	C2	12440*	11280	2490	-4640	8690
511	150-160 cm, duplicate	C2	10600*	9630	2330	-4170	7770
279	180-190 cm	C2	8760*	8160	2140	-3810	6880
280	210-220 cm	C2	9940*	9210	2240	-4100	7470
<u>South Ice Cave</u>							
258	5-31 cm	AC	5270*	5270	1740	-3160	5180
248	31-41 cm	C1	9400*	7980	2200	-3840	7060
249	41-69 cm	C2	8690*	7850	2090	-3800	6790
<u>South Ochoco Butte</u>							
259	0-18 cm	A1	-480	-60	1090	-2030	2230*
260	18-45 cm	AC	2580	2440	1440	-2590	3720*
250	45-68 cm	C1	14360*	11900	2740	-4860	9460
251	68-85 cm	C2	6690*	6000	1880	-3420	5760
<u>Day Creek</u>							
261	0-25 cm	A1	2740	2210	1470	-2600	3740*
262	25-45 cm	AC	7520*	6560	1980	-3580	6160
252	45-60 cm	C1	6810*	6130	1850	-3560	5810
253	60-72 cm	C2	8010*	7270	2020	-3710	6450
<u>Dick Spring</u>							
263	0-22 cm	A1	-9950	-7490	-60*	-400	-2370
254	22-50 cm	AC	-5110	-3720	590*	-1100	-20
255	50-68 cm	C	10940*	9630	2420	-4160	7900

* Highest discriminant value classifies the sample with this group.

Mazama ash. The classifications of other soil horizons remain in doubt because of the unresolved effects of weathering.

Weathering Effects

The abundances of transition metals tend to increase upon weathering (Table 3). If Mazama ash is assumed to be the parent material of the soils, chromium and cobalt increased by two to three times the original amounts. These effects were related to soil depth as illustrated for the Day Creek site (Figure 2). Leaching of soluble major elements such as Na, K, Ca, and Si may account for some of the increases in transition metals in upper horizons. Increases in contents of transition metals which result from leaching of the glass would be much less than 100%. It seems more likely that large relative increases in contents of Cr and Co along with smaller increases in Sc and Fe indicate the contribution of materials added to the glass, probably in the form of iron oxide coatings. Iron and scandium appeared to increase simultaneously, perhaps because scandium co-precipitates with ferric hydroxide (Norman and Haskin, 1968). Apparently, Cr and Co precipitate more rapidly from soil solutions than Fe and Sc. An analysis of the $< 2\mu$ clay fractions produced a remarkably similar depth function for the Day Creek soil (Chapter IV).

Data on the relationships between elements affected by

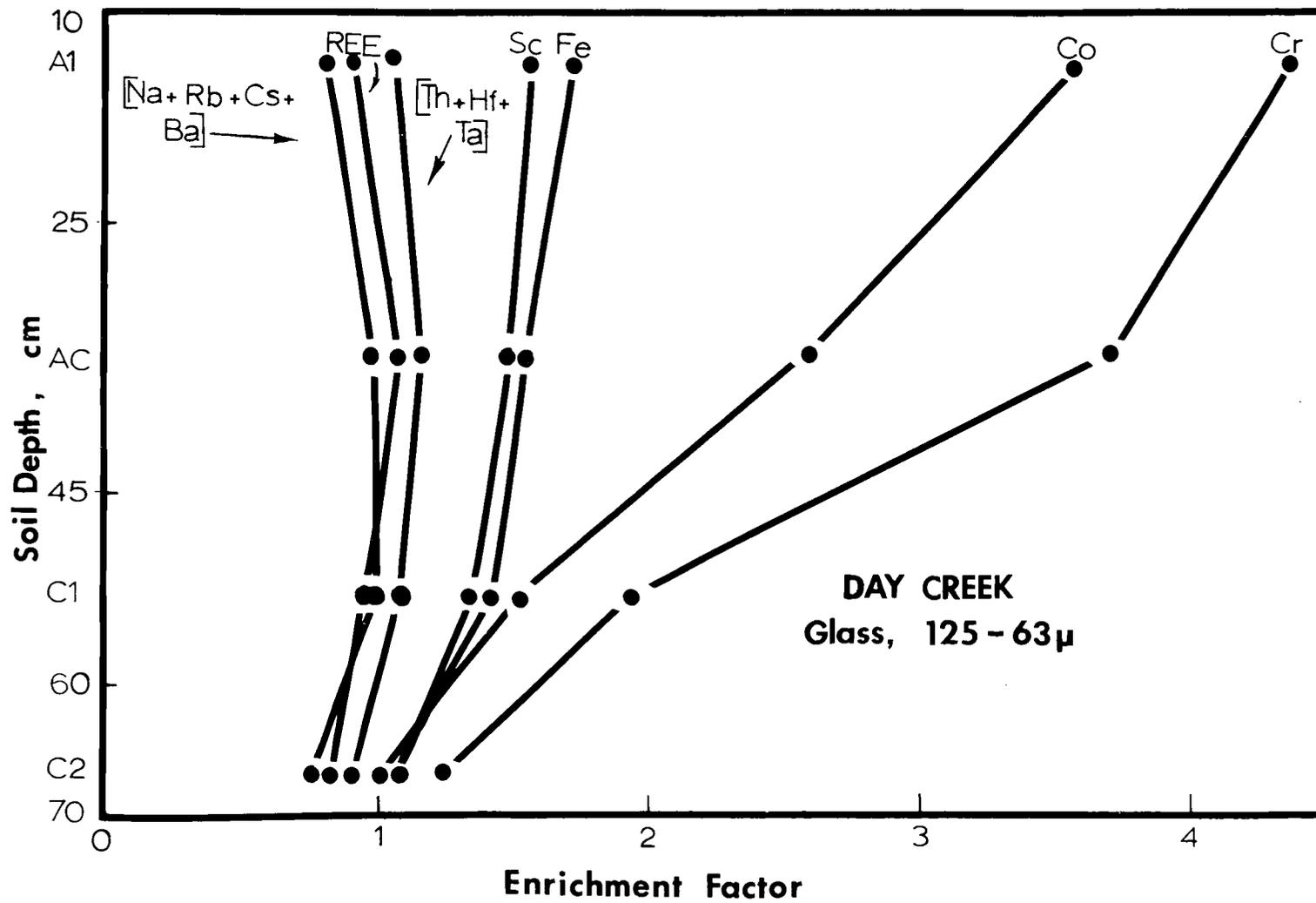


Figure 2. Elemental enrichment in Mazama volcanic glass in relation to soil depth. The factor for unweathered Mazama glass equals 1.0.

weathering processes can be obtained by dividing the concentration of one element by the concentration of another. Theoretically, easily leached sodium should decrease in weathered soil horizons while iron content should increase because of its tendency to form more insoluble compounds.

Both Na/Fe and Na/Co ratios were found to be suitable indicators of weathering intensity. These ratios for unweathered Mazama glass were 2.54 and 1.72, respectively (Table 6, sample 311). Both ratios decrease with nearness to the soil surface as a result of soil weathering. The one exception, South Ice Cave AC, may have the less weathered Mazama ash mixed into the surface by tree throw or other biological activity (see profile description in Doak, 1969).

In general, the depth of weathering in the four soils developed in fine pumiceous ash (< 4 mm) appears to decrease with distance from Crater Lake (Table 6 and Figure 1). Slight amounts of leaching of Na and/or accumulation of Fe and Co were apparent in all C horizons occurring in the fine ash. Less weathering in the Huckleberry Spring C1 (50-60 cm) probably reflects the low rainfall and coarse texture (> 4 mm) of the pumice. This site was not exactly comparable because the Huckleberry Spring samples were obtained by grinding lapilli, while the fine sand fractions of other soils were sieved directly. The lapilli from the AC horizon at Huckleberry Spring may have undergone as much weathering as the

Table 6. Elemental ratios and elemental abundances used for correlating weathered volcanic ash.

INAA No.	Horizon	Elemental ratios								ppm	
		Na/Fe	Na/Co ($\times 10^{-4}$)	Sc/Fe ($\times 10^4$)	Sc/Co	Th/Hf	La/Sm	Sm/Eu	Th/Sm	Ce	Hf
<u>Huckleberry Spring</u>											
256	AC	2.06	1.04	4.4	2.2	0.68	4.2	6.5	0.91	47	7.0
274	C1	2.53	1.44	4.3	2.5	1.06	3.8	5.9	1.21	40	6.0
311	C2	2.54	1.72	4.3	2.9	0.95	4.5	6.8	1.13	43	6.2
<u>South Ice Cave</u>											
258	AC	1.38	0.53	4.4	1.7	1.41	5.2	6.3	1.75	54	7.0
248	C1	1.19	0.43	4.4	1.6	0.89	4.4	4.9	0.94	54	7.1
249	C2	1.41	0.60	4.4	1.9	1.05	4.3	6.6	1.10	48	6.8
<u>South Ochocho Butte</u>											
259	A1	1.06	0.34	3.8	1.2	1.16	4.8	5.8	1.53	46	5.9
260	AC	1.13	0.37	4.0	1.3	1.10	5.3	5.5	1.56	46	6.1
250	C1	1.32	0.44	4.3	1.5	0.83	3.9	4.2	1.07	48	6.4
251	C2	1.61	0.66	4.3	1.8	0.90	5.5	4.4	1.28	43	6.1
<u>Day Creek</u>											
261	A1	1.02	0.28	3.8	1.1	0.95	5.2	6.2	1.34	47	6.2
262	AC	1.24	0.43	4.2	1.4	1.12	4.9	4.6	1.60	48	6.3
252	C1	1.39	0.59	4.0	1.7	1.20	4.9	4.3	1.46	49	4.9
253	C2	1.97	1.04	4.3	2.3	0.84	5.2	5.1	1.26	38	6.0
<u>Dick Spring</u>											
263	A1	0.81	0.26	3.3	1.1	1.26	5.0	5.9	1.58	55	6.6
254	AC	1.05	0.39	3.7	1.4	1.22	5.4	4.4	1.81	52	6.8
255	C	2.10	1.03	4.5	2.2	1.54	5.3	5.0	1.64	41	4.6
Mean		1.52	0.68	4.1	1.7	1.07	4.8	5.4	1.36	47	6.2
CV(%)		34	61	8	29	20	11	16	20	10	10

Day Creek C2 and Dick Spring C horizon fine sand fractions having similar Na/Fe and Na/Co ratios (Table 6).

Elemental Ratios for Correlating Soils

After obtaining some indication of the effects of weathering upon the trace element composition, an attempt was made to reduce the effects of weathering upon the correlation of upper soil horizons. Parameters such as elemental ratios and the concentrations of certain elements that were least affected by weathering were investigated.

The usefulness of trace element ratios for correlating weathered materials depends upon distinctiveness of ratios for different parent materials and low variability of ratios in the weathered material being correlated. To determine what elemental ratios would be appropriate for correlating weathered volcanic ash, it was necessary to assume that all horizons of the transect soils were derived from Mazama ash. Seventeen samples representing A1, AC, C1, and C2 horizons were selected from the five transect soils for multiple linear regression analysis (STEP program, OSU Computer Center). The relationships between all possible paired combinations of elements were ascertained in this way (Table 7).

Sodium was leached readily from volcanic glass, giving negative correlation coefficients with most of the other elements (Table

Table 7. Multiple correlation coefficients for elemental abundances determined for seventeen soil horizon samples from the Mazama transect soils (125-63 μ glassy isolates).

	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Na	1	-.34	-.51	-.34	-.33	-.67	-.32	.02	-.21	-.04	-.28	-.34	-.47	-.26	-.59	-.90	-.92	-.89	-.79
Rb		1	.28	.26	.44	.46	.13	.24	.02	.20	.30	.39	.50	-.03	.46	.26	.34	.33	.34
Cs			1	.17	.43	.49	.55	.42	.51	.29	.72	.63	.06	.32	.43	.44	.44	.69	.55
Ba				1	.29	.56	.46	.37	.14	-.11	.15	-.06	.16	.31	.29	.53	.60	.45	.60
La					1	.63	.31	.72	.33	.66	.49	.56	.62	.59	.64	.18	.27	.38	.35
Ce						1	.43	.48	.47	.37	.62	.45	.60	.56	.82	.61	.71	.75	.64
Nd							1	.47	.52	-.04	.49	.36	-.05	.21	.18	.33	.37	.47	.44
Sm								1	.53	.50	.53	.51	.26	.67	.48	-.05	.01	.19	.28
Eu									1	.26	.67	.28	.07	.34	.42	.11	.19	.43	.29
Tb										1	.52	.39	.55	.38	.47	-.17	-.05	.14	-.02
Yb											1	.49	.08	.30	.45	.16	.25	.53	.26
Lu												1	.28	.54	.48	.22	.18	.45	.40
Th													1	.24	.80	.33	.41	.37	.37
Hf														1	.43	.22	.25	.33	.38
Ta															1	.48	.52	.62	.58
Co																1	.97	.90	.91
Fe																	1	.91	.87
Sc																		1	.90
Cr																			1

7). The tendency for the transition metals to increase as sodium decreased gave negative coefficients as high as -0.92 for Na/Fe and -0.90 for Na/Co, indicating that these ratios are very sensitive to weathering. Coefficients were high for correlations among the transition elements, as might be expected from their similar chemical properties. The transition metals also have tendencies to accumulate readily to give a wide range of values conducive to high correlation coefficients. For example, Cr increased by four times the initial concentrations (Figure 2). The rare earth elements (REE), also may be closely related to each other (Haskin et al., 1966) but were not as readily accumulated. The contents of the REE did not vary appreciably with depth (Figure 2). Therefore, the correlation coefficients, for pairs of REE (ie. La vs Sm, $r = 0.72$) would not be an adequate measure of their similar chemical properties. However, La/Sm ratios might remain constant throughout weathering, and if characteristic for a particular ash layer they would be useful in correlating soils.

Ratios for correlating weathered horizons were selected from highly correlated pairs of elements in Table 7. Consideration also was given to elements with theoretically similar properties such as La and Sm. In addition, the averages for suitable elemental ratios of the 17 soil samples should have low relative deviations (Table 6). The best ratio, Sc/Fe, had a coefficient of variation of

only 8%. Also, elemental ratios that were unique for at least one of the standard ash layers were selected (Table 8). The Sc/Co ratio, for example, was 5.4 for Newberry volcanic glass, but 2.5 for Mazama and 0.9 to 1.4 for the standard ash samples from Washington. This range in values was considerably greater than the variation for the 17 soil samples (Table 6) making the Sc/Co ratio especially useful for distinguishing Newberry ash. However, the Sc/Co ratio should be used with caution because it decreases with weathering intensity much like the Na/Fe and Na/Co ratios which were sensitive to weathering.

Coefficients and constants of discriminant equations were determined for six elemental ratios and the concentrations of Ce and Hf for the standard ash samples (Table 9). Both Ce and Hf had coefficients of variation of only 10% for the average concentration in 17 soil samples (Table 6). Ce and Hf represent those elements having abundances least affected by weathering, and they would serve a function similar to the elemental ratios for correlating weathered volcanic ash. A chi-square value of 7,612 (d. f. = 32) led to rejection of the hypothesis that the mean values are the same in all five standard ash layers for the six elemental ratios and the abundances of Ce and Hf. Discriminant values calculated for five equations classified each of the standard ash samples (data not shown) with the appropriate group much like results in Chapter I,

Table 8. Elemental ratios and statistics of standard volcanic ash samples.

INAA No.	Sample names	Elemental ratios						ppm	
		Sc/Fe ($\times 10^4$)	Sc/Co	Th/Hf	La/Sm	Sm/Eu	Th/Sm	Ce	Hf
<u>Mazama</u>									
274	Huckleberry Spring C1	4.3	2.5	1.06	3.8	5.9	1.21	40	6.0
216	Antelope Unit C1	4.6	2.2	1.01	4.1	5.6	1.29	48	7.0
207	Walker Rim C1	4.3	2.2	1.04	4.7	4.9	1.49	46	6.4
209	Royce Mountain C1	4.4	2.6	0.95	4.8	5.3	1.24	44	6.9
211	Huckleberry Spring C2	4.3	2.9	0.95	4.5	6.8	1.13	43	6.2
206	Antelope Unit C2	4.3	2.9	1.04	4.2	5.2	1.47	43	6.3
208	Walker Rim C2	4.3	2.3	1.05	4.3	4.9	1.32	40	5.9
210	Royce Mountain C2	4.3	2.2	1.01	3.9	7.2	1.20	44	6.6
	Mean	4.3	2.5	1.01	4.3	5.7	1.29	44	6.4
	CV(%)	2	11	4	8	14	9	6	8
<u>Newberry</u>									
211	Weasel Butte	4.0	5.1	1.44	4.8	8.7	1.77	57	8.5
241	Pumice Butte	4.2	4.5	1.42	5.2	11.1	1.78	60	9.2
242	China Hat	4.1	6.5	1.48	5.1	9.7	1.93	60	9.1
	Mean	4.1	5.4	1.45	5.0	9.9	1.83	59	8.9
	CV(%)	2	15	2	1	3	4	2	.4
<u>Glacier Peak</u>									
212	Phelps Creek	3.4	1.3	2.70	7.0	4.6	2.87	18	1.7
243	North Sugarloaf	3.3	1.4	2.52	6.2	5.4	2.90	34	4.0
244	Steptoe Canyon	2.7	0.8	2.34	5.6	5.1	1.88	26	2.0
	Mean	3.1	1.1	2.52	6.2	5.1	2.55	26	2.6
	CV(%)	10	23	6	9	7	19	25	35

Table 8. (continued)

INAA No.	Sample names	Elemental ratios						ppm	
		Sc/Fe ($\times 10^4$)	Sc/Co	Th/Hf	La/Sm	Sm/Eu	Th/Sm	Ce	Hf
				<u>St. Helens Y</u>					
213	Randle	2.1	0.7	1.57	6.5	12.9	1.24	19	1.4
240	Longmire	2.2	1.0	1.72	6.1	4.7	1.38	26	2.8
	Mean	2.2	0.9	1.65	6.3	8.8	1.31	23	2.1
	CV(%)	0.3	19	5	3	47	5	16	50
				<u>St. Helens W</u>					
214	Mt. St. Helens	2.8	1.2	1.00	4.9	4.6	1.29	32	4.5
238	Lake Keechelus	3.5	1.5	1.32	5.6	7.1	1.87	34	5.2
239	Crystal Mountain	2.9	1.4	0.95	5.4	5.2	1.32	31	5.2
	Mean	3.1	1.4	1.09	5.3	5.7	1.49	32	4.9
	CV(%)	10	9	15	5	18	18	4	10
				<u>St. Helens T</u>					
236	Randle	2.4	0.7	1.36	4.0	5.5	1.37	33	3.5
237	Mt. St. Helens	4.0	1.8	0.94	4.5	6.1	1.22	33	5.2
	Mean	3.2	1.2	1.15	4.3	5.8	1.30	33	4.3
	CV(%)	25	44	18	5	6	6	0	25

Table 9. Coefficients and constants of the discriminant functions for INAAC with elemental ratios diminishing the effects of weathering upon classifications.

Coefficient No.	Ratio or Element	Coefficients				
		Mazama	Newberry	Glacier Peak	St. Helens	
					Y	W
1	Sc/Fe	270.	20.0	-357.	-317.	-0.772
2	Sc/Ce	27.4	32.3	-10.1	-6.92	7.48
3	Th/Hf	-11.0	546.	1300.	1107.	397.
4	La/Sm	28.5	77.7	142.	139.	71.8
5	Sm/Eu	-5.93	5.55	15.7	14.6	2.62
6	Th/Sm	-183.	-283.	-338.	-311.	-195.
7	Ce*	9.74	9.09	3.34	7.16	6.74
8	Hf*	-44.6	5.99	45.3	43.7	1.16
Constant		-608.	-780.	-1299.	-993.	-385.

*Ce and Hf abundances in soils were least affected by weathering. They serve functions similar to the elemental ratios in this discriminant function analysis.

Table 10.

Discriminant classifications derived from elemental ratios (Table 10) corroborate those obtained directly from the elemental abundances (Table 5). Two additional samples (South Ochoco Butte AC and Day Creek A₁) are now classified with the Mazama ash layer. Three out of 17 of the transect samples remain classified with the St. Helens W group. However, for the South Ochoco Butte A₁, the discriminant value of 440 for the Mazama equation was almost as large as the classifying value, 462. This was not the case for the A₁ and AC samples occurring above material correlated with Mazama ash. These horizons were found to be no more weathered than A₁ and AC horizons at other locations when the Na/Fe and Na/Co ratios were used as measures of weathering intensity (Table 6). Post-depositional mixing of other materials into the soil at Dick Spring appears quite likely. This is suggested by a discontinuity observed in a nearby Tolo soil developed in volcanic ash. Norgren (1962) stated that:

The coarse sand-size pumice, plagioclase and hypersthene which distinguish the A₁ horizon must be a very recent deposit. This youthfulness is attested to not only by superior stratigraphic position but by lack of mixing with underlying finer textured material (p. 82).

The occurrence of 3000 year old ash, which may be St. Helens Y, in a peat bog at Hurricane Creek (Chapter II) also supports this

Table 10. Discriminant values for equations derived from elemental ratios least affected by weathering in volcanic ash soils.

INAA No.	Horizon	Mazama	Newberry	Glacier Peak	St. Helens	
					Y	W
<u>Huckleberry Spring</u>						
256	AC	680*	322	-895	-605	362
274	C1	586*	348	-658	-423	378
311	C2	648*	416	-622	-374	429
<u>South Ice Cave</u>						
258	AC	626*	615	-44	115	608
248	C1	742*	478	-669	-328	492
249	C2	661*	475	-473	-251	482
<u>South Ochoco Butte</u>						
259	A1	440	396	-237	-50	462*
260	AC	493*	400	-314	-108	469
250	C1	660*	301	-837	-571	361
251	C2	622*	369	-613	-359	434
<u>Day Creek</u>						
261	A1	491*	367	-397	-174	444
262	AC	542*	385	-430	-217	447
252	C1	605*	470	-291	-101	509
253	C2	585*	298	-757	-484	370
<u>Dick Spring</u>						
263	A1	357	524	183	322	567*
254	AC	416	449	-85	88	510*
255	C	673*	600	-102	55	596

* Highest discriminant value classifies the sample with this group.

explanation. The Dick Spring site occurring between Mt. St. Helens and Hurricane Creek may have slightly more than a five cm thick layer mixed with it.

The problem of mixed ash layers is complicated by differing proportions of the size fraction used for analysis (125-63 μ) obtained from the two different layers. Also, the amount of glass isolated by the heavy liquids may depend upon how weathered the sample is. Only 27% of the very fine sand from the Dick Spring A1 horizon floated on liquid of density 2.4 g/cc compared to 72% for the C horizon (Appendix V). The most accurately determined ratios, Sc/Fe, Th/Hf, and La/Sm, had values midway between Mazama and St. Helens Y while Th/Sm ratios were higher than those for either of these groups (Tables 6 and 8). Further work with elemental ratios may help determine the extent of mixing of soil parent materials.

Removal of Iron Oxide Coatings

Iron oxide coatings and colloidal precipitates formed by weathering processes confound the chemical analysis of A1 and AC horizon samples enough to prevent definite correlations in some instances. It was hypothesized that removal of such coatings would reveal glass shards with compositions more like those unaffected by soil weathering. A control sample consisting of unweathered pumice from the Antelope Unit standard sample had the same amounts of sodium

before and after the iron removal and acid wash (Table 11). The acid wash successfully removed any sodium adsorbed to the sample during the iron removal. Except for increases in Cr and Co, there was no significant trace element contribution from the reagents.

A rigorous test of the method was performed on a glassy fine sand fraction isolated from Parkdale loam, a soil in the upper Hood River Valley, suspected of being developed from Mazama ash. Microscope observations of this untreated sample prior to irradiation revealed numerous iron oxide coatings and much devitrification of the volcanic glass. The mean ratio of Parkdale loam to Mazama ash was 3.2 and the coefficient of variation was 77% for untreated material (not shown). This soil was evidently much more weathered ($\text{Na}/\text{Fa} = 0.29$, $\text{Na}/\text{Co} = 0.07$) than soils from the Mazama transect ($\text{Na}/\text{Fe} = 0.81$, $\text{Na}/\text{Co} = 0.26$). The concentrations of the rare earth elements (REE) in the Parkdale fine sand fractions were two to five times the amounts in Mazama glass (Table 11). The Ce ratio was expected to be intermediate between La (5.53) and Nd (4.90) or Sm (2.86). Instead, the ratio for Ce was 1.64. The REE distribution pattern (such as in Chapter I, Figure 3) would show a considerable Ce depletion in relation to the other REE (La through Lu). The iron removal treatment drastically reduced the other REE to values concordant with Ce, and more nearly like abundances in Mazama ash. Ce depletion has been observed in sea water and Ce enrichment

Table 11. Effect of iron removal treatment upon 125-63 μ glassy fractions from soils.

INAA No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Ratios to Mazama glass composition X 100																			
Antelope Unit C2 (35 - 4) Control																			
206	102	80	98	92	87	98	100	88	96	120	94	89	101	98	100	87	103	102	30
\pm^*	2	10	11	11	8	2	10	2	6	20	8	7	4	2	10	6	1	1	40
Antelope Unit C2 (35 - 4) after iron removal																			
217	101	120	98	84	107	92	90	101	104	160	94	86	97	98	100	114	107	114	240
\pm	2	30	14	14	7	4	30	2	13	50	16	16	7	3	20	9	3	2	60
Parkdale C (11 - 3) Control																			
246	36	140	111	100	553	164	490	286	342	270	205	163	139	90	230	636	288	317	1130
\pm	2	50	30	30	14	5	50	4	25	70	23	48	12	6	30	28	5	5	130
Parkdale C (11 - 3) after iron removal																			
265	51	100	95	66	110	86	90	67	90	80	17	50	94	76	260	345	163	156	830
\pm	1	30	18	23	6	3	30	2	10	30	9	21	4	3	20	11	3	2	90

* \pm = one standard deviation for counting statistics.

has been noted for manganese nodules (Haskin et al., 1966). Ce^{3+} apparently oxidizes to Ce^{4+} producing highly insoluble CeO_2 accumulated by MnO_2 in the nodules. Parkdale soil contains numerous concretionary pellets (Appendix IV). Concretions would have been removed from the fine sand sample during the heavy liquid separation ($\rho = 2.4 \text{ g/cc}$).

The Sc/Fe ratios of Parkdale loam were the same as Mazama ash, both before and after treatment. The amounts of transition metals decreased after treatment, but the sample still contained eight times more Cr and three times more Co than the Mazama ash average. The mean ratio to Mazama volcanic glass composition decreased to 1.68, but the coefficient of variation increased to 108% after treatment (data not shown). Additional chemical and physical treatments might remove coatings still remaining after a single iron removal treatment. Although there were similarities between the compositions of Parkdale soil and Mazama ash, a definitive correlation can not be made with any of the standard ashes. Further work is needed to evaluate chemical treatments to aid in correlating less weathered material such as the upper horizons of the Mazama transect soils.

Conclusions

1. The trace element composition of volcanic glass from C horizons of soils along a 450 km transect in Oregon correlated with the composition of ejecta from Mt. Mazama.

2. Enrichment and leaching effects in weathered horizons prevented positive correlation with known samples. The discriminant function classified most A1 and AC and all C horizon samples with the Mazama group. Coefficients of variation of average ratios to Mazama volcanic glass were less useful for correlating weathered horizons.

3. Enrichment of transition metals in upper horizons occurred in the following order: $Cr > Co > Fe = Sc$. The abundances of Hf, Th, and the rare earth elements remained relatively unchanged throughout moderate weathering. Na/Fe and Na/Co ratios were measures of weathering intensity. The weathering depth appeared to be greatest in the pumiceous ash (< 4 mm) near the source.

4. Sc/Fe, Th/Hf, La/Sm, and Th/Sm ratios were not greatly affected by weathering. All but three of the 17 soil horizons correlated with Mazama ash when elemental ratios were used with discriminant function analysis. The A1 and AC horizon samples from Dick Spring may contain some St. Helens Y ash.

IV. TRACE ELEMENT CONCENTRATION IN AMORPHOUS CLAYS OF VOLCANIC ASH SOILS

Introduction

High trace element concentrations in fine sand-size volcanic glass from upper horizons of soils developed in Mazama volcanic ash were attributed to colloidal coatings (Chapter III). Chromium and cobalt contents in these fractions were up to four times the amounts for unweathered glass. Iron and scandium contents also increased progressively with nearness to the soil surface. Clay fractions were analyzed to verify the trace element concentrating effect of colloidal coatings.

Clays found in soils developed from Mazama pumiceous lapilli in Oregon contain about 80% amorphous material (Chichester, Youngberg and Harward, 1969). X-ray diffraction of whole clay samples produced very weak 14 \AA peaks. X-ray patterns of NaOH boiling treatment residues confirmed the presence of small amounts of a mixed suite of 2:1 clay minerals in addition to amorphous clay. Although the systems exhibited pH dependent charge, peculiar dispersive properties, low temperature endotherms, and were amorphous to X-rays, the identification of the amorphous material as allophane could not be made due to the confounding effects of 2:1 phyllosilicates. Therefore, the nature of the amorphous component remains to be elucidated. It is possible that the amorphous material is fine glass.

If so, the trace element composition should be the same as the larger size volcanic glass fraction. On the other hand, if the amorphous clay is a weathering or alteration product, a composition different from volcanic glass would be expected.

Jenne (1968) has suggested that the hydrous-oxides of iron and manganese may control the occurrence of heavy metals in natural waters, soils, and sediments. Free iron oxides can be intimately mixed with clays (Roth et al., 1966). The concentrations of the rare earth element, La, and the transition element, Sc, in soils (Kline et al., 1969) and Fe, Mn, and Co in sediments (Moore, 1963) have been shown to be related to the clay content.

Instrumental neutron activation analysis (INAA) can produce chemical composition estimates for over 20 elements with a minimum of effort. The soils from which amorphous clays were obtained have been correlated with the Mazama volcanic ash deposit (Chapter III). Volcanic ash parent material and the associated clay fractions have been compared in this study. The acceptance of certain trace elements into structural positions of pedogenic minerals could reveal information of a geochemical, as well as structural nature.

The objectives of this investigation were:

1. To determine if amorphous clays from Mazama volcanic ash were either fine glass or a new phase; and
2. If a new phase exists, to evaluate the occurrence of trace

elements in this phase.

Materials

Volcanic ash soils were sampled at intervals along a transect extending for 450 km northeast of Crater Lake, Oregon, the source of Mazama ash (Figure 1, Table 1). These soils were located on broad forested ridge tops or plateaus having less than a 5% slope. Soils developed in volcanic ash from Newberry and Glacier Peak were sampled near China Hat in eastern Oregon, and Wenatchee, Washington, respectively. Clays were also separated from volcanic ash sampled in peat bogs of Oregon and Washington.

For comparison, other soil clays containing various forms of iron were obtained from western Oregon. The Wren (now classified with the Jory series) B1 horizon clay contains an iron interlayer and free iron oxides (Singleton, 1966), while the Jory B22 clay contains large amounts of free iron oxides. The Dayton soil clay contains mostly smectite, formed under poorly drained conditions. Salem Hills bauxite was a highly weathered ferruginous material used to determine the applicability of the trace element concentration effects found for volcanic ash clays. Descriptions of peat bog sampling sites and soils from which clays were obtained are given in Chapter II and Appendix IV, and by Doak (1969).

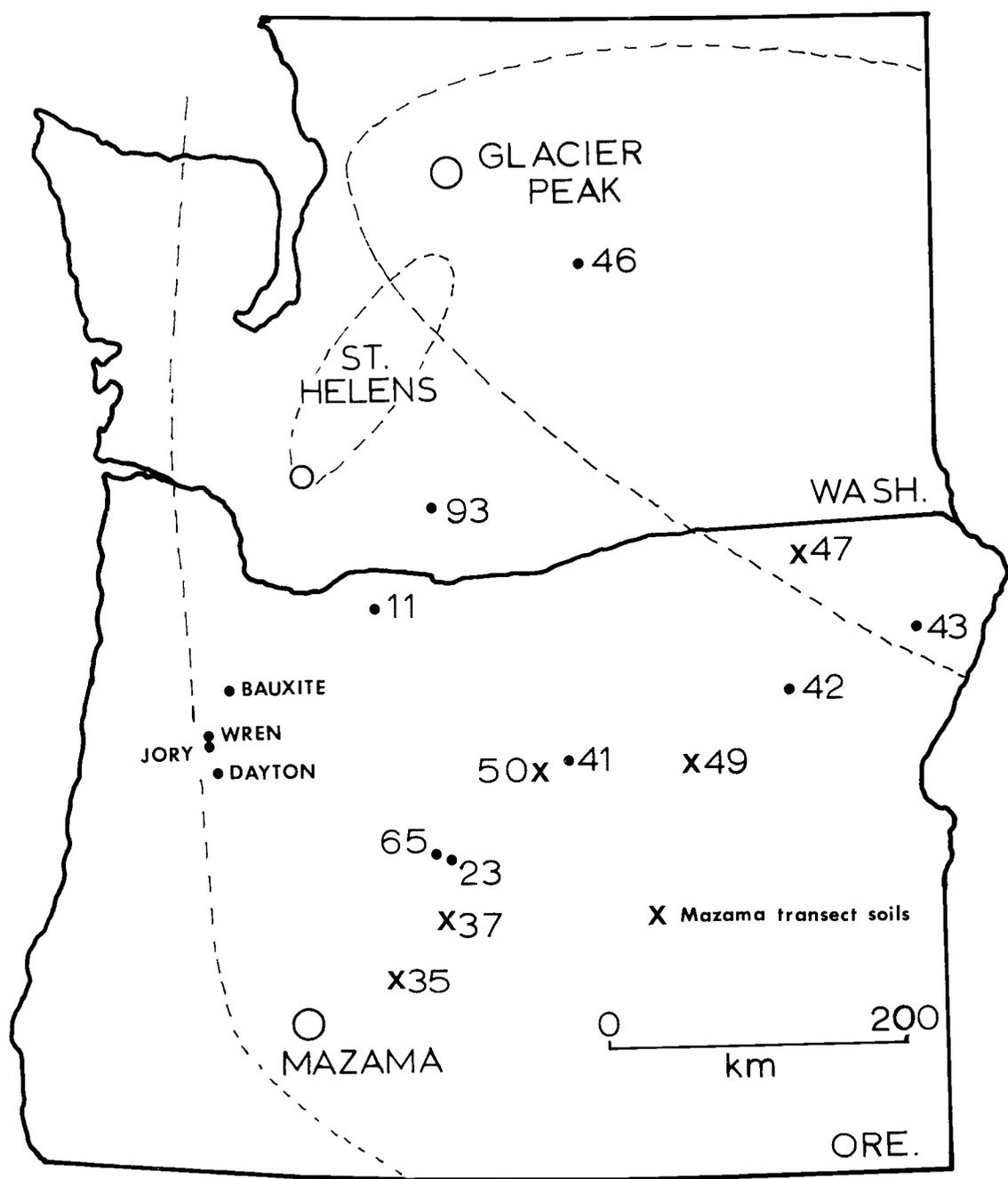


Figure 1. Locations of soils and volcanic ash deposits from which clays were obtained for activation analysis.

Table 1. Clay samples and pretreatments used.

INAA No.	Horizon and sample number	Depth	Pretreatment or comment	% Clay
		<u>Antelope Unit</u>		
342	AC (35-2)	5-28 cm		2.1
		<u>South Ice Cave</u>		
273	AC (37-1)	5-31 cm		2.8
264	AC (37-1)	5-31 cm	0.05 N HNO ₃	
		<u>South Ochoco Butte</u>		
272	AC (50-2)	18-45 cm		3.6
		<u>Day Creek</u>		
266	A1 (49-1)	0-25 cm		3.9
267	AC (49-2)	25-45 cm		2.0
288	"	"	NH ₄ NO ₃	
283	"	"	0.05 N HNO ₃	
281	"	"	Iron removal (DCB*)	
289	"	"	Amorphous removal	
268	C1 (49-3)	45-60 cm		1.8
269	C2 (49-4)	60-72 cm		1.3
		<u>Dick Spring</u>		
271	AC (47-2)	22-50 cm		2.2
287	AC (47-2)	22-50 cm	0.05 N HNO ₃	
		<u>Parkdale</u>		
270	AC (11-2)	12-43 cm		6.5
282	"	"	NH ₄ NO ₃	
286	"	"	0.05 N HNO ₃	
284	"	"	Iron removal (DCB)	
290	"	"	Amorphous removal	
		<u>Red Hill</u>		
304	AC (65-1)	5-23 cm	Soil on Newberry pumice	2.1
		<u>China Hat</u>		
312	C (23-1)	18-71 cm	Newberry lapilli	0.3
		<u>North Sugarloaf</u>		
313	C1 (46-4)	55-75 cm	Soil on Glacier Peak ash	5.6
		<u>Anthony Lakes Meadow</u>		
331	Bog (42-1)	51-61 cm	Mazama ash	3.0
332	Bog (42-3)	196-206 cm	Glacier Peak ash	11.2
		<u>Hurricane Creek</u>		
314	Bog (43-1)	122-127 cm	St. Helens Y ash (?)	4.2
315	Bog (43-2)	208-220 cm	Mazama ash	3.4
		<u>Lakebeds Meadow</u>		
333	Bog (93-1)	21-31 cm	St. Helens Y ash (?)	10.0
		<u>Wren (Jory) (S62-2-5-4)</u>		
307	B1	31-46 cm	Fe interlayer clay	33.7
		<u>Jory (S63-24-5-5)</u>		
308	B22	74-91 cm	High in Fe oxides	40.7
		<u>Dayton (S62-22-1-5)</u>		
309	B22	56-71 cm	High in smectite	24.3
		<u>Salem Hills Bauxite</u>		
310			Ferruginous bauxite	

*DCB = dithionite-citrate-bicarbonate free iron oxide removal treatment.

Methods

One hundred gram soil samples were treated with H_2O_2 acidified with a few ml of dilute HNO_3 for removal of organic matter. Nitric acid was used to avoid the trace element contamination that might have occurred with other reagents. One percent ammonium hydroxide was used to disperse the clay fraction (Appendix IX) which was then separated by centrifugation (Jackson, 1956). Certain clays (Table 1 and Appendix X) received additional pretreatments to remove exchangeable cations (1 N NH_4NO_3), hydroxylated cations (0.05 N HNO_3), free iron oxides (sodium dithionite-citrate-bicarbonate method given by Jackson, 1956), and amorphous material (boiling 0.5 N KOH). Reagent grade NH_4OH , HNO_3 , and Specpure grade NH_4NO_3 were used to minimize trace element contamination. The treatments for removal of free iron and amorphous material were followed by 0.05 N HNO_3 washing and high speed centrifugation.

Clay samples were washed free of excess salts, dried from acetone at 49°C and weighed after oven drying at 110°C . One gram clay samples were irradiated and analyzed for gamma-ray activity as described in Chapter I and by Gordon et al. (1968).

Results and Discussion

Less Than Two Micron Glass

The hypothesis that the $< 2\mu$ clay fractions of the volcanic ash

soils are fine volcanic glass was tested. Averages and coefficients of variation have been determined for trace element concentrations in eight unweathered glass samples separated from Mazama ash with heavy liquids ($\rho = 2.4\text{g/cc}$) (Table 2). Since the parent materials of the transect soils have been shown to be Mazama ash (Chapter III), all comparisons were made to the unweathered glass from this volcano. The analytical values for each clay sample were divided by the values for the unweathered glass (Table 3) so that percentage differences between samples could be noted easily. The average analysis for clays of five AC soil horizons developed on Mazama ash produced considerably higher abundances than for unweathered glass (Table 2). The variation in the concentrations of the alkali and rare earth elements within the five soil clays was only two or three times the variation for the parent material. The averages for some of the transition elements had coefficients of variation only slightly greater than those for unweathered volcanic glass. This suggests remarkably uniform weathering conditions over the transect distance of 450 km. However, all soils occur at similar elevations (4,000-6,000 ft) and probably have similar annual precipitation (15-30 in).

In relation to Mazama ash, the soil clays had a much higher content of transition metals, particularly chromium and cobalt (Table 3). The sodium content of clays was only 10% of the amount found in the volcanic glass parent material. Sodium may have leached from

Table 2. Average analyses and coefficients of variation for volcanic glass and for clays separated from AC horizons of the Mazama transect soils.

Element	Glass**			Clay			Clay/Glass
	Conc.*	±s	CV	Conc.	±s	CV	
Na%	3.44	.16	5	.31	.07	24	0.1
Rb	50.	8.	17	40.	10.	23	0.8
Cs	3.9	.7	19	5.	1.	26	1.3
Ba	660.	70.	11	690.	230.	34	1.0
La	22.	2.	9	60.	20.	33	2.9
Ce	44.	3.	6	140.	30.	20	3.3
Nd	29.	5.	17	99.	45.	45	3.4
Sm	5.0	.4	8	15.	3.	19	3.0
Eu	.89	.08	9	2.5	.6	23	2.8
Tb	.83	.14	17	2.5	.6	25	3.0
Yb	3.5	.7	19	9.3	1.4	15	2.6
Lu	.56	.07	13	1.3	.3	25	2.3
Th	6.5	.3	5	13.8	1.4	10	2.1
Hf	6.4	.4	6	10.8	.5	5	1.7
Ta	.23	.08	34	.51	.08	15	2.2
Co	2.6	.3	5	18.	2.	9	6.7
Fe%	1.48	.09	6	5.4	.5	10	3.6
Sc	6.4	.4	7	21.5	.5	7	3.3
Cr	1.6	.6	35	15.	3.	19	9.4

* Conc. = concentration, in ppm except for Na and Fe which are in %; ±s = standard deviation of the means; CV = coefficient of variation, in %; Clay/Glass = concentration in clay divided by concentration in glass.

** Average composition of eight unweathered Mazama volcanic glass samples (Chapter I, Table 5).

Table 3. Ratios to Mazama volcanic glass composition for clay fractions from AC horizons of the transect soils.

INAA No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Ratios X 100																			
Antelope Unit																			
342	12	70	180	60	474	455	640	410	400	300	330	340	222	156	220	591	312	302	730
±*	1	40	30	20	9	5	110	4	20	50	30	20	6	5	40	15	5	5	240
South Ice Cave																			
273	10	70	80	100	262	308	250	294	270	270	260	210	204	177	270	686	339	342	1030
±	0	40	20	40	5	5	30	2	20	70	20	30	6	5	40	23	5	5	130
South Ochoco Butte																			
272	7	80	130	110	219	262	260	268	240	230	230	190	185	164	170	648	361	342	960
±	0	30	30	20	5	5	30	2	20	60	20	20	9	5	40	15	5	5	170
Day Creek																			
267	7	100	120	90	208	299	230	243	210	260	220	180	247	175	210	777	378	369	1210
±	0	40	20	20	4	5	30	2	20	60	20	20	9	5	40	19	5	5	140
Dick Spring																			
271	7	120	140	170	303	324	330	316	290	450	270	230	207	169	230	655	425	316	780
±	0	30	30	20	6	5	30	2	20	70	20	20	6	5	30	15	5	5	110

* ± = one standard deviation for counting statistics.

< 2 μ glass, as was observed for glassy fine sand fractions in upper horizons of the same soils (Chapter III). Traces of plagioclase were found in clay fractions from the Antelope Unit A1 horizon (Chichester, 1967). Clay size feldspars would be expected to survive soil weathering for a greater length of time than volcanic glass. This apparently was true for clay from the more intensely weathered Parkdale soil, although plagioclase was not detected in clay from the Day Creek AC horizon (Figures 2 and 3). Data calculated from Chichester (1967) reveal that the amorphous component of the Antelope AC horizon contained about 35% SiO₂, whereas volcanic glass from Mt. Mazama has about 70% SiO₂. Available data, therefore, indicate the presence of phases other than volcanic glass in the clay fractions of soils from Mazama ash. The hypothesis that the clays consist of <2 μ volcanic glass is rejected.

Trace Element Concentration as a Function of Depth

Four soil horizons were observed at the Day Creek site. Clay fractions from this soil exhibit interesting chemical depth functions (Table 4, Figure 4). The sodium content was lower in clays from upper horizons, possibly reflecting the presence of lesser amounts of plagioclase feldspar crystals. This may be one indication of increased weathering at the soil surface. The rare earth element (REE) content remains uniform with only a slight tendency to decrease near the soil

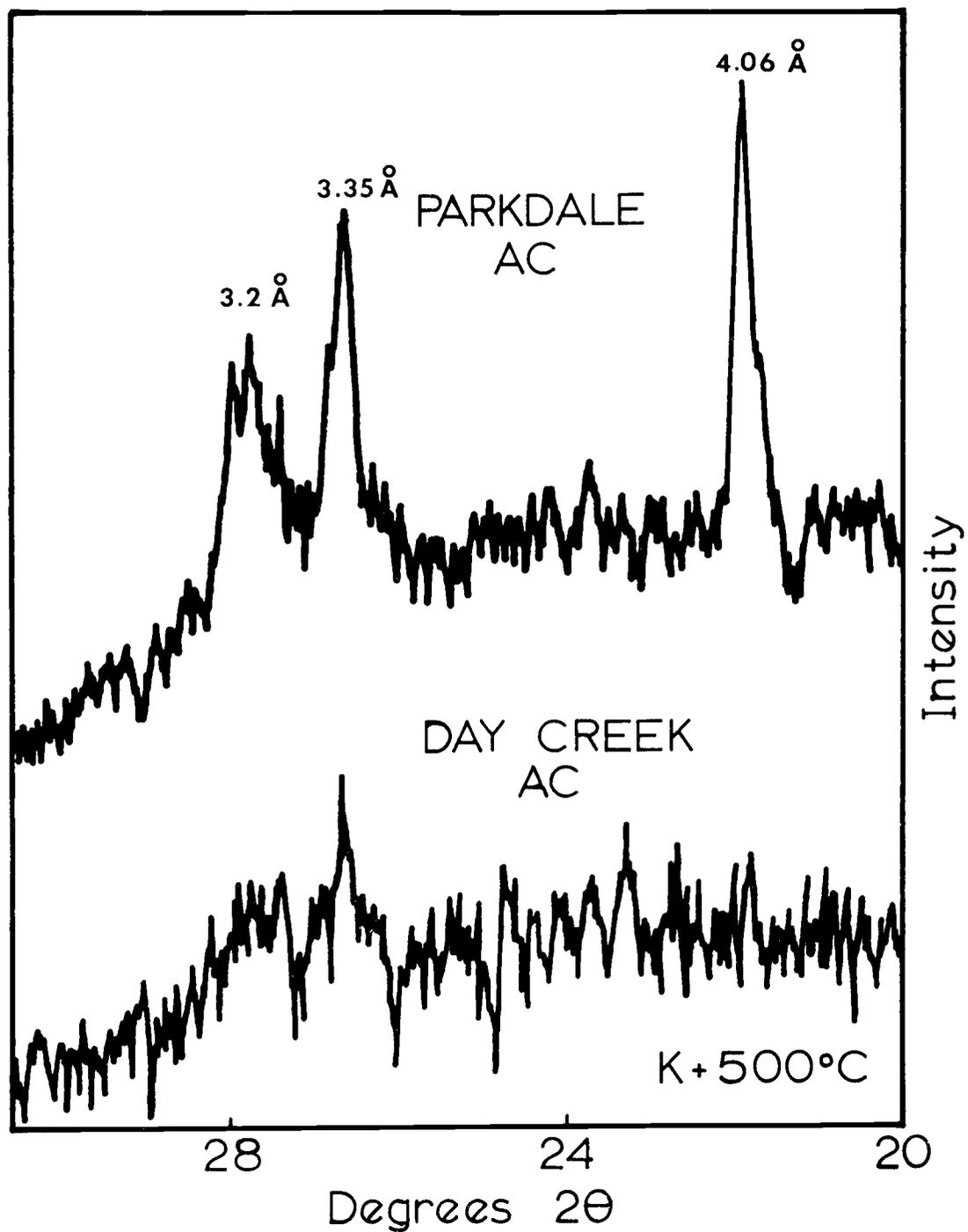


Figure 2. High angle X-ray diffraction patterns of residues from clays treated for removal of amorphous material.

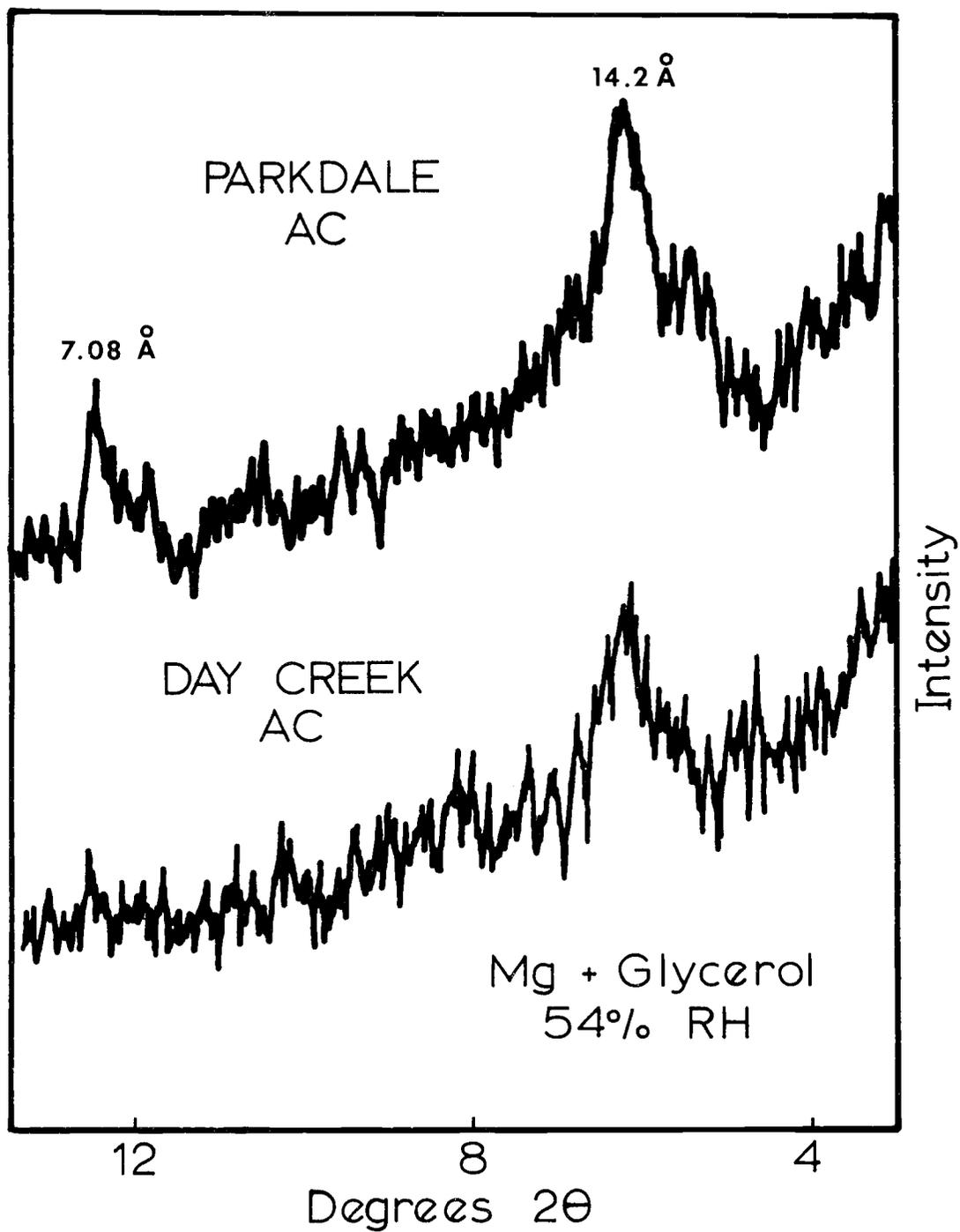


Figure 3. Low angle X-ray diffraction patterns of residues from clays treated for removal of amorphous material.

Table 4. Ratios to Mazama volcanic glass composition for clays from a depth sequence for the Day Creek site.

INAA No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Ratios X 100																			
A1 (0 - 25 cm)																			
266	7	160	100	180	180	267	180	201	198	210	150	140	218	153	220	820	407	400	1290
±*	0	40	20	30	4	5	30	2	18	60	20	20	8	5	40	20	6	5	130
AC (25 - 45 cm)																			
267	7	100	120	90	208	299	230	243	206	260	220	180	247	175	210	780	378	369	1210
±	0	40	20	20	4	5	30	2	17	60	20	20	9	5	40	20	5	5	140
C1 (45 - 60 cm)																			
268	9	70	70	70	232	310	260	294	251	170	250	200	244	200	260	430	317	336	800
±	0	20	30	40	5	5	40	2	20	50	20	20	11	5	30	20	6	5	120
C2 (60 - 72 cm)																			
269	15	150	60	110	236	257	230	280	204	200	230	180	182	191	260	370	280	277	440
±	1	40	20	40	6	5	30	2	15	50	20	20	6	5	30	20	5	3	160

* ± = one standard deviation for counting statistics.

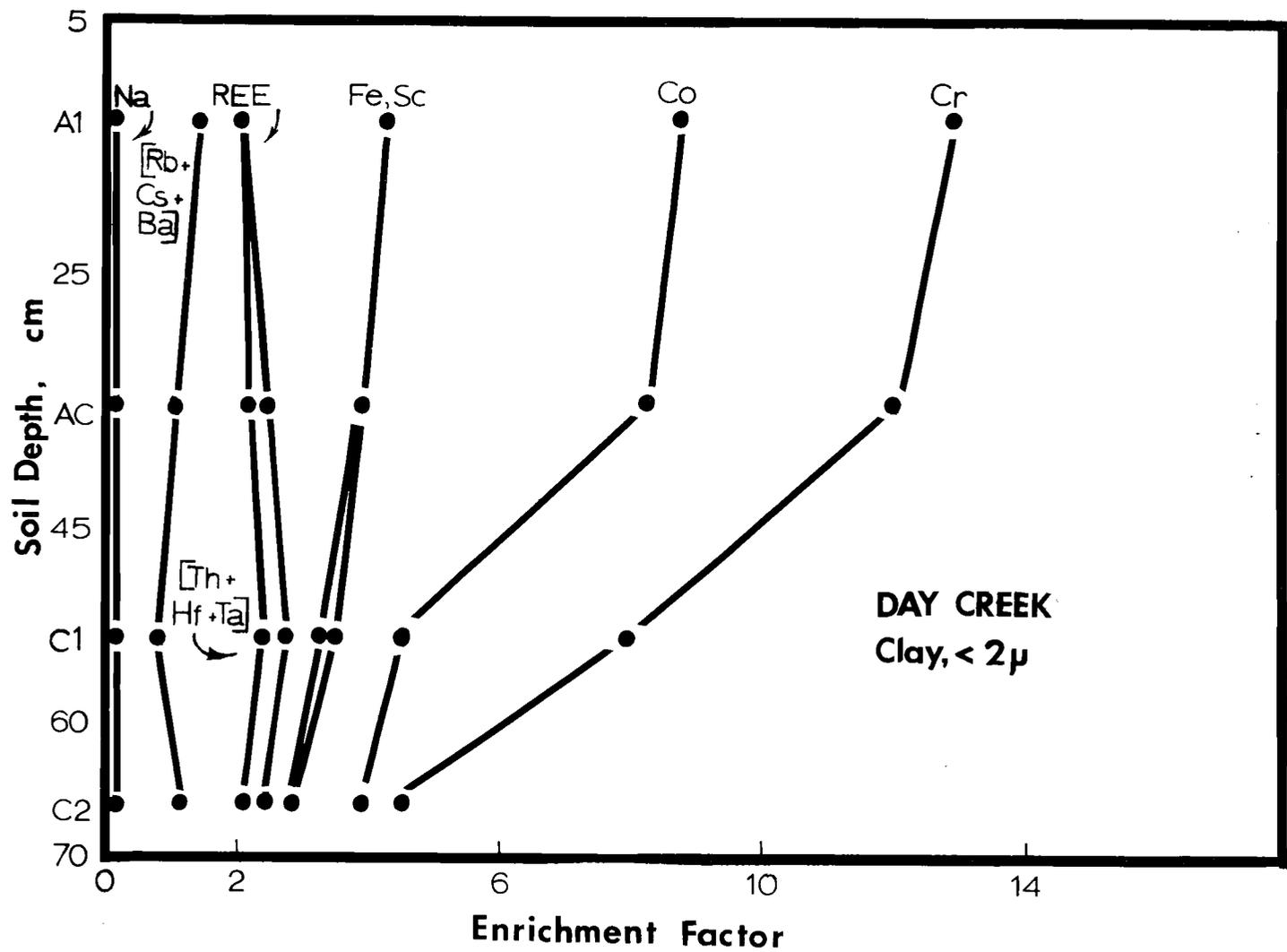


Figure 4. Effect of soil weathering on elemental enrichment in soil clays derived from Mazama ash. The factor for unweathered Mazama glass equals 1.0.

surface, probably as a result of dilution by other elements. The transition metals have one and one half to three times higher abundances in clay from upper horizons than in clay from the C horizons. Chromium enrichment during weathering was greater than that of cobalt.

Iron and scandium increased in conjunction with one another, reflecting their similar chemistry. The Sc/Fe ratio for each horizon remained at 4×10^{-4} , as found for the soils from which the clays were separated. The depth relationships for soils and clays were essentially identical (Chapter III, Figure 2). This is illustrated for Sc content in the clay versus the content in the fine sand fractions from the Day Creek soil (Figure 5). The other transition metals, Cr, Fe, and Co, produced similar relationships with correlation coefficients greater than 0.9.

The significance of enrichment of transition metals in upper horizons can be explained by the theory proposed by Jenne (1968). He suggested that the heavy metals are associated with and controlled by iron and manganese hydrous-oxides in natural waters, soils, and sediments. Clays from Mazama ash probably contain significant amounts of free iron oxides existing as coatings on soil particles prior to the dispersion treatment. Soil weathering may result from dissolution and leaching of finer particles, followed by redeposition of the least soluble compounds onto larger particles. The tendency for an

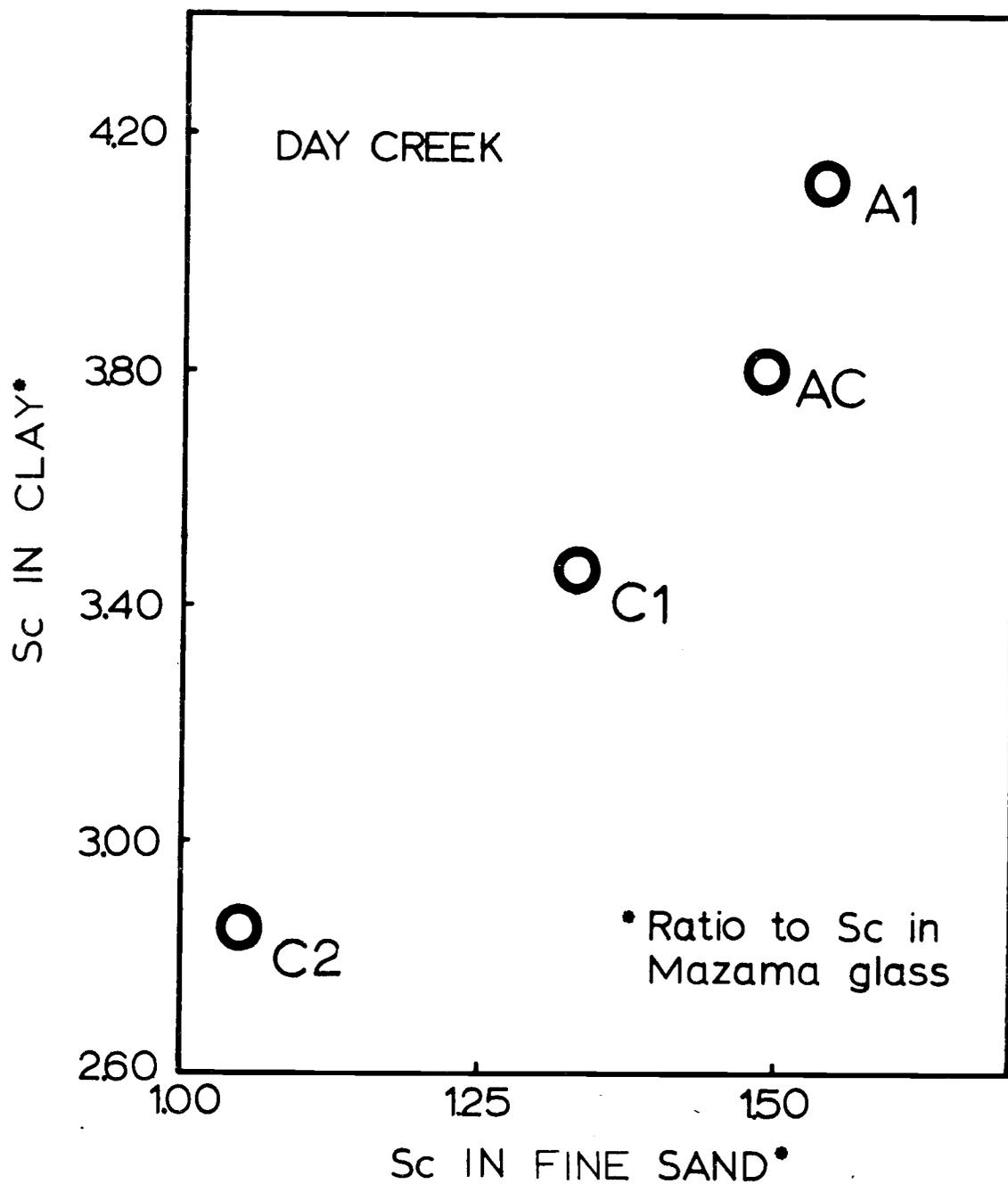


Figure 5. Scandium in clay and very fine sand-size glass of Day Creek soil horizons.

element to accumulate in upper horizons of soils may be predicted from the solubility product of the hydroxide. The mobility of chromium, for example, is so low that its migration has been observed only in desert soils (Vinogradov, 1959).

Chemical Pretreatments

Successively more rigorous treatments were used to ascertain the strength with which the trace elements were held within the clay. The four classifications: hydroxylated cations, free iron oxides, amorphous material, and crystalline minerals are used largely as a matter of convenience. This does not imply that other phases were not dissolved with a particular chemical treatment. Saturation with 1 N NH_4NO_3 (Specpure grade) showed that the elements analyzed either were not exchangeable cations or were removed during the dispersion and clay separation with 1% NH_4OH (Tables 5 and 6). The analyses of the control sample and the NH_4NO_3 saturated sample were considered duplicates. Their averages were used for comparisons with the other treatments.

Washing the Mazama soil clay samples with 0.05 N HNO_3 considerably reduced the amounts of the rare earth elements, La through Lu (Tables 5 and 7). Cerium, however, was not significantly affected by the treatment. Ce^{3+} is one of the few rare earth elements (REE) capable of attaining a higher oxidation state, forming more

Table 5. Ratios to Mazama volcanic glass composition for Day Creek AC horizon clay receiving various pretreatments.

INAA No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Ratios X 100																			
Control, dispersed with 1% NH ₄ OH																			
267	7	100	120	90	208	299	230	243	210	260	220	180	247	175	210	780	378	369	1210
±*	0	40	20	20	4	5	30	2	20	60	20	20	9	5	40	20	5	5	140
NH ₄ NO ₃ saturated, duplicate of above																			
288	8	100	150	60	228	315	150	280	250	270	180	160	262	177	310	880	416	409	1120
±	1	40	40	30	7	7	40	2	20	90	20	40	12	6	40	30	8	6	140
0.05 N HNO ₃ saturated to remove hydroxylated cations																			
283	11	160	190	70	68	244	60	85	70	0	10	50	281	202	800	920	470	297	1340
±	0	60	40	30	4	7	30	2	20	30	20	20	11	6	70	30	8	5	130
Dithionite-citrate-bicarbonate iron removal (DCB)																			
281	14	200	180	80	48	70	70	53	110	80	0	100	140	159	770	990	272	232	1340
±	0	60	30	30	4	6	50	1	70	70	10	40	14	6	70	30	6	3	180
0.5 N KOH + DCB for amorphous material removal																			
289	28	160	360	70	100	102	0	93	80	210	40	110	265	89	1070	1000	275	425	2410
±	1	30	40	20	4	3	0	1	20	60	10	20	8	5	40	30	5	5	130

* ± = one standard deviation for counting statistics.

Table 6. Ratios to Mazama volcanic glass composition for Parkdale AC horizon clay receiving various pretreatments.

INAA																			
No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Ratios X 100																			
Control, dispersed with 1% NH ₄ OH																			
270	8	110	80	46	314	262	290	249	250	180	140	150	221	119	350	860	468	372	1450
±*	0	20	20	12	5	2	20	2	10	40	10	10	6	3	20	20	5	5	80
NH ₄ NO ₃ saturated, duplicate of above																			
282	8	80	80	57	304	244	210	225	240	240	170	130	199	109	340	860	452	356	1360
±	0	30	20	18	5	5	30	2	20	50	10	10	8	3	30	20	5	5	90
0.05 N HNO ₃ saturated to remove hydroxylated cations																			
286	9	160	100	67	268	260	220	217	200	150	140	140	247	123	420	940	518	389	1680
±	0	50	30	20	6	5	30	2	20	50	20	20	8	5	30	20	5	5	130
Dithionite-citrate bicarbonate iron removal (DCB)																			
284	19	180	120	82	156	184	60	99	90	110	40	100	154	107	470	760	342	232	1580
±	1	50	20	22	6	3	30	1	20	50	10	20	6	4	30	20	4	3	140
0.5 N KOH + DCB for amorphous material removal																			
290	36	330	370	125	114	89	80	76	100	20	30	80	167	88	740	880	268	303	2580
±	1	50	30	19	6	4	30	1	20	30	10	20	8	3	30	20	5	5	140

* ± = one standard deviation for counting statistics.

Table 7. Ratios to Mazama volcanic glass composition for additional soil clays receiving the 0.05 N HNO₃ treatment compared to untreated clays.

INAA No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Ratios X 100																			
<u>South Ice Cave AC</u>																			
Control																			
273	10	70	80	100	262	308	250	294	270	270	260	210	204	177	270	690	339	342	1030
±*	0	40	20	40	5	5	30	2	20	70	20	30	6	5	40	20	5	5	130
0.05 N HNO ₃ saturated to remove hydroxylated cations																			
264	11	90	130	40	156	294	130	189	130	130	130	150	241	192	390	780	382	344	860
±	0	40	30	20	4	5	30	2	20	50	20	20	9	5	30	20	5	5	130
<u>Dick Spring AC</u>																			
Control																			
271	7	120	140	170	303	324	330	316	290	450	270	230	207	169	230	660	425	316	780
±	0	30	30	20	6	5	30	2	20	70	20	20	6	5	30	20	5	5	110
0.05 N HNO ₃ saturated to remove hydroxylated cations																			
287	9	130	160	90	153	285	120	207	190	230	140	120	256	172	330	690	475	305	880
±	0	40	30	20	4	5	30	2	20	60	20	20	8	5	30	20	5	3	90

* ± = one standard deviation for counting statistics.

insoluble compounds (Chapter III; Robinson, Bastron and Murata, 1958; Haskin et al., 1966).

The next treatment involved reduction and removal of free iron oxide compounds with dithionite-citrate-bicarbonate (DCB). The HNO_3 insoluble Ce was removed by the reducing agent (dithionite) in the free iron oxide removal treatment, confirming the results of Robinson et al. (1958).

Boiling 0.5 N KOH followed by DCB treatment dissolved 80% of the clay from both Day Creek and Parkdale AC horizons (Appendix X). The abundances of Na, Rb, Cs, Ta, and Cr were highest in the crystalline minerals surviving the treatment (Tables 5 and 6). Increases in the amount of sodium indicated the treatment was concentrating minerals containing sodium, probably plagioclase (3.2 Å peak, Figure 2).

Table 8 illustrates a method of data presentation that considers the weight loss undergone by the clay sample during dissolution treatments. For example, the Day Creek KOH treated sample residue had 100 units of La but the residue weight was only 18% of the original clay weight. Thus only 18 units of La occurred in resistant minerals, while 218 units (average of samples 267 and 288) were present in the original sample. The resistant minerals had 8% of the total La, the remainder being removed by HNO_3 , DCB, or KOH. Negative values obtained as a result of large analytical error due to counting statistics

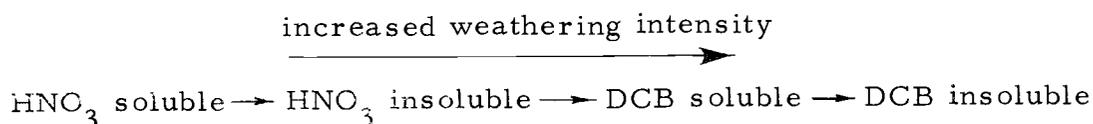
Table 8. Trace element allocation to the chemical phases present in Day Creek and Parkdale clay fractions.

Phase	Percentage of untreated concentration																		
	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
<u>Day Creek AC</u>																			
Hyd*	3	0	3	36	79	48	80	79	76	86	95	72	27	24	0	27	22	50	25
FeOx	0	0	26	8	9	40	0	11	0	0	2	0	44	28	24	11	42	19	15
Amor	29	71	21	38	3	6	20	4	18	2	0	17	10	38	39	40	23	11	23
Crys	67	29	50	17	8	6	0	6	6	13	3	11	19	9	37	22	13	20	38
<u>Parkdale AC</u>																			
Hyd	0	0	0	0	21	7	19	17	27	32	17	10	0	2	0	1	0	3	0
FeOx	0	44	34	41	57	61	72	65	57	45	72	60	70	57	46	60	68	69	54
Amor	14	9	0	18	15	25	3	12	8	21	8	19	15	26	15	19	21	11	12
Crys	86	47	66	41	7	7	6	6	8	2	3	11	15	15	39	20	11	17	34

* Hyd = hydroxylated cations (0.05 N HNO₃ soluble fraction); FeOx = free iron oxides (dithionite-citrate-bicarbonate soluble fraction (DCB)); Amor = amorphous material soluble in 0.5 N KOH + DCB following the first iron removal; Crys = crystalline material resistant to the treatments above.

were set equal to zero (Appendix XII). Less significance should be attributed to allocations calculated from less accurate values.

The alkali elements tended to remain with the more resistant fractions, while the rare earth elements were removed more easily (Table 8). Significant amounts of the transition metals, Co, Fe, Sc, and Cr, were removed from the Day Creek clay with the nitric acid wash. The transition metal content in Parkdale clay remained unaffected by 0.05 N HNO₃. The iron removal treatment was necessary to extract major portions of the rare earth and transition elements from the Parkdale clay. As in the Day Creek clay, cerium was less soluble than the other REE. Most of the Ce not removed by HNO₃ or DCB was removed by the KOH boiling treatment. Assuming the Parkdale clay to be a product of more intense weathering of volcanic glass compared to Day Creek clay, the following sequence might explain the behavior of Ce:



The hydrous-oxides of iron in soils become more anhydrous and more crystalline as they age (Schwertmann, 1966). Data of Table 8 seem to indicate an association between the REE and other transition metals as well as iron. This relationship is evaluated later in the discussion concerning other weathered materials containing large amounts of iron oxides.

The relationship between Sc and Fe was of theoretical interest because these elements have similar chemical properties and Sc/Fe ratios tend to remain constant during volcanic ash weathering (Chapter III). Sc was removed to a greater extent than Fe from Day Creek clay by HNO_3 , while both Fe and Sc remained unaffected in the Parkdale clay (Table 8). A total of 2/3 of the Fe and Sc were removed from both clays after the iron removal treatment. The amorphous material (KOH + DCB soluble fraction associated with Al and Si) contained higher allocated amounts of Fe than Sc by a ratio of 2:1 (Table 8). On the other hand, the crystalline minerals in the residue (Figures 2 and 3) contained higher allocated amounts of Sc than Fe by a ratio of 2:1. Sc^{3+} (radius = 0.81 Å) should enter Fe^{2+} (radius = 0.74 Å) rather than Fe^{3+} (radius = 0.64 Å) positions. Since Sc-O bonds are more ionic than Fe-O bonds, this may also aid in capture of Sc in Fe^{2+} positions (Taylor, 1965).

Origin of 2:1 Layer Silicates

The pedogenic origin of 2:1 layer silicates occurring in soils developed from coarse Mazama pumice has been proposed (Chichester *et al.*, 1969). Perhaps a detrital origin should be considered as well. Minute amounts of biotite observed with a light microscope in silt fractions of Mazama pumice might have been concentrated in the $<2\mu$ clay fractions of soils weathered from Mazama ash. This would

explain the relatively high Sc/Fe ratios that would be predicted for detrital biotite containing considerable Fe^{2+} . The lower Sc/Fe ratios for the fraction associated with amorphous Si and Al would be consistent with pedogenic formation of the amorphous component. Iron in pedogenic minerals of well drained soils would be expected to be predominantly in the +3 oxidation state (radius = 0.64 \AA). Certain structural positions in pedogenic minerals might have difficulty admitting the larger Sc^{3+} (radius = 0.81 \AA).

Only 2% clay was found for the Day Creek AC horizon (Table 1) and since only 20% of this survived the KOH boiling treatment, the content of 2:1 layer silicates was less than 0.5% of the Day Creek soil sample. This was representative of the quantity of layer silicates found for other soils derived from Mazama ash. Certainly, pedogenic formation of 2:1 layer silicates has not been a major reaction in Mazama volcanic ash during the past 6,600 years of soil formation. The transformation of detrital biotite to vermiculite and chloritic intergrades remains a distinct possibility for the origin of 2:1 layer silicate clays developed in Mazama ash.

Comparison of Mazama Soil Clays to Weathering Products of Other Materials

Soil clays from western Oregon containing high amounts of free iron oxides and a ferruginous bauxite were selected as examples of weathering products of non-ash materials. The Wren soil clay was

characterized by disordered kaolin and iron interlayered smectite (Singleton, 1966). The Jory soil clay sample was similar to the Wren soil clay except for the presence of less iron in the interlayer component of the clays. Very low amounts of sodium indicated the absence of plagioclase in these clay fractions -- the usual observation for soil clays (Table 9). The Wren clay had over three times more Co and five times more Cr than the Jory clay. It was not known if this could be associated with the presence of iron interlayers. The Sc/Fe ratios for both upland soils were nearly identical, perhaps suggesting development from the same parent material. These upland soil clays had high amounts of Fe associated with equivalent amounts of Sc, higher amounts of Co, and still higher amounts of Cr relative to compositions in Mazama volcanic glass (Table 9). The expression describing elemental enrichment during volcanic ash weathering, $Cr > Co > Fe = Sc$, therefore applies to clays unrelated to Mazama ash. Tantalum was the only other element exhibiting extremely high concentrations relative to Mazama ash. The rare earth element (REE) contents were slightly lower than those for Mazama soil clays.

An untreated sample of ferruginous bauxite from the Salem Hills area of western Oregon was included as an example of a highly weathered iron oxide concentrate. The absence of sodium indicated the intensive leaching undergone by the bauxite deposit (Table 9). This sample had relatively high amounts of transition metals except for Co

Table 9. Ratios to Mazama volcanic glass composition for clays from western Oregon soils and for ferruginous bauxite.

INAA																			
No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Ratios X 100																			
Wren B1																			
307	1	190	40	26	138	150	180	159	200	0	89	200	70	133	540	2940	905	913	11800
±*	0	60	30	12	4	5	90	2	20	20	27	20	7	5	60	50	14	16	370
Jory B22																			
308	1	100	140	25	164	184	150	155	250	130	16	120	126	86	420	890	653	672	2360
±	0	40	40	18	3	6	50	1	20	80	25	10	6	4	40	30	7	12	240
Dayton B22																			
309	4	130	240	56	211	202	160	215	310	260	189	230	187	80	430	880	682	566	3980
±	1	50	30	19	5	5	60	2	30	110	34	20	8	5	40	30	7	9	290
Salem Hills bauxite																			
310	0	70	40	21	24	16	nd	12	40	10	0	110	461	342	2080	150	986	415	4300
±	0	30	20	12	1	3		1	10	10	0	10	6	5	50	20	7	8	230

* ± = one standard deviation for counting statistics.

which was similar to the amount in Mazama ash. Tantalum was 20 times the amount in Mazama ash. Th and Hf concentrations were three times the values for soil clays from western Oregon and about twice the values for Mazama soil clays. Hf commonly substitutes for Zr in zircon, a resistant mineral tending to become concentrated in extremely weathered materials (Jackson, 1964). Judging by their low abundance, the REE probably were not associated with zircon in the ferruginous bauxite. Zircon from granitic rocks tends to concentrate REE to a greater extent than zircon from more basic rocks (Haskin et al., 1966). The geochemistry of such iron concentrates needs more study, but it appears that other transition metals become concentrated along with iron, and that the REE are not as closely interrelated.

Clays from Other Volcanic Ash Deposits

The trace element similarities between clays from AC horizons of five different Mazama transect soils (Tables 2 and 3) suggested that weathered pyroclastics from other volcanoes might have similar abundances. However, if clays derived from different sources have unique abundances, it might be possible to make distinctions between weathered soils from different volcanic ash layers. To test these possibilities, clay was separated from an AC horizon developed in Newberry ash at Red Hill, and from a C horizon at China Hat also developed in Newberry ash, and a weathered "C1" horizon developed

from Glacier Peak ash at North Sugarloaf (sites described by Doak, 1969). Clays were also obtained from volcanic ash layers deposited in peat bogs (Chapter II) for assessing the effects of such diverse environments.

Comparison to Mazama Volcanic Glass

Both of the clays from Newberry pumice had high amounts of Ta relative to Mazama volcanic glass composition (Table 10). Newberry volcanic glass also had about four times more Ta than Mazama glass (Chapter I, Table 5). Equal Sc and Fe values in Table 10 are equivalent to the Sc/Fe ratio of 4.3×10^{-4} for Mazama volcanic glass (Table 2). The AC horizon clay of Newberry pumice had a considerably lower Sc/Fe ratio, while the C horizon clay had a much higher Sc/Fe ratio than found for Newberry glass (Chapter III, Table 8). These observations contradict the Sc/Fe constancy found for soils and clays derived from Mazama ash. Clays from the Glacier Peak soil had Sc/Fe ratios more like Mazama ash than Glacier Peak ash. All of these soil clays had high relative amounts of Cr, Co, Fe, Sc, and rare earth elements, also observed for Mazama soil clays. Sodium contents in clays from Glacier Peak C1, and Newberry AC and C horizons were about 1/8, 1/4, and 1/2 of the amounts found for volcanic glass from the respective ash layers. This might indicate the presence of small quantities of volcanic glass or plagioclase in the $< 2\mu$ clay

Table 10. Ratios to Mazama volcanic glass composition for clays separated from Newberry, Glacier Peak, St. Helens Y, and Mazama volcanic ash samples.

INAA No.	Na	Rb	Cs	Ba	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Th	Hf	Ta	Co	Fe	Sc	Cr
Ratios X 100																			
Red Hill AC, Newberry soil																			
304	23	120	123	65	180	164	210	195	160	270	100	214	211	1421	1210	420	424	252	900
±*	1	30	31	14	7	5	80	3	27	80	30	16	8	6	70	30	6	5	240
China Hat C, Newberry soil																			
312	45	210	79	90	238	538	150	290	211	380	310	371	332	205	670	360	284	398	710
±	1	40	23	22	7	7	80	2	25	90	50	16	9	6	60	20	5	8	230
North Sugarloaf C, Glacier Peak soil																			
313	8	50	147	83	425	446	380	340	380	270	310	273	279	122	320	630	327	299	1540
±	1	30	31	16	7	7	80	2	28	50	40	13	6	5	40	30	5	5	210
Anthony Lakes bog, Mazama layer																			
331	27	80	84	79	120	106	100	117	96	120	70	98	100	112	40	180	82	114	410
±	1	20	14	14	5	3	50	2	11	30	20	20	4	3	30	10	3	2	160
Anthony Lakes bog, Glacier Peak layer																			
332	29	80	35	41	103	93	0	95	108	50	7	66	202	80	320	150	61	78	540
±	1	20	7	9	5	2	40	2	9	20	10	13	3	2	30	10	1	2	90
Hurricane Creek bog, St. Helens Y layer																			
314	47	120	89	42	104	108	200	190	108	80	50	136	73	50	200	620	305	185	1880
±	1	40	23	12	6	5	60	2	18	40	30	13	5	3	40	20	5	3	210
Hurricane Creek bog, Mazama layer																			
315	30	110	80	117	130	154	330	406	120	0	130	207	79	72	130	520	247	162	1580
±	1	30	15	15	5	4	40	3	17	30	40	9	5	4	40	20	4	3	180
Lakebeds Meadow bog, St. Helens Y layer																			
333	11	60	90	28	165	167	200	185	188	90	50	95	93	75	200	120	77	174	1670
±	1	20	18	10	4	3	70	2	11	20	20	13	4	3	30	10	2	31	170

* ± = one standard deviation for counting statistics.

fractions. Clays from different ash layers in the same bog tended to have similar trace element compositions.

Variation Analysis

Similarities and differences between analyses for clays could be detected by variation analysis (Table 11). The analysis for each clay sample was divided by the following analyses: 1) the averages of five Mazama soil clays (Table 2), 2) Newberry soil clay, 3) Glacier Peak soil clay, and 4) clay from Mazama ash in Anthony Lakes bog. Mean ratios near 1.00 and coefficients of variation less than 20% (Chapter I) indicated similar samples.

Coefficients of variation ranged from 11 to 23% and mean ratios were between 0.89 and 1.10 when each of the five Mazama soil clays was compared to the average analysis (Table 11). Clay from the Antelope Unit AC derived from coarse Mazama pumice was most similar to clay from coarse Glacier Peak pumice. Clays occurring at different depths in the Day Creek soil were most similar to other clays from Mazama soils.

The analysis of clay from Newberry soil was unlike other clays, while clays from Glacier Peak pumice and Parkdale soil were most similar to clay from Mazama ash (Table 11). Clays from volcanic ash layers in peat bogs had compositions unlike those found in any of the soils (lowest CV for all comparisons was 50%). The landscape

Table 11. Coefficients of variation (%) for clays found in pyroclastics of the Pacific Northwest.

INAA No.	Description	Av. ratio for lowest CV	Mazama		Glacier	Newberry
			Soil 1*	Bog 2	Peak 3	
<u>Mazama transect soils (AC horizons)</u>						
342	Ant. Unit	1.10	23	41	19**	52
273	S. Ice Cave	0.98	11**	49	27	43
272	S. Ochoco B.	0.89	11**	44	30	40
267	Day Creek	0.93	19**	49	32	40
271	Dick Spring	1.04	17**	46	37	45
<u>Day Creek soil profile</u>						
266	Day Creek A1	0.93	33	57	54	46
288	Day Creek AC	1.04	21	56	34	37
268	Day Creek C1	0.94	16**	48	33	44
269	Day Creek C2	0.90	30	50	51	42
<u>Clays from other ash samples</u>						
304	Red Hill AC (Soil from Newberry pumice)	1.16	101	184	84	-
270	Parkdale AC	0.99	31	70	38	41
313	N. Sugarloaf C1 (Soil from Glacier Peak ash)	1.14	22	48	-	50
315	Hurricane Ck. (Mazama ash - bog)	1.04	80	53	93	50
332	Anthony Lakes Md. (Glacier Peak ash - bog)	0.55	119	127	136	53

* Chemical compositions of the clays were divided by the chemical compositions of (1) the average analysis of the five AC horizon clays from soils developed in Mazama ash, (2) clay from Mazama ash at Anthony Lakes bog (sample 331), (3) clay from North Sugarloaf C1 derived from Glacier Peak ash (sample 313), and (4) clay from Red Hill AC derived from Newberry pumice (sample 304).

** Lowest CV classifies the sample with this group.

position of peat bogs might have allowed clay-containing seepage water from the surrounding uplands to filter into the ash layers. This may account for the large clay contents ($> 10\%$) found for ash samples from Glacier Peak (sample 332) and St. Helens Y (sample 333) (Table 1). Weathering of volcanic ash in peat bogs has been noted as well (Chapter II).

This study indicated the possibility of using variation analysis to correlate clays derived from the same parent material and to evaluate chemical differences between clays from diverse environments. A larger number of clay samples from Glacier Peak, Newberry, and St. Helens volcanic ash derived soil horizons would be needed to do the discriminant analysis for INAAC (Chapter I). An additional consideration involves clays derived from different volcanic ash layers becoming more similar to each other after longer periods of weathering.

REE Distribution Patterns

The rare earth elements (REE) produce distribution patterns distinctive for various geologic materials (Haskin et al., 1966). A straight line along the bottom axis in Figure 6 would correspond to the relative abundances found for chondritic meteorites representing nebular material (Haskin et al., 1966). Most sediments would have a curve similar to the one for Glacier Peak clay.

Whole samples of Mazama volcanic ash (Chapter I, Table 4)

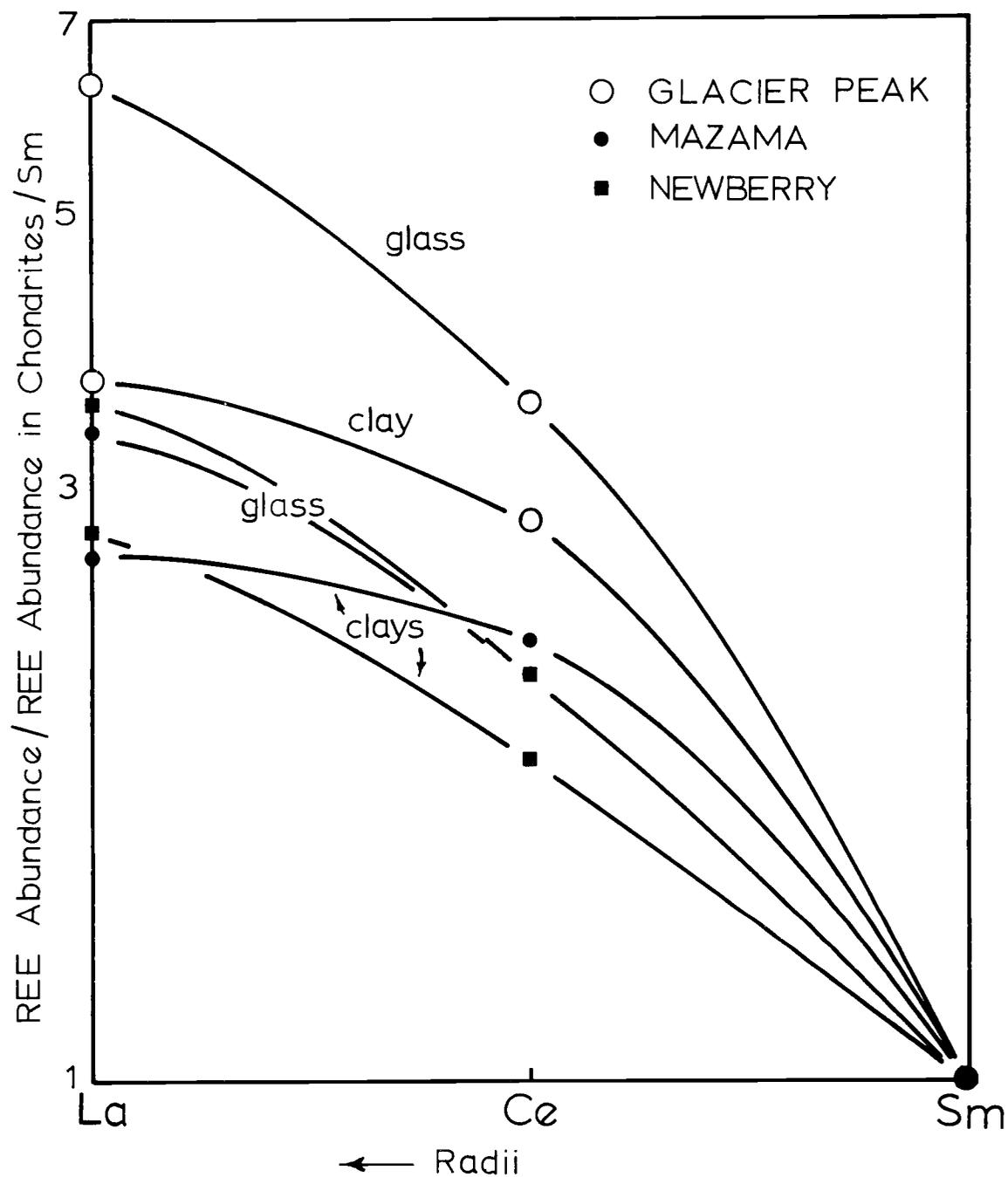


Figure 6. La and Ce in relation to Sm for clays and glass from Mazama, Newberry, and Glacier Peak volcanic ash. The abundances of La, Ce, and Sm were divided by the abundances of La, Ce, and Sm in chondrites.

and crystalline clay minerals (Table 5) had REE patterns similar to the volcanic glass (data not shown). In relation to the other REE, La and Ce abundances were higher in Glacier Peak glass than in Mazama glass (Chapter I, Figure 3). Clays separated from these materials produced La, Ce, and Sm distributions somewhat similar to the volcanic glass from which they were partly derived (Figure 6). The lower relative values for La and Ce in the clay may reflect the influence of REE dissolved from certain easily weathered minerals other than glass. The Ce/La ratio of the clay fraction increases with nearness to the soil surface at the Day Creek site (data not shown). This probably reflects the accumulation of HNO_3 insoluble oxides of Ce^{4+} rather than preferential leaching of La during soil formation. Further study of REE distribution patterns may reveal the nature of the reactions, as well as the products of soil weathering.

Conclusions

1. Clay fractions of soils developed from Mazama ash were not $< 2\mu$ volcanic glass. The amorphous clays were weathering products containing large amounts of hydrous iron oxides associated with the colloidal coatings found on volcanic glass.
2. Rare earth element (REE) abundances in the clay fractions were about three times the amounts found for unweathered volcanic glass. Sodium was only 10% of the value for glass while the transition

metals were as much as nine times higher in clay than in glass. Such increases were remarkably similar for clays from five soils along a 450 km transect of the Mazama fallout area.

3. Abundances of Cr and Co, as well as Fe and Sc in the clay fractions decreased with depth in clays from a typical volcanic ash soil. The Sc/Fe ratio was about 4×10^{-4} for clay fractions and for Mazama volcanic glass from which they were derived.

4. Chemical treatments indicated that solubilities of REE in Day Creek clay were greater than those in the more intensely weathered Parkdale clay. High Sc/Fe ratios indicated a possible detrital origin for crystalline clay minerals comprising 20% of the clay fractions of both soils.

5. Clays from soils of western Oregon also contained high concentrations of the trace elements. Iron concentration in laterite included the transition elements, but apparently not the rare earth elements.

6. An attempt to correlate clays from different volcanic ash layers revealed some chemical similarities between Glacier Peak and Mazama soil clays, while the chemical composition was different for Newberry soil clays.

BIBLIOGRAPHY

- Allison, I. S. 1945. Pumice beds at Summer Lake, Oregon. Geological Society of America, Bulletin 56:789-807.
- _____ 1966a. Fossil Lake Oregon: Its geology and fossil faunas. Corvallis, Oregon State University. 48 p.
- _____ 1966b. Pumice at Summer Lake, Oregon -- A correction. Geological Society of America, Bulletin 77:329.
- Borchardt, G. A. and A. A. Theisen. 1968. Unpublished research on rapid X-ray spectrographic determination of major element homogeneity in Mazama pumice. Corvallis, Oregon, Dept. of Soils, Oregon State University, 1968.
- Borchardt, G. A., A. A. Theisen and M. E. Harward. 1968. Vesicular pores of pumice by mercury intrusion. Soil Science Society of America, Proceedings 32:735-737.
- Chichester, F. W. 1967. Clay mineralogy and related chemical properties of soils formed on Mazama pumice. Ph. D. thesis. Corvallis, Oregon State University. 152 numb. leaves.
- Chichester, F. W., C. T. Youngberg and M. E. Harward. 1969. Clay mineralogy of soils formed on Mazama pumice. Soil Science Society of America, Proceedings 33:115-120.
- Crandell, D. R., D. R. Mullineaux, R. D. Miller and M. Rubin. 1962. Pyroclastic deposits of Recent age at Mount Rainier, Washington. U. S. Geological Survey, Professional Paper 450-D:D64-D68.
- Czamanske, G. K. and S. C. Porter. 1965. Titanium dioxide in pyroclastic layers from volcanoes in the Cascade Range. Science 150:1022-1025.
- Doak, W. H. 1969. A qualitative and quantitative characterization of porosity in volcanic ash. M. S. thesis. Corvallis, Oregon State University. 90 numb. leaves.
- Ewart, A. 1963. Petrology and petrogenesis of Quaternary pumice ash in the Taupo area, New Zealand. Journal of Petrology 4:392-431.

- Fryxell, R. 1965. Mazama and Glacier Peak volcanic ash layers: Relative ages. *Science* 147:1288-1290.
- Gordon, G. E., K. Randle, G. G. Goles, J. B. Corliss, M. H. Beeson and S. S. Oxley. 1968. Instrumental activation analysis of standard rocks with high-resolution γ -ray detectors. *Geochimica et Cosmochimica Acta* 32:369-396.
- Griffiths, J. C. 1966. Application of discriminant functions as a classification tool in the geosciences. In: *Computer application in the earth sciences: Colloquium on classification procedures*, ed. by D. F. Merriam. Lawrence, University of Kansas. p. 48-52. (Kansas. State Geological Survey. Computer Contribution 7)
- Hansen, H. P. 1947. Postglacial forest succession, climate, and chronology in the Pacific Northwest. *American Philosophical Society, Transactions, new ser.*, 37 (Part I):p. 1-130.
- Haskin, L. A., F. A. Frey, R. A. Schmitt and R. H. Smith. 1966. Meteoritic, solar and terrestrial rare-earth distributions. In: *Physics and chemistry of the earth. Vol. 7.* New York, Pergamon. p. 167-321.
- Higgins, M. W. and A. C. Waters. 1968. Newberry caldera field trip. In: *Andesite conference guidebook.* Portland. p. 59-77. (Oregon. Dept. of Geology and Mineral Industries. Bulletin 62)
- Jackson, M. L. 1956. *Soil chemical analysis-advanced course.* Madison, Wisconsin, author. 991 p.
- _____ 1964. Chemical composition of soils. In: *Chemistry of the soil*, ed. by F. E. Bear. 2d ed. New York, Reinhold. p. 71-141. (American Chemical Society. Monograph Series 160)
- Jenne, E. A. 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe oxides. In: *Trace inorganics in water: A symposium.* Washington, D. C., American Chemical Society. p. 337-387. (Advances in Chemistry Series 73)
- Kline, J. R. and S. S. Brar. 1969. Instrumental analysis of neutron irradiated soils. *Soil Science Society of America, Proceedings* 33:234-238.

- Kline, J. R., J. E. Foss and S. S. Brar. 1969. Lanthanum and scandium distribution in three glacial soils of western Wisconsin. Soil Science Society of America, Proceedings 33:287-291.
- Knox, J. B. and N. M. Short. 1963. Diagnostic model using ash fall data to determine eruption characteristics and atmospheric conditions during a major volcanic event. Berkeley. 29 numb. leaves. (University of California. Lawrence Radiation Laboratory. Report on Contract W-7405-eng-4B, UCRL 7197)
- Krumbein, W. C. and F. A. Graybill. 1965. An introduction to statistical models in geology. New York, McGraw Hill. 475 p.
- Moore, J. R. 1963. Bottom sediment studies, Buzzards Bay, Massachusetts. Journal of Sedimentary Petrology 33:511-558.
- Nelson, C. H., L. D. Kulm, P. R. Carlson and F. R. Duncan. 1968. Mazama ash in the northeastern Pacific. Science 161:47-49.
- Norgren, J. A. 1962. Thin-section micromorphology of eight Oregon soils. M. S. thesis. Corvallis, Oregon State University. 122 numb. leaves.
- Norgren, J. A. and M. E. Harward. 1968. Assistant in Soils and Professor, respectively. Corvallis, Oregon, Dept. of Soils, Oregon State University. Personal communication. Sept. 1968.
- Norman, J. C. and L. A. Haskin. 1968. The geochemistry of Sc: A comparison to the rare earths and Fe. Geochimica et Cosmochimica Acta 32:93-108.
- Powers, H. A. and H. E. Malde. 1961. Volcanic ash beds as stratigraphic horizon markers in basin deposits near Hagerman and Glens Ferry, Idaho. U. S. Geological Survey, Professional Paper 424-B:B167-B170.
- Powers, H. A. and R. E. Wilcox. 1964. Volcanic ash from Mount Mazama (Crater Lake) and from Glacier Peak. Science 144: 1334-1336.
- Robinson, W. O., H. Bastron and K. J. Murata. 1958. Biogeochemistry of the rare-earth elements with particular reference to hickory trees. Geochimica et Cosmochimica Acta 14:55-67.

- Roth, C. B., M. L. Jackson, J. M. de Villiers and V. V. Volk. 1966. Surface colloids on micaceous vermiculite. In: Soil chemistry and fertility: Transactions of the meeting of Commissions II and IV of the International Society of Soil Sciences, Aberdeen, Scotland, 1966. Aberdeen, University of Aberdeen. p. 217-221.
- Schwertmann, U. 1966. The formation of goethite and hematite in soils and sediments. In: Proceedings of the International Clay Conference, ed. by L. Heller and A. Weiss. Jerusalem, 1966. Vol. 1. Jerusalem, Israel Program for Scientific Translations, 1966. p. 159-165.
- Singleton, P. C. 1966. Nature of interlayer materials in silicate clays of selected Oregon soils. Ph. D. thesis. Corvallis, Oregon State University. 84 numb. leaves.
- Smith, D. G. W. and J. A. Westgate. 1969. Electron probe technique for characterizing pyroclastic deposits. *Earth and Planetary Science Letters* 5:313-319.
- Steen, V. C. and R. Fryxell. 1965. Mazama and Glacier Peak pumice glass: Uniformity of refractive index after weathering. *Science* 150:878-880.
- Taylor, S. R. 1965. The application of trace element data to problems in petrology. In: *Physics and chemistry of the earth*, ed. by L. H. Ahrens, F. Press, S. K. Runcorn, and H. C. Urey. Vol. 6. New York, Pergamon. p. 133-213.
- Theisen, A. A., G. A. Borchardt, M. E. Harward and R. A. Schmitt. 1968. Neutron activation for distinguishing Cascade Range pyroclastics. *Science* 161:1009-1011.
- Tidball, R. R. 1965. A study of soil development on dated pumice deposits from Mount Mazama, Oregon. Ph. D. thesis. Berkeley, University of California. 235 numb. leaves.
- Vinogradov, A. P. 1959. *The geochemistry of rare and dispersed chemical elements in soils*. 2d ed. New York, Consultants Bureau. 209 p.
- Westgate, J. A. and A. Dreimanis. 1967. Volcanic ash layers of Recent age at Banff National Park, Alberta, Canada. *Canadian Journal of Earth Sciences* 4:155-161.

Wilcox, R. E. 1965. Volcanic ash chronology. In: The Quaternary of the United States: Review volume for the Seventh Congress of the International Association for Quaternary Research, Boulder, Colorado, 1965, ed. by H. E. Wright, Jr. and D. G. Frey. Princeton, Princeton University. p. 807-816.

_____ 1969. Geologist. Dept. of Interior, Geological Survey, Denver Federal Center, Denver. Personal communication. Pendleton, Oregon. June 22, 1969.

Wilcoxson, K. 1967. Volcanoes. London, Cassell. 237 p.

Williams, H. 1942. The geology of Crater Lake National Park, Oregon. Washington, D. C. 162 p. (Carnegie Institute of Washington. Publication no. 540)

APPENDICES

Neutron Activation for Distinguishing Cascade Range Pyroclastics

Abstract. Neutron activation of glassy separates of volcanic ash resulted in 21 nuclides measurable with instrumental techniques. The relative activities of most of the nuclides distinguish samples from Mount Mazama, Newberry Crater, and Glacier Peak. The usefulness of the technique was assessed by comparing the values for known sources with those from fine ash of uncertain origin. The data strongly suggest Mount Mazama as the source.

Volcanic ash layers may be used as stratigraphic horizon markers, but this approach depends upon the ability to distinguish different ash deposits. One of the principal sources of volcanic ash in Oregon was an eruption of Mt. Mazama about 6600 years ago (1). Another major source of volcanic ash in the Pacific Northwest was Glacier Peak, with an eruption about 12,000 years ago (2). Material from both of these sources may occur in northeastern Oregon (2). In certain areas, they can be further confused with materials from Newberry Crater, Mt. St. Helens, and Mt. Rainier. An investigation is in progress to determine the mineralogy and weathering products across a transect of soils from Mazama pumice and ash. It is, therefore, necessary to determine that the selected sample sites do indeed represent Mazama pyroclastics.

Glacier Peak and Mazama pyroclastics have been distinguished previously on the basis of mineralogy, major element composition, and index of refraction (3, 4). Titanium dioxide contents were used with some success to distinguish between a majority of Glacier Peak and Mazama ash samples (5). Overlap in such parameters and bimodal frequency distributions sometimes hinder unequivocal distinctions between the deposits. Neutron activation analysis has been successfully applied to rocks and meteorites (6, 7). The method has the advantage of providing a large number of trace element abundances which can be used to increase the reliability for distinguishing samples. We therefore began an investigation of the merits of instrumental neutron activation analysis to discriminate between ash deposits. This report presents the results of preliminary studies. Specifically, it outlines what elements can be determined in volcanic glass, what relative differences are obtained for samples from different sources, some of the methods and problems, and an assessment of the technique.

Mazama pumice was sampled northwest of China Hat in Deschutes County,

Oregon (Sec. 9, T22S, R14E, Willamette Meridian). An upper coarse layer (I) and a finer-textured lower layer (II) can be distinguished in Mazama pumice at this and other locations. Samples from both layers were obtained. The textural differences between layers I and II of Mazama ash reflect the increasing violence of later eruptions of Mt. Mazama (8). Newberry Crater pumice overlying Mazama pumice with an abrupt, smooth boundary was obtained at the same location. Volcanic ash from Glacier Peak was sampled in Steptoe Canyon in southwestern Washington [previously described by Fryxell (2, 9)].

Fractions the size of fine sand (125 to 63 μ) were sieved from bulk samples of pumice and volcanic ash. Contamination of layers of pyroclastics by primary minerals and possible differences due to mineral sorting might contribute to geochemical variability and confound the interpretations. Glassy components, therefore, were

isolated from the sieved fractions with bromoform-bromobenzene, $\rho = 2.4$ g/cm³. Contamination of trace elements from the bromoform-bromobenzene separation was found to be negligible. The success of the separation was checked on the Mazama ash sample. About 80 percent of the sieve fraction had a density less than 2.4 g/cm³. Crystal inclusions occurring within the glassy separate were less than 5 percent of the sample. We subsequently determined that for soils, an additional separation at 2.2 g/cm³ removes dark fragments that appear to be plant residues.

The method of instrumental neutron activation analysis has been demonstrated by Schmitt *et al.* (6) with NaI(Tl) detectors and by Gordon *et al.* (7) with Ge(Li) detectors. We used the method of Gordon *et al.* (7) except that the counting equipment consisted of a 3.6-cm³ Ge(Li) semiconductor detector and 4096 Nuclear Data Multichannel analyzer. Contributions of the low-energy peaks of Fe, Yb, and Eu activities were subtracted from the peaks of Ce, Pa(Th), and Tb, respectively (10). Quantitative estimates of the abundances of the 21 elements found were obtained by comparison with similarly activated standard solutions of the elements. Final calibrations of standard solutions are being completed and, therefore, the concentrations given for Mazama ash, layer I,

Table 1. Approximate elemental abundances in Mazama ash (layer I) and relationship to activities found for samples of volcanic ash from Mazama layer II, Newberry Crater, and Glacier Peak.

Element	Mazama (layer I) (ppm) ^a		Ratios		
			Mazama II/ Mazama I	Newberry/ Mazama I	Glacier Peak/ Mazama I
Sm	5.21 ± 0.18 [†]	1.21 ± 0.05 [†]	1.66 ± 0.07 [†]	0.45 ± 0.02 [†]	
Fe (%)	2.93 ± .12	1.29 ± .05	0.60 ± .03	.69 ± .03	
Sc	13.3 ± .30	1.27 ± .05	.69 ± .03	.53 ± .02	
Ta	0.46 ± .01	1.14 ± .07	2.00 ± .09	.52 ± .05	
Na (%)	3.41 ± .24	1.13 ± .08	1.45 ± .11	.75 ± .06	
Co	9.5 ± .9	1.26 ± .08	0.36 ± .04	.84 ± .06	
Ce	45.1 ± 2.7	1.26 ± .10	1.68 ± .08	.56 ± .05	
Mn	450 ± 16	1.03 ± .10	0.92 ± .10	.64 ± .06	
Eu	1.21 ± 0.15	1.27 ± 0.23	0.74 ± 0.19	0.60 ± 0.14	
Nd	15.7 ± 2.7	1.23 ± .25	1.22 ± .25	.58 ± .14	
La	25.7 ± 5.7	1.07 ± .34	1.76 ± .44	.61 ± .21	
Lu	0.55 ± 0.12	1.09 ± .21	1.47 ± .42	.42 ± .38	
Th	7.7 ± 1.8	1.00 ± .63	1.64 ± .47	.56 ± .50	
Yb	3.20 ± 0.21	1.26 ± 0.75	1.65 ± 0.65	0.21 ± 0.22	
Cr	17.0 ± 9.0	1.84 ± 1.06	0.61 ± .58	.29 ± .29	
Cs	3.9 ± 1.8	1.02 ± 0.48	1.02 ± .39	.51 ± .34	
Ba	837 ± 420	0.98 ± .59	0.99 ± .61	.26 ± .41	
Hf	6.0 ± 3.3	1.03 ± .64	1.90 ± 1.20	.37 ± .23	
Dy	5.7 ± 3.0	1.12 ± .77	1.43 ± 0.89	.51 ± .39	
Rb	39 ± 30	1.32 ± 1.35	1.80 ± 1.50	1.87 ± 1.77	
Tb	0.9 ± 0.9	0.89 ± 1.18	0.95 ± 0.39	0.40 ± 0.82	
Mean ratio, \bar{X}		1.18	1.26	0.58	
Coefficient of variation		16%	38%	56%	

^a Elemental abundances are in parts per million, except iron and sodium, which are in percent.
[†] Three standard deviations based on counting statistics.

Table 2. Activity ratios for two soil samples. Abbreviations: O.V.P., Ochoco View Point; \bar{X} , mean ratio; C.V., coefficient of variation.

Element	O.V.P. AC2/ Mazama I	Whisky Flat AC2/ Mazama I
Sm	0.85 ± 0.04*	0.73 ± 0.05*
Fe	.85 ± .05	1.01 ± .04
Sc	.80 ± .04	1.00 ± .04
Ta	.71 ± .07	0.72 ± .06
Na	.97 ± .09	.94 ± .09
Co	.86 ± .09	1.11 ± .09
Ce	1.15 ± .08	1.01 ± .08
Mn†	2.26 ± .20	1.57 ± .14
Eu	0.97 ± 0.23	0.91 ± 0.20
Nd	1.20 ± .23	.82 ± .16
La	1.22 ± .32	1.10 ± .23
Lu	0.85 ± .44	0.66 ± .26
Th	1.10 ± .32	1.01 ± .37
Yb	0.79 ± 0.49	0.83 ± 0.41
Cr	.89 ± .45	1.50 ± .76
Cs	.67 ± .48	0.88 ± .58
Ba	1.23 ± .96	.89 ± .65
Hf	0.52 ± .44	.84 ± .53
Dy	.87 ± .87	.77 ± .64
Rb	1.14 ± 1.25	1.09 ± 1.17
Tb	0.70 ± 1.28	0.47 ± 0.87
\bar{X}	0.92	0.91
C.V.	21%	23%

* Three standard deviations based on counting statistics. † The values for Mn are not included in mean and C.V.

are to be regarded as preliminary (Table 1). The first group of elements could be determined the most accurately and the last group was determined with the least accuracy. The precision of the results is estimated from counting statistics using three standard deviations. Refinements of technique in future analyses will include the use of a 30-cm³ Ge(Li) crystal rather than the 3.6-cm³ crystal with which these data were obtained. Use of a 30-cm³ crystal will considerably increase the precision of determinations.

Since the question we are dealing with concerns the ability to distinguish between different samples, the absolute levels are less important than relative differences. Activities of the nuclides in the different ash samples were compared with the activities found for

Table 3. Elements whose activity ratios are within three standard deviations of ratios for the known materials.

Source	Ochoco View Point AC2 horizon	Whisky Flat AC2 horizon
Mazama	Na, Co, Nd, La, Ce	Na*, Fe*, Sc*, Ce*, Eu, Co, La, Yb, Lu
Newberry Crater	Nd, La, Ce	La, Yb
Glacier Peak	Co	Lu

* Ratios for these elements are within the range for layer I. Other elements listed under "Mazama" have ratios within the ranges of both Mazama layer I and layer II.

Mazama (I) by using the ratio $[A^o(x)]$ for sample of unknown/ $[A^o(x)]$ for Mazama (I), where $A^o(x)$ is the counts per minute per gram of sample for the nuclide formed from element x (Table 1). For Mazama (I) samples, the activity ratio for a given element should be 1 by definition. The mean ratio for all elements in the sample should also be 1 and the coefficient of variation should be low (12). Low coefficients of variation (based upon all activity ratios) are a measure of the similarity to Mazama (I). Relative to Mazama layer I, the elemental abundances generally were higher in samples from Mazama layer II, mean ratio 1.18, and Newberry, mean ratio 1.26. The Glacier Peak sample yields much lower activity ratios with a mean value of 0.58. The coefficient of variation for Mazama II (16 percent) contrasts with Newberry (38 percent) and Glacier Peak (56 percent) as expected for samples unrelated to Mazama. Although the mean ratios and coefficients of variation are informative, the ratios for individual elements are of interest. The compositions of particular elements are expected to be of use for discrimination. Relative to Mazama (I), the Newberry sample is significantly higher in Sm, Ta, Na, Ce, La, and Th; it is lower in Fe, Sc, and Co. Contents of most elements in the Glacier Peak sample are lower than for Mazama (I).

We desire to extend the findings obtained on coarse pumice of known origin to the identification of fine ash deposits of uncertain origin encountered at considerable distance from possible sources. An assessment of the technique was made by comparing the values of known materials with those from two ashy soils of uncertain origin. One soil developed from volcanic ash was sampled at Ochoco Viewpoint in the Ochoco National Forest, Crook County, Oregon (Sec. 28, T12S, R19E). Another soil was sampled at Whisky Flat in the Malheur National Forest, Grant County, Oregon (Sec. 20, T10S, R32E). Glassy fractions were isolated from 125- to 63- μ fractions of AC2 soil horizons and analyzed as previously described.

Activity ratios (relative to the Mazama I sample) for the Ochoco View Point and Whisky Flat soil samples averaged 0.92 and 0.91 with coefficients of variation of 21 and 23 percent, respectively (Table 2). The soil samples also were compared to the Newberry and Glacier Peak samples by calculation of appropriate activity ratios. Relative to Newberry, the Ochoco View-

point sample has a mean ratio of 0.87, but the coefficient of variation is 56 percent. The Whisky Flat sample has a mean ratio of 0.72, but the coefficient of variation is 75 percent. Relative to Glacier Peak, the Ochoco Viewpoint sample has a mean ratio of 1.94 and a coefficient of variation of 48 percent. The Whisky Flat sample has a mean ratio of 1.93 and a coefficient of variation of 54 percent.

Manganese was not included in the above averages since the enrichment of Mn is thought to result from MnO₂ coatings or concretionary forms in the soil. One of the soil samples was subsequently treated with sodium dithionite-citrate (11). This treatment yielded Mn contents in general agreement with the Mazama I sample. However, the addition of reagents to a sample always presents some chance of adding other contaminants to the system. Until these effects and purity of reagents are determined, we prefer to omit the analyses for Mn.

The activity ratios for some of the more accurately determined individual elements provide further information as to probable source of volcanic ash for the two soils (Table 3). More of the elements for the soil samples have ratios overlapping the ratios for Mazama than for Newberry or Glacier Peak. The data in Tables 2 and 3 strongly suggest Mazama as the source of volcanic ash for these soils.

The primary purpose of this study was to determine the potential usefulness of instrumental neutron activation analysis for distinguishing different volcanic materials. We conclude that neutron activation analysis is a very promising technique for the characterization of pumice from different sources and for the correlation of volcanic ash soils. Further refinements are necessary. Greater precision in counting statistics is desired. This should be obtained with other crystal detectors. For correlation work, it is necessary to have reliable estimates of confidence limits for elemental abundances in the different deposits. The data presented here are not necessarily intended to characterize the deposits. The confidence limits for a given material should include sampling and deposit variability as well as counting statistics.

ARTHUR A. THEISEN
GLENN A. BORCHARDT
MOYLE E. HARWARD
ROMAN A. SCHMITT

Oregon State University,
Corvallis 97331

References and Notes

1. I. S. Allison, *Fossil Lake Oregon: Its Geology and Fossil Faunas* (Oregon State Univ. Press, Corvallis, 1966).
2. R. Fryxell, *Science* **147**, 1288 (1965).
3. H. A. Powers and R. E. Wilcox, *ibid.* **144**, 1334 (1964).
4. V. C. Steen and R. Fryxell, *ibid.* **150**, 878 (1965).
5. G. K. Chamanske and S. C. Porter, *ibid.* **150**, 1022 (1965).
6. R. A. Schmitt, R. H. Smith, G. G. Goles, *J. Geophys. Res.* **70**, 2419 (1965).
7. G. E. Gordon, K. Randle, G. G. Goles, J. B. Corliss, M. H. Beeson, S. S. Oxley, *Geochim. Cosmochim. Acta* **32**, 369 (1968).
8. H. Williams, *Carnegie Inst. Wash. Publ.* **540** (1942).
9. The cooperation of Roald Fryxell in collecting the Glacier Peak sample is appreciated.
10. S. C. Choy and R. A. Schmitt, *Nature* **205**, 758 (1965).
11. M. L. Jackson, *Soil Chemical Analysis: Advanced Course* (Univ. of Wisconsin, Madison, published by the author, 1956).
12. Appreciation is expressed to R. G. Petersen, Oregon State University, for advice on statistical applications. Technical Paper No. 2439, Oregon Agricultural Experiment Station. Supported in part by AEC contract AT (45-1) 2062.

18 June 1968

■

Reprinted from *Science*

6 September 1968, Volume 161, pp. 1009-1011

Appendix II

Reprinted from the *Soil Science Society of America Proceedings*
Vol. 32, no. 5, September-October
677 South Segoe Road, Madison, Wisconsin 53711 USA

VESICULAR PORES OF PUMICE BY MERCURY INTRUSION¹

G. A. BORCHARDT, A. A. THEISEN, AND M. E. HARWARD²

Abstract

The pore size distribution of pumice was measured with a mercury intrusion porosimeter. Effects of particle to particle pores were minimized by use of separates based on size and density. Vesicular pores constituted about 98% of the fine porosity (<120 μ diameter) in 1-0.5 mm fractions of pumice. Average diameters of internal pores of pumice were found to be in the range of 3 to 7 μ . Distinctive curves were obtained for samples from Mt. Mazama, Glacier Peak, and Newberry Crater.

Additional Key Words for Indexing: Mt. Mazama pumice, Glacier Peak pumice, Newberry Crater pumice, Oregon, porosimeter, soils from volcanic ash.

SOILS DEVELOPED from pumice have unique physical (Cochran, Boersma, and Youngberg, 1967)³ and chemical properties (Chichester, 1967). To a large extent, these properties are related to the vesicular structure of the particles. Characterization of porosity of soils from volcanic ash is fundamental to ion exchange, diffusion, and translocation studies.

The objectives of the study reported here were to evaluate mercury intrusion for measurement of the vesicular pore size distribution of pumice, to develop the methods, and to obtain preliminary information on the characteristics of samples from different origins.

An Aminco-Winslow porosimeter (5,000 psi model) was used to measure vesicular pore size distribution with mercury penetration (Winslow and Shapiro, 1959). Data for whole samples of volcanic ash varied with particle size (Fig. 1). The average pore size of nonvesicular material is approximately one-fourth the average particle diame-

¹ Technical paper no. 2453, Oregon Agr. Exp. Sta. Corvallis. Supported in part by NSF Grant no. GA 1355. Received Mar. 21, 1968. Approved May 24, 1968.

² Graduate Assistant, Assistant Professor and Professor, Oregon State University, respectively.

³ Appreciation is expressed to L. Boersma for initial discussions and providing data which demonstrated the potential usefulness of Hg intrusion for study of pores in soils from pumice.

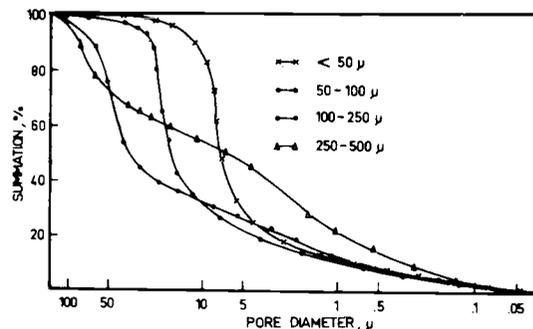


Fig. 1—Pore size distribution curves (volume percentage of measurable pores vs pore diameter) from various size fractions obtained from Mt. Mazama ejecta.

(Groton and Frazer, 1935; Klock, 1968). The pore-size distribution curves in Fig. 1 indicate that to a large extent normal particle-to-particle pores were being measured for fractions less than 250 μ in diameter. The average particle size of the 50-100 μ sample was about 75 μ and the observed average pore diameter was about 19 μ , one-fourth the particle diameter. However, the 250-500 μ fraction had a large percentage of very small pores, more than would be expected from particle-to-particle effects. The pore-size characteristics are due therefore to the combined effects of particle-to-particle pores and the internal pores of the vesicular particle. The type of system under investigation is illustrated in Fig. 2.⁴ As the particle size decreases, the relative contribution of the particle-to-particle pores increases and the contribution of vesicular pores decreases. The maximum pore aperture that can be measured with the mercury porosimeter is 200 μ . By using particles with diameters about 4 times this value the effects of particle-to-particle pores can be minimized.

The pore-size distributions of 1-0.5 mm samples of granitic sand and pumice were compared (Fig. 3). Only 0.02 cc Hg was intruded into 1 g of the granitic sand

⁴Microscopic examination of Hg-intruded pumice revealed parallel tubular pores. Unpublished data. W. H. Doak, Soils Department, Oregon State University.

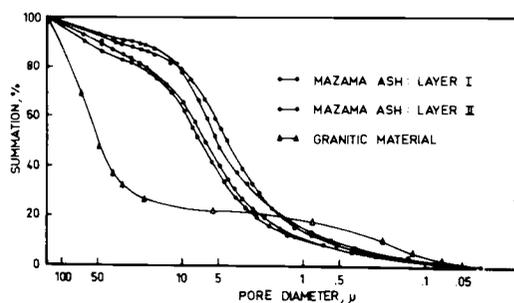


Fig. 3—Pore size distribution curves (volume percentage of measurable pores vs pore diameter) for samples from two sites and two different layers of Mt. Mazama pumice compared to granitic material. (1.0-0.5 mm fraction).

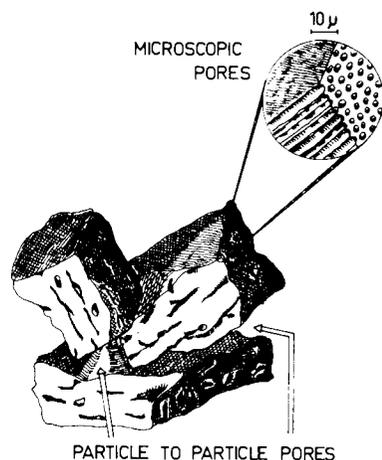


Fig. 2—Schematic drawing of pumice fragments depicting the types of pores found in pumice.

whereas about 1.00 cc Hg was intruded into 1 g of Mazama pumice. The particle-to-particle porosity in this size range therefore amounts to only 2%. The remainder of the study was confined to analyses using this size fraction.

Data shown in Fig. 3 for the Mazama ash are for samples from two locations sampled by different people. One site was on the Antelope Unit, 60 km from the source (Chichester, 1967) and the other was at China Hat, 123 km from the source. At these locations, two textural layers can be distinguished. Two points are worthy of note. First, the agreement between data for samples of the same layer is good even though different locations and sampling were involved. This suggests low variability in analyses and in the deposit. Second, the samples from the two layers appear to have different pore size distributions. The difference between layers was greater than differences between locations. The trace element composition for samples of the two layers appeared to be different as well (Theisen et al. 1968). Work is in progress to ascertain the significance of the two layers.

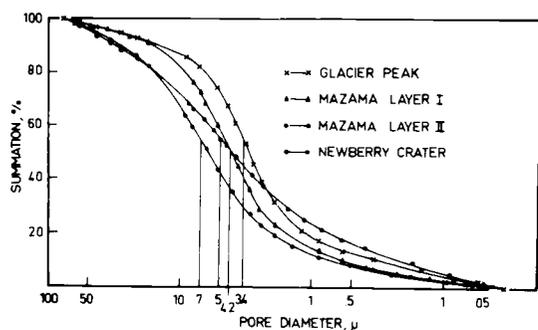


Fig. 4—Pore size distribution curves (volume percentage of measurable pores vs pore diameter) for samples of pumice from various sources separated on the basis of size (1.0–0.5 mm) and specific gravity ($\rho < 1.6$ g/cc).

Deposits of volcanic ejecta contain varying proportions of primary minerals. This arises from sorting of heavier minerals over distance and from contamination by non-pyroclastic materials. It was reasoned that inclusion of primary minerals in the sample would contribute to variability. The techniques were modified by separation of porous components from non-porous mineral grains by flotation in carbon tetrachloride ($\rho = 1.6$ g/cc). The remainder of data reported were obtained in this manner.

The type and amount of vesicular pores in pumice supposedly depend upon gas pressure and viscosity in the magma at the time of eruption (Williams, 1942). It is therefore likely that pumice ejected from different volcanoes will have different vesicular pore-size distributions. This was investigated and pumice samples from different sources exhibited distinguishing pore size distribution curves (Fig. 4). The average vesicular pore diameter for Glacier Peak pumice³ was 3.4μ . For Mazama pumice, layer I, the value was 4.2μ and for layer II the value was 7.0μ . The Newberry Crater pumice had an average pore size of 5.0μ , but the pore size distribution curve was distinctly flatter reflecting a wider range of pore sizes. Ejecta from Newberry Crater is restricted to a much smaller area than that from the more violent eruptions of Mt. Mazama and Glacier Peak. Vesicular pore size distribution curves thus appear to be useful for distinguishing between volcanic ashes of different origins. A sampling study designed to evaluate the variability of the deposits and to establish confidence limits is in progress.

The observed range and relatively small size of vesicular pores in pumice is expected to be significant in moisture movement, salt trapping, ion exchange, leaching, and clay mineral formation.

³ Collected from the lower Grand Coulee in Washington and supplied through the courtesy of Roald Fryxell, Washington State University.

Literature Cited

- Chichester, F. W. 1967. Clay mineralogy and related chemical properties of soils formed on Mazama pumice. Ph.D. thesis, Corvallis, Oregon State University. 152 numb. leaves. Diss. Abstr. 27:3749B.
- Cochran, P. H., L. Boersma, and C. T. Youngberg. 1967. Thermal properties of a pumice soil. Soil Sci. Soc. Amer. Proc. 31:454–459.
- Groton, L. L., and H. Frazer. 1935. Systematic packing of spheres with relation to porosity and permeability. J. Geol. 13:785–909.
- Klock, G. O. 1968. Pore size distributions as measured by the mercury intrusion method and their use in predicting permeability. Ph.D. thesis, Corvallis, Oregon State University. 91 numb. leaves. Diss. Abstr., Vol. 8, No. 12.
- Theisen, A. A., G. A. Borchardt, M. E. Harward and R. A. Schmitt. 1968. Neutron activation analysis of Cascade range pyroclastics (submitted to Science).
- Williams, H. 1942. The geology of Crater Lake National Park, Oregon. Carnegie Institute of Washington, Publication no. 540. 162 p.
- Winslow, N. M., and J. J. Shapiro. 1959. An instrument for the measurement of pore-size distribution by mercury penetration. ASTM Bulletin, Feb., 39–44.

APPENDIX III

SEPARATION OF GLASS FROM VOLCANIC ASH

Procedure:

1. Clean samples of ash with the ultrasonic vibrator to remove less than 63μ particles from the surface of the 125- 63μ fraction, to float off organic matter, and to break up aggregates of finer particles.
 - A. Wash 40 ml. (10 cm. long) tubes in 0.1N HNO_3 (50 ml. conc. HNO_3 per two liters double distilled water).
 - B. Place 125- 63μ fraction in tube, add water, and place in ultrasonic vibrator (Disintegrater System 40) using a wire basket for support.
 - C. After convection currents stop, allow particles to settle for at least 2.5 sec. per cm.
 - D. Discard suspended particles and floating organic matter.
 - E. Repeat steps B through D until suspension is clear.
2. If the percent glass is to be determined weigh after heating at 110°C . Place oven dried whole sample of 125- 63μ volcanic ash into 20 ml heavy-walled Sorvall test tube.
3. Add 3.0 ml bromobenzene (high purity) and 3.25 ml bromoform to the test tube with a graduated pipette to get a solution of density 2.2 g/cc.

4. Place tube in desiccator and use aspirator to remove air from desiccator and consequently from the sample. The pressure should be about five psi and the evacuation should last for about 15 minutes. Loss of heavy liquids on evaporation was 0.02 ml/day/cm² in air and 0.02 ml/hr/cm² when the sample was in the aspirated desiccator.
5. Cap tube with cap from two dram polyvial, shake, and centrifuge at about 700 rpm for one minute. Then shake to get crystals remaining on sides of tube into the upper part of the suspension.
6. Repeat step five two times, centrifuge the last time for five minutes, and remove the organic matter occurring in the floating fraction ($\rho < 2.2 \text{ g/cc}$) by sieving the suspension on a 63 μ sieve.
7. Add 2.42 ml bromoform and repeat step five two or three times. The density of the heavy liquid will be 2.40 g/cc if transfer loss during the previous sieving has been insignificant.
8. Place in -10^oF freezer overnite or freeze in dry ice and acetone bath. The top part of the suspension does not freeze.
9. Pour floating material (< 2.4 g/cc) into 63 μ sieve and save the bromoform-bromobenzene solution for redistillation.
10. Wash the glassy fraction on the sieve first with ethanol and then acetone. Dry from acetone in air or at a temperature no higher

than 49°C . Weigh sample after 110°C heating for percent glass determination.

11. Place tube in warm water to melt bottom half of suspension, sieve, and discard the fraction greater than 2.4 g/cc .

APPENDIX IV

SAMPLE SITE DESCRIPTIONS

PARKDALE LOAM: Site 11

Sampled 10-13-66, by A. A. Theisen, G. A. Borchardt, and E. G. Knox.
Hood River County, Oregon, Hood River area, center of S 1/2, NE 1/4, sec. 29, T1N, R10E; about 1 1/2 miles north of Parkdale, in brushy area east of road and west of railroad, 50 feet east of road from point 100 feet north of slight bend which is about 300 feet north of intersection. About 1480 feet elevation, 2% N slope, well drained soil from apparently water-transported ash, on undulating valley floor. Vegetation of dogwood, vine maple, willow, hazel, strawberry, and other herbs.

Soil Profile (depths in cm):

01 and 02	Fresh to decomposed leaves.
2-0	
A1	Dark brown (7.5YR 3/2) loam, brown (10YR 5/3) dry; moderate very fine granular structure; soft, nonplastic, nonsticky; abundant roots;
0-12	abundant interstitial pores; 5% 1 to 5 mm, very hard aggregates; boundary clear, smooth.
(11-I)	
AC	Dark brown (7.5YR 3/4) loam, yellowish brown (10YR 5/4) dry; moderate very fine granular structure; soft, nonplastic, nonsticky; abundant roots;
12-43	abundant interstitial pores; boundary gradual.
(11-II)	
C	Dark brown (7.5YR 4/4) loam, yellowish brown (10YR 5/4) dry; weak very fine granular structure; soft with some chunks slightly hard and brittle,
43-70+	nonplastic, nonsticky; common roots; abundant interstitial pores.
(11-III)	

GLOWING AVALANCHE: Site 24

Sampled 10-27-66 by A. A. Theisen, G. A. Borchardt, and C. T. Youngberg.
Klamath County, Oregon, NW 1/4, SW 1/4, sec. 16, T28S, R8E; about 6 miles south of Chemult, from road cut, about 1/2 mile east of Diamond Lake Siding.
Samples taken from 60 to 90 cm.

24-I	Excludes large pieces of pumice.
24-II	Consists of large pieces of pumice.

PUMICE FLAT: Site 34

Sampled 7-17-67 by A. A. Theisen, G. A. Borchardt, J. Moore, and C. T. Youngberg.
Klamath County, Oregon, NE 1/4, sec. 16, T26S, R10E; Pumice Flat.
The sample (34-I) consists of pumice fragments from the surface in an area with no vegetation, in an opening in lodgepole pine and ponderosa pine forest.

SIMPSON PLACE (Last Chance Bog): Site 41

Sampled 10-10-67 by A. A. Theisen, J. A. Norgren, and M. E. Harward.
 Wheeler County, Oregon, Ochoco area, between SW 1/4 and NW 1/4, sec. 32, T12S, R21E;
 from bog south of road, about 1/4 mile east of National Forest boundary, east of Simpson Place.
 About 5400 feet elevation, bog has no apparent inflowing or outflowing stream, drainage area
 probably less than 50 acres.

Section (near sample pits, depths in cm):

0-51	Mucky peat
51-118	Fibrous peat
118-150	Ash (41-I, II, III, IV, V)
150+	Peat

The peat layers were thinner in the section that was sampled.

ANTHONY LAKES MEADOW: Site 42

Sampled 10-12-67 by A. A. Theisen, J. A. Norgren, and M. E. Harward.
 Union County, Oregon, Anthony Lakes area, SE 1/4, sec. 7, T7S, R37E; at southwest side of bog
 east of Mud Lake, 200 feet north of F. S. road S73.
 About 5100 feet elevation, bog on bench above Mud Lake, drainage area probably less than 50
 acres, no apparent inflowing stream.

Section (depths in cm):

0-51	Peat
51-69	Upper ash (42-I, II)
69-196	Peat
196-206	Lower ash (42-III)
206+	Clay, unoxidized.

HURRICANE CREEK: Site 43

Sampled 10-13-67, by A. A. Theisen, J. A. Norgren, and M. E. Harward.
 Wallowa County, Oregon, Enterprise area, SE 1/4, SW 1/4, sec. 13, T2S, R44E; north of road,
 Cruikshank property, about midway between Enterprise and Joseph.
 About 3900 feet elevation, large bog in glacial outwash channel and on stream flood plain.

Section (depths in cm):

0-122	Peat
122-127	Upper ash (43-I)
127-208	Peat and mineral matter

208-226	Lower ash (43-II, III)
226-241	Peat and mineral matter
241-254	Gravel

TOLLGATE SUMMIT: Site 44

Sampled 10-13-67 by A. A. Theisen, J. A. Norgren, and M. E. Harward.
Union County, Oregon, Tollgate area, NE 1/4, NE 1/4, sec. 34, T3N, R38E; west of Oregon Highway 204, 0.2 miles south of junction with Black Mountain road, at S end of elongated north-south bog area.

About 5040 feet elevation, bog at the head of a drainage way on a broad drainage divide.

Section (depths in cm):

0-69	Peat
69-104	Ash (44-I, II)
104-168	Clay, unoxidized

DEVILS HILL: Site 67

Sampled on 8-3-68 by G. A. and M. R. Borchardt.

Century Drive Highway east of road at Trail No. 20.

Irregular layer about 10 cm thick over Mazama soil. Sample appears to be representative of natural particle size distribution, but it may contain other rocks.

STAGE GULCH: Site 95

Sampled on 9-19-68 by M. J. Dudas, J. A. Norgren, and M. E. Harward.
Sec. 6, T3N, R31E.

0-43 cm Loess

Upper ash (95-I), coarse

A layer of loess separates this from a finer silty ash which is greater than 6 meters thick.

SQUAW CREEK: Site 97

Sampled on 9-24-68 by W. H. Doak, M. J. Dudas, and M. E. Harward.

Along F. S. road 2823 near sec. line 4-9, T31S, R14E.

Alluvial fan which may be older ash, and is cemented.

128-152 cm Coarse layer (97-I)

178-203 cm Fine layer (97-II)

STEPTOE CANYON: Sites 26 and 27

Sampled by M. E. Harward, A. A. Theisen, E. G. Knox, and R. Fryxell.
Steptoe Canyon, Washington.

Mazama ash (26-1) was sampled on the upstream side of an alluvial fan. Same site as site No. 65-S-36 of Czamanski and Porter (1965).

Glacier Peak (27-1) ash was much thinner and occurred in small pockets on the downstream side of the fan where it was sampled.

APPENDIX V

TABLE AI. PERCENT GLASS IN VOLCANIC ASH SAMPLES.

INAA No.	Site Name	Site and Sample Number	Horizon	Percent Glass *
GROUND LUMP PUMICE				
256	Huckleberry Spring	62-3	AC	66
257	Huckleberry Spring	62-5	C1	82
274	Huckleberry Spring	62-6	C1	85
275	Huckleberry Spring	62-7	C1	78
276	Huckleberry Spring	62-10	C2	79
277	Huckleberry Spring	62-13	C2	77
278	Huckleberry Spring	62-16	C2	85
279	Huckleberry Spring	62-19	C2	84
280	Huckleberry Spring	62-22	C2	82
Average of Huckleberry Spring C Horizons				82
285	Huckleberry Spring (dark grey pumice) ***	62-10B	C2	72
206	Antelope Unit	35-3	C1	84
207	Walker Rim	WRC1	C1	86
209	Royce Mountain	RMC1	C1	83
247	Pumice Flat	34-1	C	80
245	Glowing Avalanche	24-2	C	63
242	China Hat (Newberry)	23-1	C	95+
243	N. Sugarloaf (Glacier Peak)	46-4	C	30
303	South Camp (St. Helens Y)	70-1		33
305	Devils Hill (Devils Hill pumice)	67-1	C	78
320	Lakebeds Meadow (St. Helens Y)	91-2		40
326	Sycan Marsh	94-1		79
327	Sycan Marsh	94-2		80
328	Sycan Marsh	94-3		81

A1 (Continued)

INAA No.	Site Name	Site and Sample Number	Horizon	Percent Glass *
329	Squaw Creek	97-1		98
330	Squaw Creek	97-2		98
FINE ASH (125-63 μ very fine sand)				
258	South Ice Cave	37-1	AC	24
248	South Ice Cave	37-2	C1	24
249	South Ice Cave	37-3	C2	8
259	South Ochoco Butte	50-1	A1	28
260	South Ochoco Butte	50-2	AC	25
250	South Ochoco Butte	50-3	C1	29
251	South Ochoco Butte	50-4	C2	40**
261	Day Creek	49-1	A1	38
262	Day Creek	49-2	AC	33
252	Day Creek	49-3	C1	46
253	Day Creek	49-4	C2	59**
263	Dick Spring	47-1	A1	27
254	Dick Spring	47-2	AC	38
255	Dick Spring	47-3	C	72**
265	Parkdale (after Fe removal, <2.6g/cc)	11-3	C	19
234	Steptoe Canyon	26-1		48
244	Steptoe Canyon (Glacier Peak)	27-1		36
301	Marine Sediment	N-377		40
302	Marine Sediment	N-378		12
316	Waha Soil	77-1		33
317	Lakebeds Meadow	93-2		79
319	Lakebeds Meadow	91-1		18
321	Stage Gulch	95-1		33
322	Bald Mountain Saddle	96-1		17
323	Olinger Meadow	78-1		28
324	Olinger Meadow	78-2		98
325	Olinger Meadow	78-3		18

A1 (Continued)

INAA No.	Site Name	Site and Sample Number	Horizon	Percent Glass *
COARSE SILT (53-20 μ)				
346	Marine Sediment	N-54		63
347	Marine Sediment	N-277		56

* % glass=material floating on 2.4 g/cc bromoform-bromobenzene.

** Unweathered C horizons.

*** Eight percent of the 16-8 mm fraction of sample 62-10B was dark grey pumice. This was hand picked and treated like the other pumice samples.

APPENDIX VI

Table A2. CONCENTRATIONS OF MONITORS AND GAMMA-RAY PEAKS USED FOR CALCULATION OF ABUNDANCES *

Element	Gamma-ray energy:**	Conc. ($\mu\text{g/ml}$)	OSU Identification	Product Nuclide
Sodium	1368	1025.	Std III NaNO_3	^{24}Na
Rubidium	1077	5000.	Car I RbNO_3	^{86}Rb
Cesium	796	100.	Std IV CsNO_3	^{134}Cs
Barium	496	10060.	Car II $\text{Ba}(\text{NO}_3)_2$	^{131}Ba
Lanthanum	1596	45.6	Std III $\text{La}(\text{NO}_3)_3$	^{140}La
Cerium	145***	998.	Std II $\text{Ce}(\text{NO}_3)_2$	^{141}Ce
Neodymium	91	1000.	Car III $\text{Nd}(\text{NO}_3)_3$	^{147}Nd
Samarium	103	10.01	Std III $\text{Sm}(\text{NO}_3)_3$	^{153}Sm
Europium	1408	.974	Std II $\text{Eu}(\text{NO}_3)_3$	^{152}Eu
Terbium	966***	98.8	Std II $\text{Tb}(\text{NO}_3)_3$	^{160}Tb
Ytterbium	63	102.	Std II $\text{Tb}(\text{NO}_3)_3$	^{169}Yb
Lutetium	208	96.7	Std III $\text{Lu}(\text{NO}_3)_3$	^{177}Lu
Thorium (Pa)	312***	100.	Std IV $\text{Th}(\text{NO}_3)_4$	^{233}Pa
Hafnium	133	100.	Std III HfOCl_2	^{181}Hf
Tantalum	68	99.5	Std II $\text{Ta}(\text{F}, \text{NO}_3)$	^{182}Ta
Cobalt	1332	100.	Std IV $\text{Co}(\text{NO}_3)_2$	^{60}Co
Iron	1100	211400.	Spex Fe_2O_3 #1232	^{59}Fe
Scandium	1120	9.73	Std II $\text{Sc}(\text{NO}_3)_3$	^{46}Sc
Chromium	320	956.	Std III CrCl_3	^{51}Cr

* The preparation and standardization of many of these monitors was done by Drs. R. A. Schmitt and T. A. Linn.

** kev

*** Contributions of nuclides of Fe, Eu, and Yb have been subtracted by using the ratios calculated from 1202, 1408, and 63 kev gamma-ray peaks, respectively.

APPENDIX VII

TABLE A3. MICROSCOPIC OBSERVATIONS ON GLASS SEPARATES USED FOR INAAC.

INAA No.	Site*	Percent Crystal	Percent OM	Comments**
206	35-4 AU (M)	3.0	0	Some lg. crystals w/o glass, grey
207	WRC1 (M)	1.1	0	Slightly weathered, brownish tinge
208	WRC2 (M)	0.5	0	Grey, slightly oxidized
209	RMC1 (M)	2.0	0	Slightly weathered, brownish
210	RMC2 (M)	2.3	0	Grey, crystals in glass
211	39-1 WB (N)	0.2	0	Grey, many bubbles, differs from Mazama in appearance
212	45-6 PC (G)	8.0	0	Fine crystals in glass, grey
213	51-1 R (Y)	3.3	0	Grey, many very small bubbles and crystals in glass
214	56-1 MSH (W)	2.5	0	Same as 213
215	35-3 AU	3.8	0	Grey, unweathered, tubular pores
216	35-3 AU (M)	2.2	0	Same as 215
217	35-4 AU, -Fe	2.0	0.8	OM present, glass bleached
218	8-2 WF, -Fe	2.0	5.0	Fe coatings removed, much devit.
219	35-3, AU, wh	25.0	0	Many different size crystals
223	41-1 SP	2.4	1.5	Devit., weat., Fe stains
224	41-5 SP	2.5	0.3	No devit., weat. biotite?
225	42-2 AL	1.1	0.1	No devit., grey
226	42-2 AL	1.5	0.1	Weat., devit., Fe stains
227	42-3 AL	4.7	0.1	Many small crystals in glass
228	43-1 HC	7.0	7.6	Weathered, many crystals
229	43-2 HC	2.1	0.7	Slightly devit., brownish
230	43-3 HC	1.9	0.6	No devit., grey-brown
231	44-1 TS	1.7	0.1	Slightly devit., grey-brown
232	44-2 TS	1.8	0.1	No devit., grey, unweat.
233	40-1 E	2.5	0.6	Slightly devit.
234	26-1 SC	1.5	0	Grey, unweat.
235	55-1 KBC	2.5	0	Grey, sl. devit., Mazama?

A3 (Continued)

INAA No.	Site	Percent Crystal	Percent OM	Comments
236	61-1 R (T)	6.0	1.0	Sl. weat., inclusions, many bubbles, different
237	60-1 MSH (T)	1.5	0	Grey, bubbles, like 236
238	59-1 LK (W)	2.0	1.0	Equidimensional, fine bubbles and inclusions
239	58-1 CM (W)	4.0	9.0	High OM, inc. and bubbles
240	52-1 L (Y)	6.3	0.2	Sl. devit., equi. crystals all in glass
241	38-1 PB (N)	0.3	0	Grey, very clean
242	23-1 CH (N)	0.3	0	Same as 241
243	46-4 NS (G)	10.0	0.5	Fe stains, many crystal inc.
244	27-1 SC (G)	17.0	0.3	Devit., low Fe stains, like 243 otherwise
245	24-2 GA	8.0	0.3	Hematite present
246	11-3 P	4.0	15.0	V. highly weat., red coatings, high OM
247	34-1 PF	3.5	0	Grey, no OM
248	37-2 SIC	4.5	2.0	Devit., many crystal inclusions
249	37-3 SIC	2.0	1.0	Devit., Fe oxid.
250	50-3 SOB	7.1	5.4	Devit., inc., like 248
251	50-4 SOB	3.0	4.0	Devit., inc., Fe stains
252	49-3 DC	3.0	1.0	Similar to 251
253	49-4 DC	5.0	0.3	Devit. less than 252
254	47-2 DS	6.0	7.0	Devit., Fe stains
255	47-3 DS	3.0	0.3	Low devit. and low Fe staining
256	62-3 HS	3.0	0	Sl. devit., sl. Fe staining
258	37-1 SIC	3.0	1.0	High devit., many inc., Fe st.
259	50-1 SOB	3.0	3.1	Weathered
260	50-2 SOB	1.5	3.0	Weathered
261	49-1 DC	2.0	1.0	Same as 260, low OM
262	49-2 DC	1.5	1.0	Same as 261
263	47-1 DS	1.0	4.0	Similar but shorter, more round crystals, higher OM
265	11-3 P	25.0	2.0	(-Fe), high devit., high Fe oxid.
274	62-6 HS	3.0	0	Grey, devit. low, Fe staining
276	62-10 HS	2.2	0	V. sl. devit., no Fe stains

A3 (Continued)

INAA No.	Site	Percent Crystal	Percent OM	Comments
279	62-19 HS	3.5	0	Devit. low as above
285	62-10B HS	5.0	0	More devit., sl. oxid., lg. crystals, equi. glass
301	N-377 MS	12.0	0	Glass like Mazama, Biotite?
302	N-378 MS	7.9	0	Like 301, brown glass
303	70-2 SC	4.7	0	Not Maz., unweathered, no. of bubbles, red shards
305	67-1 DH	3.1	0	Shape between Mazama and Y
316	77-1 WS	2.5	0.2	High devit., few Fe stains
317	93-1 LBM	8.7	0	Unweat., many bub., many crystal inc.
318	93-2 LBM	7.5	0.5	Fe stains, weat., devit., many inc., biotite rare
319	91-1 LBM	25.0	0	Unweat., Fe stains, many lg. crystals
320	91-2 LBM	20.2	0.2	Similar to 319
321	95-1 SG	5.0	0	Looks like Mazama, tubular pores, few bubbles
322	96-1 BMS	13.5	4.5	Fe stains, high devit., red shards, 1% diatoms
323	78-1 OM	5.5	0	High devit., Fe stains, 18% diatoms
324	78-2 OM	17.2	1.0	Weat., devit., many small crystal inc., like 246
325	78-3 OM	10.0	1.0	High devit., Fe stains, red shards, crystal inc. 0.3% diatoms
326	94-1 SM	1.5	0	Unweathered
327	94-2 SM	2.0	0	Like 326
328	94-3 SM	1.0	0	Like 326
329	97-1 SC	1.0	0	Unweat., tubular pores, few bubbles
330	97-2 SC	0.7	0.2	Like 329
346	N-54 MS	3.0	0	Unweat., undevitrified
347	N-277 MS	3.0	0	Like 346

* Site and sample numbers including letter designations representing the beginning letters of words in site names found in Table A1 and in tables in the text describing the samples. Letters in parentheses represent the standard ash layers as follows: M=Mazama, N=Newberry, G=Glacier Peak, Y=St. Helens Y, W=St. Helens W, and T=St. Helens T. Wh=Whole sample, -Fe=treated to remove iron.

** Rough approximations of crystal and organic matter estimated by counting the crystals and organic particles in a field of about 300 particles. Abbreviations are: sl=slightly, devit=devitrification, OM=organic matter residue, Fe=iron, oxid=oxidation, weat=weathered, inc=inclusions, v=very, bub=bubbles, lg=large, equi=equidimensional.

APPENDIX VIII

PREPARATION OF VOLCANIC ASH SAMPLES

Bog Samples

Samples were taken from vertical sections representative of the particular layer. The outside particles (about 1 cm) were scraped off with a small stainless steel spatula and discarded. The sample was then scraped into a 125 μ and 63 μ sieve nest and placed in a shaker for 5-10 minutes to complete the sieving. Noncoherent samples were mixed in a plastic bag and then sampled by pouring into the sieve. The sieves were washed with acetone on the ultrasonic vibrator (Disintegrater System 40) after the preparation of each sample.

Pumice Lumps

When samples of ash contained lumps of pumice, these were considered to be the best available material for trace element analysis. At least ten lumps greater than 2 mm in diameter were crushed in a diamonite mortar and pestle to pass a 125 μ sieve. The mortar and pestle were cleaned with acetone and Kimwipe after grinding each sample. The Sycan Marsh pumice samples were scrubbed with ultrasonic vibration (Biosonic III) for five minutes at 100 kilocycles per sec. to remove organic and iron oxide stains.

Fine Ash Samples

Air dried soil samples and ash collected in alluvial fans were sieved directly as for the bog samples. Care was taken to clean all equipment with double distilled water and acetone. The A1 soil horizon samples received the additional separation at a density of 2.2 g/cc. Samples 317, 319, 320, and 323 contained large amounts of organic matter. These were the only samples to receive the following treatment. The samples were washed twice with 0.025 N HNO₃ in a 20 ml centrifuge tube. A few ml of 0.025 N HNO₃ and a few drops of H₂O₂ (containing less than 2.5 ppm PO₄) were added. The tube and sample were warmed in a hot water bath until the dark color of the organic matter disappeared. The sample was washed with double distilled water and centrifuged for two minutes at 750 rpm. The cloudy supernatant was discarded.

Samples 322 and 325 were obtained by floatation with heavy liquid of density 2.5 g/cc. Sample 316 would not float even at this density. Therefore it was obtained by removing the lighter colored upper part of the sediment after centrifugation at a liquid density of 2.5 g/cc.

Insignificant amounts of sand size particles were obtained from marine ash samples N-54 and N-277 so a separation was made by gravity sedimentation in distilled water to obtain a 53-20 μ fraction (samples 346 and 347).

APPENDIX IX

DISPERSION OF CLAY WITH AMMONIUM HYDROXIDE

This procedure was used because NH_4OH was the only reagent that would disperse the clays without contributing elements that would interfere with INAA. Sample 313 would not disperse during the procedure. It was obtained by alternate washes of 0.05 N HNO_3 and water.

One hundred gram samples of air dried soil (< 2mm diameter) were placed in clean two liter beakers (cleaned with HNO_3 , acetone, and double distilled water). Prior to NH_4OH treatment sample 37-1 which was very coarse, was ground to pass through a 500 μ sieve to get clay from the pores. The soils were acidified with a few ml. of 0.05 N HNO_3 . H_2O_2 (<2.5 ppm PO_4) was added to the soils while they were being heated on a hot plate until the dark color resulting from the organic matter disappeared. One percent (0.23 N) NH_4OH (15 ml. conc. $\text{NH}_4\text{OH}/1. \text{H}_2\text{O}$) was then used to transfer clay samples to clean plastic bottles for centrifugation. Dispersion of the clay occurred on all samples after the second NH_4OH wash. Washings were repeated 5-10 times with 125 ml of 1% NH_4OH solution. Clay suspensions were stored in two liter plastic bottles. Upon completion of the separations, 30 ml of conc. HNO_3 was added to neutralize each two liters of suspension. After mixing, a few ml. of conc.

NH_4OH was added until flocculation occurred (pH 6 to 8).

The next day, the clear supernatant was siphoned off with a clean glass tube. The samples were transferred to Nalgene wide mouth bottles, centrifuged, and then washed five times with acetone followed by drying at 49°C .

APPENDIX X

CLAY PRETREATMENTS

NH₄NO₃ Displacement of Exchangeable Cations (samples 282, 288)

These samples were washed five times with 20 ml of 1 N NH₄NO₃ (Specpure grade), five times with acetone, and then dried at 49°C.

HNO₃ Displacement of Hydroxylated Cations (samples 264, 283, 286, 287)

These samples were washed three times with 0.05 N HNO₃. As dispersion began to occur, washings were completed using a high speed centrifuge (7000 rpm) for ten minutes. Samples were washed five times with acetone followed by drying at 49°C.

Removal of Free Iron Oxides (samples 281, 284, 265)

Sodium citrate and sodium bicarbonate (Reagent grade) were used with a fresh bottle of Reagent grade dithionite for iron removal treatment (Jackson, 1956). Samples were then washed twice with sodium citrate, three times with 0.05 N HNO₃, and five times with acetone before drying at 49°C. Sample 265 was cleaned by ultrasonic vibration (Disintegrater System 40) instead of centrifuging since it

was a very fine sand. Much silt and organic matter was removed from this sample by the treatment.

Removal of Amorphous Material (samples 289, 290)

Samples dried from acetone at 49°C followed by 110°C to get the basic weight, were shaken with water for 15 minutes. An iron removal treatment was given as previously described for other clay samples. Potassium hydroxide (0.5 N) was prepared from Reagent grade B&A pellets and double distilled water. The Day Creek clay (sample 289) was added to seven liters of boiling KOH in a stainless steel beaker. Five liters of KOH was used for the Parkdale clay. The supernatant was siphoned off after the samples cooled and settled for eight hours. The boiling KOH treatment was repeated, followed by another iron removal. Samples were then washed twice with sodium citrate, three times with 0.05 N HNO₃, five times with acetone, and dried at 49°C.

Table A4. Results of amorphous material removal.

INAA No.	Sample	Basic Weight (g)	% Residue	% Amorphous
289	Day Creek clay (49-2)	5.506	18.2	81.8
290	Parkdale clay (11-2)	3.278	19.9	80.1

APPENDIX XI

*SPECTRA

A Computer Program for the Analysis of Gamma-Ray Spectra

I. General Description

This program accepts gamma-ray energy spectra and determines peak locations, peak areas, and elemental abundances. This is done first for a set of standard spectra and then for unknown samples. The peaks found in the unknown sample are matched against the standards previously determined to identify the isotopes present in the unknown sample and their abundances.

The program has facilities for correcting interferences and for smoothing of the original data if desired.

II. MethodA. γ -ray calibration

1. Five photopeak locations (specified by the user) together with five corresponding γ -ray energies are read.
2. Using successive pairs of energies, four linear equations are determined from which four spectral regions are calibrated.

B. A spectrum is read in for analysis.

C. If user options, the data is edited to correct for instrumental errors.

D. If user options, the spectrum is smoothed using the method described by Savitzky and Golay [Analytical Chemistry, Vol. 36, No. 8, July 1964, pp. 1627-1639].

E. Photopeaks are located by the following method:

1. Let X_i be the count rate in channel i .

Let X_{i+1} be the count rate in channel $i+1$.

Etc.

*Major contributions to the development of this program were made by G. W. Hoagland, Computer Programmer, Department of Mathematics, and Dr. R. A. Schmitt, Associate Professor, Department of Chemistry.

2. $\Delta = (X_{i+1} - X_i)$
 3. $\Delta' = \sqrt{\frac{X_i + X_{i+1}}{2}}$
 4. Define: (+) to mean $\Delta > \Delta'$,
 (-) to mean $|\Delta| > \Delta'$ and $\Delta < 0$
 (0) to mean $|\Delta| < \Delta'$.
 5. A photopeak is determined when a condition of at least 2 (+)'s followed by one or no (0)'s followed by at least 2 (-)'s occurs. (Note: The number of (0)'s may be changed at the option of the user. See section pertaining to Spectrum-ID Card Parameters).
 6. When a peak is located, the left boundary channel (LBC), the peak channel (PCL), and the right boundary channel (RBC), are tabulated. The (LBC) and (RBC) are then adjusted to the "true" boundaries of the peak as described in Appendix B.
 7. If the user options to apply Covell's method, the peaks are examined for special cases.
 - a. If two photopeaks are separated by less than three successive Δ where $|\Delta| < \Delta'$, and the first photopeak (PCL) is followed by at least four $\Delta < 0$, then Covell's method will be used in calculating Peak area.
 - b. If the first photopeak (PCL) is followed by less than four $\Delta < 0$, we tabulate (PCL) only and make no area calculations.
- F. Calculation of net photopeak areas (total area method).
1. Compute total area; TA.

$$TA = \int_{LBC}^{RBC} X_i = \sum_{i=LBC}^{RBC} X_i$$

2. Sum n channels immediately preceding LBC; L .

$$L = \int_{LBC+1-n}^{LBC} X_i = \sum_{i=LBC+1-n}^{LBC} X_i$$

3. Sum n channels immediately following RBC; R .

$$R = \int_{RBC}^{RBC+n-1} X_i = \sum_{i=RBC}^{RBC+n-1} X_i$$

4. Calculate NC, the number of channels in the photopeak.

$$NC = (RBC - LBC) + 1$$

5. Calculate Compton Contribution; COM.

$$COM = [(L+R) / 2n] * NC$$

6. Calculate net photopeak area; NA.

$$NA = TA - COM$$

7. Calculate error in NA; ER.

$$ER = [TA + \frac{COM * NC}{2}]^{1/2}$$

- G. Calculation of net photopeak areas (Covell's method).

1. Locate PCL for first peak in pair.

2. Sum counts in PCL + m channels immediately preceding and m channels immediately following PCL; TCV.

$$\text{TCV} = \int_{\text{PCL}-m}^{\text{PCL}+m} X_1 = \sum_{i=\text{PCL}-m}^{\text{PCL}+m} X_1$$

3. Calculate Compton Contribution; CMC.

$$\text{CMC} = (2m+1) (X_{\text{PCL}+m} + X_{\text{PCL}-m})/2.$$

4. Calculate net area; NCV.

$$\text{NCV} = \text{TCV} - \text{CMC}$$

5. Calculate error in NCV; ECV.

$$\text{ECV} = \left[\text{TCV} + \frac{\text{CMC} * (2m+1)}{2} \right]^{1/2}$$

- H. Store areas calculated and γ -energy for each peak. Then if the spectrum was a standard, go back to Step B. If the spectrum was an unknown sample, continue to Step J.

- J. Match unknown peaks to standard.

1. Matching is accomplished by comparison of PCL \pm g (channel drift) or γ -energy \pm K (energy drift), at the option of the user.
2. If there are any standard peaks for which no match is found in the unknown sample, a special method is used to determine the existence of a matching peak. This is called the G-method and is described in Appendix C.
3. For matched peaks we continue with the following procedures:
 - a. If interference corrections are optioned on a given peak, corrections are applied. (See Appendix D for method).

b. Calculate

$$RA+ERR = \frac{(NA+ER)/CD \text{ for sample}}{(NA+ER)/CD \text{ for standard}}$$

$$\pm \left[\left(\frac{ER}{NA} \right)_{\text{sample}}^2 + \left(\frac{ER}{NA} \right)_{\text{standard}}^2 \right]^{1/2}$$

where CD is the counting duration.

c. Calculate the time interval between sample counting time and standard counting time; CTD.

$$CTD = (MCT_{\text{sample}} - MCT_{\text{standard}})$$

where MCT is mean counting time.

d. Calculate ELT.

$$ELT = e^{\lambda \tau}$$

where $\tau = CTD$

$$\lambda = 0.693/HL$$

HL = half-life of the isotope

e. Calculate the abundance in ppm and the associated error; $AMT \pm ERA$.

$$AMT = (RA) (STM) (ELT) / (SAM)$$

$$ERA = (AMT) (ERR)$$

where STM = standard mass in micrograms

SAM = sample mass in grams

III. Input

1. Parameter cards will be input by the user containing options, and basic data for the **program**. These are described in Section VI.
2. The spectrum will be read from magnetic tape prepared before the run. It is read using a BUFFER IN statement and expects binary information.

The data on the tape is in the form:

Record 1 - 1 word tape ID (4 characters) (This corresponds to tape ID in columns 27-30 of TAPE-OPTIONS card and/or columns 77-80 of spectrum parameters card described in Section VI).

Record 2 - 4127 words (floating point)

word

1 - 4 alphanumeric characters for file-ID. (This corresponds to columns 77-80 of Spectrum-ID card, described in Section VI).

2-21 - contains Spectrum label, 80 character header.

22-30 - floating point parameters (These are not currently used by SPECTRA, but must be present).

31 - number of channels with information.

32-4127 - 4096 channels (count rates in each) in floating point.

Record 3 - ---- same as record 2.

.

.

.

continue for as many Spectra as you may desire to analyze.

3. An alternate form of input, is to have the Spectrum counts/channel punched on Hollerith cards.

IV. Standard Output is the following table:

SAMPLE ID: xxxx

<u>PEAK CHANNEL</u> <u>LOCATION</u>	<u>γ-RAY</u> <u>ENERGY</u>	<u>ISOTOPE</u>	<u>(PPM)</u> <u>ABUNDANCE + ERROR</u>	
173	104.00	SM	1.450	0.07
193	116.00	GD	0.880	0.08
203	121.00	EU	0.910	0.09
---	----	--	---	--
719	430.00	ND	0.770	0.07
ETC.	ETC.	ETC.	ETC.	ETC.

V. Deck Setup for running on CDC 3300 under OS-3

- A. OS-3 JOB card.
- B. OS-3 EQUIP cards (see Appendix E).
- C. *SPECTRA
- D. Calculations and Printing options Card (optional).
- E. Tape-Options Card (required).
- F. Calibration package (required).
- G. SPECTRUM-ID Card (required).
- H. SPECTRUM PARAMETERS Card (required).
- I. Standard Selection Card, (Ea). (optional).
- J. Interference Correction Card, (Eb). (optional).
- K. Variable format card. (optional).
- L. Spectrum Data. (if on Cards).

- M. Repeat Cards G through L for each Spectrum.
(Standards must come first, unknowns after all standards have been read in).

OR

Repeat Cards F through L for each Spectrum when re-calibration is required for that Spectrum.

- N. FINISH card (required).
O. Repeat cards D through N if desired.
P. OS-3 LOGOFF card.

VI. Description of Input Control and Parameter Cards

A. Calculations and Printing Options Card (optional)

- | | |
|-----------|--|
| Col 1-16 | 'PRINTING OPTIONS' |
| Col 21-22 | Dump option for array 'PEAK' |
| Col 23-24 | Dump option for array 'STAND' |
| Col 25-26 | Dump option for unknown Spectrum (input data) |
| Col 27-28 | Dump option for standard Spectrum (input data) |
| Col 29-30 | Dump option for supplementary data (from parameters cards) |
| Col 31-32 | Dump option for photopeak area Calculations (recommend using Col 43-44 instead) |
| Col 33-34 | Dump option for Peak matching Calculations (recommend using Col 45-46 instead) |
| Col 35-36 | Dump option for smoothed unknown Spectrum |
| Col 37-38 | Dump option for smoothed Standard Spectrum |
| Col 39-40 | Option to ignore peak matching (i.e. Calculate areas only). (If this option is exercised, the user should also exercise option in Col 43-44 using <lun> = 61). |

- Col 41-42 <lun> to print Δ and Δ' for each calculation, if desired. Leave blank otherwise. (If <lun> is specified, the user must equip the unit given. See Appendix E).
- Col 43-44 <lun> on which to print area calculations (if desired). Leave blank otherwise. (If <lun> specified, prepare Equip card).
- Col 45-46 <lun> for peak match calculations dump, if desired. Otherwise leave blank. (If <lun> is specified, prepare Equip card).
- Col 47-48 RLS. Number of channels to the right and left of RBC and LBC to use in adjusting Peak boundary. (See Appendix B). (No adjustment made if left blank).
- Col 49-50 FACTOR. Factor used in editing of data. (See Appendix A).
- Col 51-54 RANGE. Lowest count rate to be edited. (See Appendix A). This number is read in as a floating point number - punch decimal point. All other entries on this card are integers and should be right adjusted).

NOTE: In each of the above, 00 means do not execute this option; 99 means execute this option.

(Assumes 99.0 if this is blank).

NOTE: For options in Col 43-44 and 45-46, the following output formats are used:

1. Col 43-44 option.
 FORMAT (1X,I6,2X,I5,8E14.6)
 Variables are: Spectrum number, PCL,
 Total area, L, R, NC, COM, NA, ER
2. Col 45-46 option.
 FORMAT (1X,A8,I5,8E14.6)
 Variables are: Spectrum name, PCL,
 PA, ERR, CTD, LAMBDA, ELT, (STM)
 (ELT)/SAM, AMT, ERA.

B. Tape-options card (required)

- Col 4-5 <lun> on which control and parameter cards will be read. This will be 60 if card reader is used. (If anything else, an Equip card must be prepared).
- Col 9-10 <lun> on which output is to be written. This is normally 61 (i.e., the line printer). (If anything else is used, prepare an Equip card). If user is running program from a teletype console, <lun> should be equipped to 'LP' and 61 should not be used.
- Col 14-15 61 if user is at teletype. Otherwise leave blank.
- Col 19-20 <lun> from which Spectra will be read. This must be an integer from 1 to 20 unless input is on Hollerith cards, in which case it will be 60. (Prepare Equip card if <lun> \neq 60).
- Col 27-30 Alpha-numeric tape-ID if Spectra is on binary tape, (or file). This is overridden by Col 77-80 of the Spectrum parameters card if <lun> in Spectrum parameters card is non-zero.

C. Calibrations Package (3 cards)

1. Calibrations option card (optional)

- Col 1-11 'CALIBRATION'
- Col 20 0 normal calibration
- 1 normal calibration + print equations
- 2 normal calibration + print equations
+ print calibrations for channels 1 through 4096.
- 3 use energy to match peaks instead of channel number (normal calibration).
- 4 combination of 3 and 1
- 5 combination of 3 and 2

NOTE: Program assumes 0 if this card is omitted.

2. Channel Card --- Format (5I10) (required)

Col 1-10	Channel of first photopeak for γ -energy calibration
Col 11-20	Channel of second photopeak for γ -energy calibration
Col 21-30	Channel of third photopeak for γ -energy calibration
Col 31-40	Channel of fourth photopeak for γ -energy calibration
Col 41-50	Channel of fifth photopeak for γ -energy calibration

3. Energy Card --- Format (5F10.0) (required)

Col 1-10	γ -energy corresponding to first photopeak on channel card
Col 11-20	γ -energy corresponding to second photopeak on channel card
Col 21-30	γ -energy corresponding to third photopeak on channel card
Col 31-40	γ -energy corresponding to fourth photopeak on channel card
Col 41-50	γ -energy corresponding to fifth photopeak on channel card

D. Spectrum-ID Card (required)

FORMAT (I5, 3A8, I1, I5, 5X, 3I5, 4X, I1, 2(I2, 1X), I1, 2X, I4, I2, I1, A4)

Col 1-5	Sample number
Col 6-29	Sample (or isotope) name. (alphanumeric)
Col 30	0 Process this spectrum as a standard 1 Process this spectrum as an unknown

- 2 Process this spectrum as an unknown and then read new standards (i.e., a new data set, complete set of control cards beginning with printing options) or read the finish card
 - 3 Process this spectrum as an unknown, then read a new calibration package and recalibrate before processing next spectrum
 - 4 Process this spectrum as a standard, then rewind spectra data tape
 - 5 Process this spectrum as a standard and then read new calibration package, re-calibrate before continuing
 - 6 Combine both options 4 and 5
- Col 31-35 Approximate channel to begin searching for peaks. (Program assumes channel 1 if this field is blank).
- Col 41-45 Channel number of first channel to be read in. (This field is used only if a partial spectrum is being read in from Hollerith cards, otherwise leave blank).
- Col 46-50 Channel number of last channel to be read in. (Same restrictions as in Col 41-45).
- Col 51-55 Cut-off channel for data smoothing (e.g., if you only wish to smooth through channel 1250 and leave the rest unsmoothed, put in 1250). This field used only when smoothing is optioned. Program assumes 4096 if left blank.
- Col 60 0 if no smoothing desired
1 if data smoothing is desired

- Col 61-62 Type of smoothing desired.
- 0 uses 5-point smoothing
 - 1 uses 5-point smoothing
 - 2 uses 7-point smoothing
 - 3 uses 9-point smoothing
 - 4 uses 11-point smoothing
 - 5 uses 13-point smoothing
 - 6 uses 15-point smoothing
 - 7 uses 17-point smoothing
 - 8 uses 19-point smoothing
 - 9 uses 5-point mean smoothing
 - 10 uses 7-point thru channel 1200 and
13-point smoothing from there on
- Col 64-65 NPK. The number of peaks to find on this spectrum, if specified by user. (If blank, all peaks are found). This is used to specify peaks on Standard Spectra. If this is not blank, card Ea must be present.
- Col 67 0 no interference corrections needed for this standard
- 1 interference corrections needed. Card Eb must be present. (leave blank if spectrum is unknown)
- Col 70-73 number of channels in the spectrum (assumes 4096 if blank)
- Col 75 Maximum number of (0)'s [i.e. $|\Delta| < \Delta'$] to allow in the center of the photopeak. (Program assumes 1 if left blank). (2 or 3 will sometimes cause 1 or 2 more peaks to be found).

- Col 76 9 if Covell's method is to be used.
 (blank otherwise).
- Col 77-80 Alpha-numeric file-ID for this spectrum.
 (this is used in searching the data tape
 to read in the correct spectrum. (See
 Section III (Input))).

E. Spectrum Parameters Card (required)

Format (3(F9.0,A1),2F10.0,2I5,F5.0,I5,2(I2,1X),A4)

- Col 1-9 Mean counting time for the sample
- Col 10 Time units for mean counting time (see
 options below)
- Col 11-19 Counting duration for the sample
- Col 20 Time units for counting duration
- Col 21-29 Half-life of the isotope
- Col 30 Time units for half life
- Col 31-40 Sample mass in grams (if unknown sample)
- Col 41-50 Standard mass in micrograms (if standard
 sample)
- Col 51-55 Number of channels (n) used for calculation
 of Compton Contribution. (Program assumes
 n=1 if left blank). If peaks are close
 together, best results are obtained by leaving
 this blank.
- Col 56-60 Number of channels (m) used in Covell's
 method. (Assumes m=1 if blank).
- Col 61-65 Allowable energy drift (K) if matching by
 energy. Punch decimal point. If blank,
 program assumes matching by PCL. See
 Appendix F for determining what K to use.
- Col 66-70 Number of channels allowable for drift (g)
 [used in G-method, Appendix C , G Also
 used if matching by PCL].

- Col 71-72 Number of variable format cards if reading Hollerith cards; otherwise leave blank.
- Col 74-75 $\langle \text{lun} \rangle$ from which this spectrum will be read (if different than Col 16-20 of tape-options card). This must be a number between 1 and 20 if binary file, or unit 60 if Hollerith cards. Leave blank if you are using $\langle \text{lun} \rangle$ specified on tape-options card. (Prepare Equip card).
- Col 77-80 Alphanumeric tape-ID (if Col 74-75 is not blank).

Time Unit Options for Spectrum Parameters Card.

- K if units are milliseconds
- S if units are seconds
- blank or M if units are minutes
- * if units are hours and minutes (e.g. 1.05 means 1 hour and 5 minutes)
- H if units are hours
- D if units are days
- Y if units are years

Ea. Standard Selection Card. (Present only when Col 64-65 of Spectrum-ID Card are not blank).

FORMAT (16I5)

Let C_i be the approximate channel number of a peak to be used as a Standard on this Standard Spectrum. Define $C_i^* = C_i + 10$

Col 1-5	C_1^*
Col 6-10	C_2^*
.	.
.	.
Col 76-80	C_{16}^*

NOTE: Terminate with C_{NPK}^* . If NPK > 16 continue on another card.

VIII. Limitations and Time Requirements (CDC 3300)

- A. SPECTRA will hold up to 200 standard peaks in memory while processing the unknown Spectra. Each unknown Spectra may have up to 200 peaks.
- B. A sample problem using 16 standard peaks and 125 unknown Spectra (2048 channels each) using interference corrections, $g=5$, plus a dump of all area calculations, averaged about 18 seconds per unknown Spectra.
- C. If only 4 elements (standards) were used and area calculations were dumped, the same problem averaged about 6 seconds per unknown spectra.

IX. Appendices

Contents

<u>Appendix</u>	<u>Title</u>
A	Spectrum Edit
B	Peak Boundary Determination
C	G-Method for Peak Location
D	Interference Correction
E	Equip Cards
F	Energy Drift Allowance
G	G-Search
H	Standard Peak Selection
I	Sample Deck Setup

Appendix ASpectrum Edit

Purpose: to correct input Spectrum for obvious instrumental errors.

Method:

1. Define C_i = counts in channel i
Define n = total number of channels in Spectrum
2. For $i = 1, 2, 3, \dots, n$
Set $C_i = |C_i|$
3. For $i = 1, 2, 3, \dots, n-2$ do the following
 - a. if $C_{i+1} < \text{range}$ go to d.
 - b. if $C_{i+1} \leq \text{FACTOR} * C_i$ go to d.
 - c. set $C_{i+1} = \frac{C_i + C_{i+2}}{2}$
 - d. continue scan beginning again with Step a.

NOTE: if Col 49-50 of Printing Options card is blank, no edit is performed. We used Factor = 3 for an energy calibration of 0.8 kev/channel. Range is assumed = 99.0 unless otherwise specified.

Appendix BPeak Boundary Determination

1. Left boundary channel, LBC, is chosen to be the first channel for which a (+) was obtained and was followed by at least one (+), one or no (0)'s, and at least 2 (-)'s.
2. The last (-) in the previous, determines RBC, Right Boundary Channel.
3. Then these bounds are adjusted as follows:

- a. Beginning at LBC and scanning backwards continue for RLS (see c.) channels or until we find a (-). Set LBC = right hand channel of the pair giving the (-) condition. Now look at counts in channels LBC-1, LBC, LBC+1. Set LBC = channel having the lowest count rate.
- b. Beginning at RBC and scanning forward continue for RLS channels or until we find a (+). Set RBC = left hand channel of the pair causing the (+) condition. Now look at counts in RBC-1, RBC, RBC+1. Set RBC = channel having the lowest count rate.
- c. RLS is defined by the user in Col 47-48 of calculations and Printing Options card.
- d. In test runs, we found RLS = 5 gave very good results.

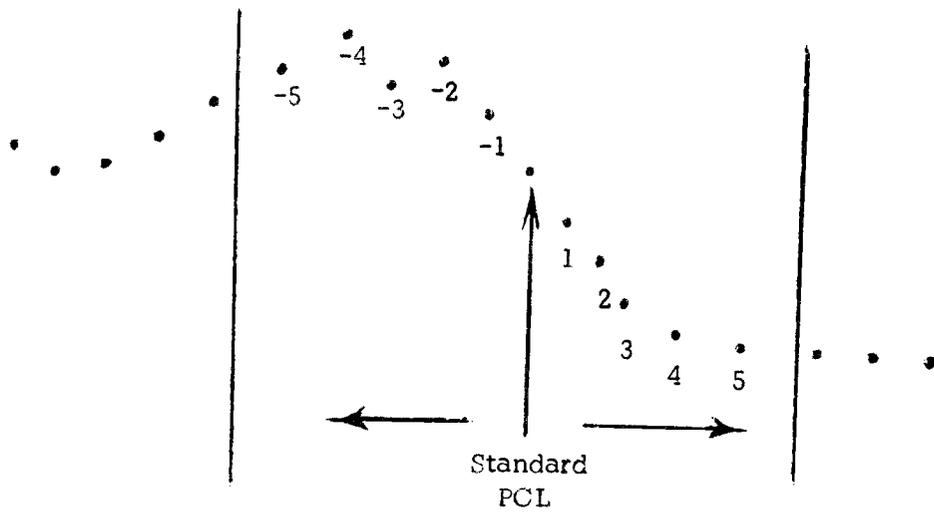
Appendix C

G-Method for Peak Location

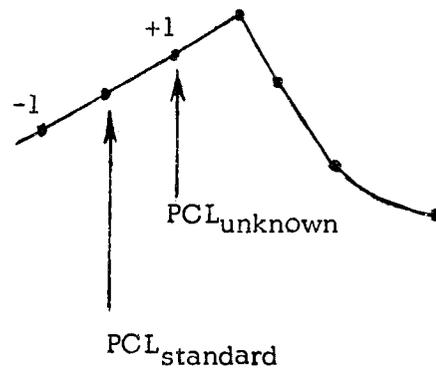
If there is a standard peak for which no corresponding peak was found in the unknown spectrum, the G-method is used. We check the region of the unknown spectrum corresponding to the location of the standard peak for which no match was found. The PCL of the standard is assumed to be the PCL of the unknown. Now a series of g (defined in Col 66-70 of Spectrum parameters card) psuedo peaks are defined and recorded as true peaks, along with their areas, etc. These peaks are determined as

$$P_i = PCL-i, PCL, PCL+i = LBC, PCL, RBC \text{ for } i=1, 2, \dots, g$$

under the condition that when $i=1$, the channel (of PCL-1, PCL, PCL+1) having the highest count rate is defined to be PCL for the unknown peak. LBC and RBC are then determined as in normal peaks. (See Appendix B). Hence if $g=5$ we could still get a peak calculation for the spectrum:



NOTE: About half the time when $i=1$, negative values will appear in the abundance calculations. In this case, PCL_{unknown} becomes RBC also and only half the peak is calculated. Negative and/or very low values signify this problem.



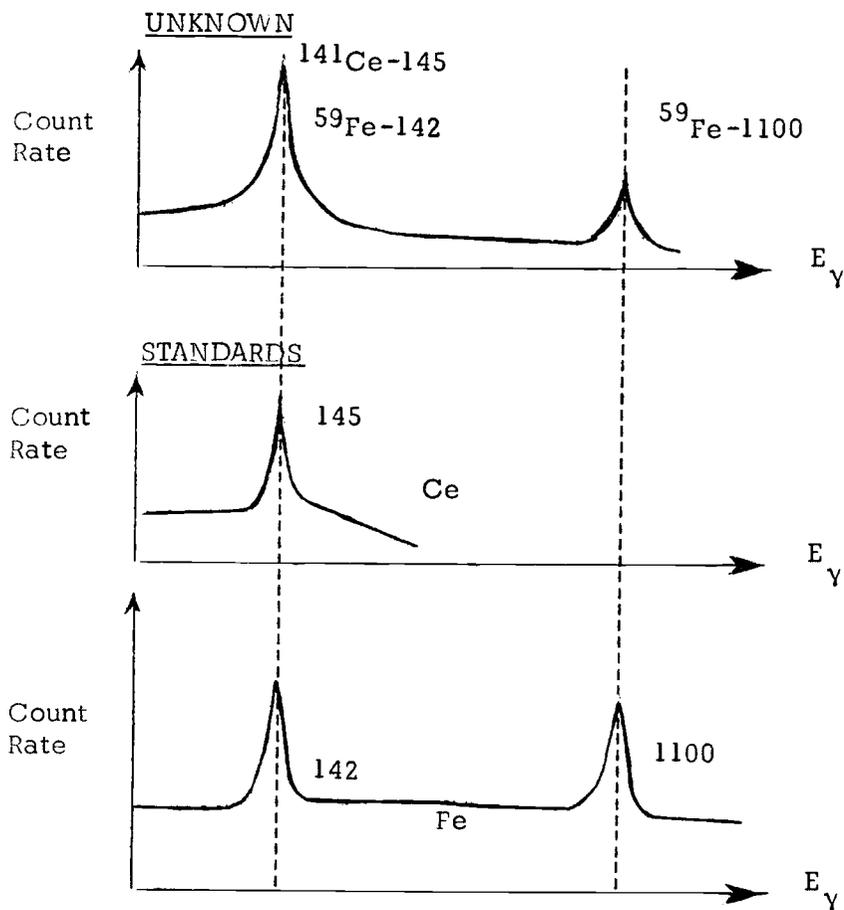
A dump of the count rates in channels between $LBC-8$ and $RBC+8$ occurs after the $i=1$ abundance calculation, and so the user can examine the peak visually. The dump of area calculations can be of further help in choosing the correct calculation. In general, the output abundance having best statistics, highest value, and correct energy will prove to be the best choice.

Appendix D

Interference Correction

Each standard peak can be used either for correcting an interference or for having an interference subtracted from it.

An example of interference corrections is as follows:



Assuming E_γ is the channel number, an additional card (Eb) may be placed behind the γ standard selection card (Ea). Card Eb has a format similar to the Ea card. See Section VI descriptions of cards Ea, Eb, and notation I_i^* to determine values for I_i^* , odd numbers are used for interfering peaks, and even numbers (1 greater than the odd) for non-interfering peaks used for

making the correction. These numbers must be unique. The peak to be corrected (Ce_{145} in our example) gets a similar card. The I_1^* here is always equal to $1000 +$ (the number used to specify the interfering peak (Fe in this example)). This is always an odd number. In addition a "1" is placed in Col 67 of the Spectrum-ID card.

For our example, then cards Ea and Eb would be

Ea (For Ce)

Col 1-5 155

Eb (for Ce)

Col 1-5 1005

Ea (for Fe)

Col 1-5 152

Col 6-10 1110

Eb (for Fe)

Col 1-5 5

Col 6-10 4

*FOOTNOTE:

This same peak could be used for more than one operation if it was calculated more than once by re-winding the tape. A different standard ID name could be used to specify the calculation in the output.

Appendix EEquip Cards

All logical units (i.e. tape drives, disk files, etc.) other than 60 (card reader) and 61 (on-line printer) must be defined by an OS-3 EQUIP card.

For example, if you say the spectra is on a magnetic tape at 800 BPI, reel number 1287, and will be read from unit 4, an equip card would be as follows:

EQUIP, 4=MT, 1287, Read Only, 800 BPI

For further details, refer to:

A Control Mode Manual for OS-3

Version 2.0

by Walter W. Massie

available at the OSU Bookstore.

Appendix FEnergy Drift Allowance

- A. For matching unknown peaks with standard peaks using energy:

Define E_s = Energy of the standard peak

E_u = Energy of the unknown peak

K = Energy drift allowed

Then we say we have a match whenever the condition

$$\left| E_s - E_u \right| < K$$

is met.

- B. For matching unknown peaks with standard peaks using channel number:

Define P_s = PCL of standard

P_u = PCL of unknown

g = Channel drift allowed

Then we say we have a match whenever the condition

$$|P_s - P_u| < g$$

is met.

- C. Choosing a value for K (Energy matching only)

The energy drift allowed, K , should be chosen such that K is less than the difference in energies between two adjacent peaks, in the unknown spectrum, where one of these adjacent peaks matches a standard. (For example, this becomes critical in $^{147}\text{Nd-91}$.) For most spectra, $K = 2.5$ works fairly well. Caution: The user should check this for a small sample of his data, before running everything. If drift becomes greater than K , recalibrate.

- D. Choosing g (When matching by channel)

Choose as we did K , only consider channel numbers instead of energy. (It is usually preferable to match by energy).

- E. Choosing g (When matching by energy)

Appendix C gives details on use of g here. Possibly a g of 4 or 5 is sufficient.

Appendix GG-Search

In determining a peak using the G-method, we actually determine g peaks instead of 1. It becomes necessary to select one of these for use in interference corrections if corrections are indicated in the corresponding standard peak.

If the area calculated for a "G peak" is positive, the corresponding error is divided by the area: ER/NA . The peak with the smallest ER/NA is selected as the "best" peak. If none of the "G peaks" have area greater than zero, then no correction is made and the output is flagged (**) indicating interference is non-significant.

Appendix HStandard Peak Selection

Select the peaks in the standard spectrum which you desire to use for matching -- for example, suppose you have a standard with peaks at channels 390, 1000, and 1097 but you wish to use only the peaks in channels 390 and 1000. Then on card Ea for this spectrum, you would enter the values of C_1^* , C_2^*

$$C_1 = 390$$

$$C_2 = 1000$$

$$C_1^* = 400$$

$$C_2^* = 1010$$

in columns 1-5 and 6-10, respectively.

Appendix I

Sample Deck Setup

```

CJOB,85177,CODE,BORCHARDT
CTIME=600
CMFRLKS=500
CFEQUIP,7=MT 3728 AT 556
CFEQUIP,1=MT 3727 AT 556 NO RING
CFEQUIP,10=FILE
C*SPECTRA
PRINTING OPTIONS 000000000000000000 10 5 3
 60 61 1 BA2
CALIBRATION 4
 62 129 343 602 1593
 91.10 145.43 320.05 531.01 1332.48
 205 CERIUM 0 1 1 2048 CFB
568.78 * 10.M 33.0 D 998. 21.7
 138
 1003
 206 COBALT 0 2 2048 CFB
569.35 *10. 5.26 Y 921.5 1
 1405 1592
 207 CHROMIUM 0 1 2048 CRB
569.56 * 10.M 27.8 D 945. 21.7
 353
 294 NEODYMIUM 0 2 2048 NFB
569.77 * 10.M 11.1 D 988. 21.7
 71 612
 296 RUBIDIUM 0 1 2048 RFB
569.94 *10. 18.7 D 4947. 1
 1285
 295 THORIUM 0 1 1 2048 THB
570.51 * 10.M 27.0 D 998. 21.7
 342
 1007
 204 BARIUM 5 4 1 2048 BAB
571.93 * 100.M 12.0 D 998. 21.7
 123 225 418 569
 1 2
CALIBRATION 4
 112 204 688 1295 1531
 133.03 208.36 604.74 1099.85 1291.40
 208 CESIUM 0 2 CFB
821.82 * 10.M 2.05 Y 1001.6 21.7
 701 935
 293 LUTETIUM 0 1 LFB
822.66 * 10.M 6.7 D 1020. 21.7
 215
 291 IRON PERCENT 0 3 1 FFB
823.39 * 11.06M 45.0 D 47.69 21.7
 138 1310 1548
 3 4
 292 HAFNIUM 0 2 1 2048 HFB
823.56 * 10.M 42.5 D 998. 21.7
 122 550
 1001
 2011 YTTERBIUM 5 4 2 2048 YFB
320.54 * 10.M 32.0 D 1020. 21.7
 16 37 202 336
 8 7

```


APPENDIX XII

FORTRAN IV PROGRAMS DEVELOPED FOR
AUTOMATED DATA PROCESSING OF
ACTIVATION ANALYSIS RESULTS

Program RATIOS

This program accepts single data cards with the concentrations for 19 elements (Y) and divides the values on each card by the values of a comparison sample (Z). The Z values used here were the average concentrations for eight unweathered Mazama volcanic ash samples. Each data card for this and the following programs has been identified by a sample number in the first four columns of the IBM punch card. Output for RATIOS was printed and also punched on cards for further data analysis. The estimated counting error (one standard deviation in ppm or %) was converted to ratio units also. Data cards were preceded by a label card (NO. NA RB . . . CR).

Program INAAC

INAAC was used to calculate the discriminant values for each sample after the coefficients and constants had been determined with the BMDO5M discriminant analysis program. The first card contains the number of groups (N) and the number of variables (M). The next

card (or cards) contains(s) the constant (CON) and the coefficients (COE) for the equation of the first group. Coefficients and constants appear on the cards for the rest of the groups. Next, a data card containing the RATIOS or concentrations is read in and the discriminant values are calculated and outputed on the printer and on punch cards. The probability of correct classification (P) is calculated for each discriminant value by using the equation given in the BMDO5M program used at the OSU Computer Center.

Program INAAC2

INAAC2 was used for the variation analysis based upon the coefficient of variation and average comparison ratios. The first card contains the number of comparisons to be made (K). The average analyses (Z) for the K group are included next (eg. average RATIOS for Mazama C1, Mazama C2, Newberry, Glacier Peak, St. Helens Y, and St. Helens W). The unknown sample RATIOS (Y) were read in next followed by the error values (X) used for weighting the results. The formula:

$$P (J) = 1.00 - [X(J)/Y(J)]/0.333$$

was used for weighting. The most accurate elemental determinations had P values near 1.00 and elements determined with accuracies of less than 33% were not used at all. For each comparison, the weighted values (concentrations or ratios) of the unknown sample were

divided by the values for the known samples. An average ratio was then calculated for the comparison to each group along with the coefficient of variation. Ratios were printed for each comparison. The weighting coefficients (P) for the unknown samples and the mean ratios and CV's of seven comparisons were printed and punched for each unknown.

Program MEANCV

MEANCV calculates a mean ratio for all 19 ratios to Mazama volcanic ash on each card (Y) punched by the RATIOS program. The CV for the variation about this mean is then calculated without using weighting factors. The error card (X) follows each RATIOS card for calculation of an average percent error due to counting statistics for all elements in the sample. After each unknown has been calculated the program prints and punches the mean, CV for ratios, and the average error for all analyses on that card. At the end of the run the average analytical error for each element is printed.

Program RAT

RAT calculates elemental ratios (eg. Sc/Fe) and averages for certain element combinations specified by the user. Input consists of RATIOS cards along with the weighting coefficients calculated with the INAAC2 program. The following ratios and averages were

calculated with the program: Rb/Cs, Ba/Cs, Ba/Rb, La/Sm, Sc/Fe, Th/Hf, rare earth element average (REAV), La+Ce+Sm average (CAV), Tb+Yb+Lu average (YAV), CAV/YAV, Th+Hf+Ta average divided by REAV, REE normalizations to REE abundances of chondrites and Yb for: La, Ce, Nd, Sm, Eu, Tb, and Lu. These values were printed and punched on single cards.

Program MARILYN

MARILYN is a variation of the MEANCV program which accepts cards Y and X from program RATIOS. The average analyses for eight unweathered ash samples and for five Mazama soil clays were obtained in this way. Output included a printer line and a punched card for the average analysis, coefficient of variation for sample to sample (field) variability, and coefficient of variation for counting statistics. Each group to be averaged is followed by an identification number (less than 100). Program MARILYN2 is a variation of this program that does not require the X cards and, therefore does not calculate the coefficient of variation for counting statistics.

Program GENESIS

GENESIS can be used to calculate up to 54 elemental ratios much like those for program RAT. The original analyses are used (ppm and %) instead of ratios and some of the resulting elemental

ratios are multiplied by a factor so that the result will fit the four column format. The elemental analyses for each unknown are numbered from 1 to 19 (eg. Y(4)/Y (7) is element 4 divided by element 7). The first card has the number of elemental ratios to be calculated (L). The next set of cards contains the subscripts for dividends (J) on the first card and the subscripts for divisors (K) on the second. The elemental ratios are calculated as per these instructions and outputed on the line printer and on the card punch.

Program CLAY

CLAY was used to estimate the percentages of the elements occurring in the HNO_3 extractable, iron oxide, amorphous, and crystalline fractions of the clay samples. The first card contains the weighting factors for HNO_3 (V), iron removal (Y), and KOH boiling treatments (Z). For example if the KOH residue was 20%, the factor would be $100\%/20\% = 5.00$. Five RATIOS cards were used for each treated soil clay. The first two are averaged to obtain duplicate results for the untreated chemical composition. The next three cards are divided by V, Y, and Z, respectively. The first quotient is subtracted from the pretreatment average, the second quotient from the first, the third quotient from the second. The total number of units for each element was obtained by adding the positive remainders to the weighted residue value. Percentages of each of these fractions

were then determined. Output on the line printer included remainders and percentages for the HNO_3 , iron oxide, amorphous, and crystalline fractions.

FORTRAN IV Programs

```

FORTRAN VERSION 2.1          08/14/69  185R
PROGRAM RATIOS
C
C
C   THIS IS THE FORMAT SECTION
99  FORMAT ( I3, 1X, 19F4.0)
150 FORMAT ( 1H , I3,      1X, 19F6.2)
151 FORMAT      ( I3,  1X, 19F4.0 )
190 FORMAT (I5, 3A8 )
195 FORMAT ( 1H-, I3, 25X, 3A8 )
196 FORMAT      (/I3, 25X, 3A8 )
300 FORMAT ( 31H      INAAC RATIOS TO MAZAMA ASH ////)
210 FORMAT (10A8 )
220 FORMAT (1H , 10A8 )
C
C   DIMENSION RATIO (19),      Z (19), Y (19)
C   DIMENSION ASH(3),  ELEM(10)
C   WRITE (61, 300)
C   READ (60, 210) (ELEM(I) , I = 1, 10)
C   WRITE (61, 220) (ELEM (I), I = 1, 10 )
C   READ (60, 99) STD, Z
C   WE JUST READ THE SAMPLE CARD USED FOR NORMALIZATION
200 READ (60, 190) LAM, ( ASH(K) , K = 1, 3 )
C   IF (99999-LAM) 102, 102, 100
100 WRITE (61, 195) LAM, (ASH(K) , K = 1, 3)
C   WRITE (62, 196) LAM, (ASH(K) , K = 1, 3 )
C   I=0
105 READ (60,99) NC, Y
C   I=I+1
C   DO 108 J=1,19
108 RATIO(J) = (Y(J)*Z(J))/100.
C   WRITE (61,150) NC, RATIO
C   WRITE (62, 151) NC, RATIO
C   IF ( I .EQ. 2 ) GO TO 200
C   GO TO 105
102 STOP
END

```

FORTRAN VERSION 2.1
PROGRAM INAAC

08/14/69 1858

```

C
C
C   FORMAT SECTION
C
  10 FORMAT (I3,I1X,
1      2F4.2,I6X,F4.2,AX,2(4X,F4.2),F4.2/24X,F4.0,28X,F4.0)
  20 FORMAT(10X,7F10.0/2F10.0)
  60 FORMAT (1H-, I3, 5F15.2)
  170 FORMAT (4X,I4,I4)
  390 FORMAT (1H ,I3, 5F15.5)

C
C   FORMAT FOR PUNCHING
C  380 FORMAT (I3, 5F15.2)

C
C   DIMENSIONED FOR N=5, M=15
  DIMENSION A(5), P(5)
  DIMENSION COE(5,15), CON(5), RATIO(15), DISC(5), PROD(15 )
  N=0
  M=0
  READ (60,170) N , M
  IF (N.GT. 6 ) GO TO 102
C   READ THE COEFFICIENTS AND CONSTANTS FOR N GROUPS AND M VARIABLES
  DO 130 I= 1, N
  130 READ (60,20) CON(I),(COE(I,J), J = 1, M )
C   READ AND CALCULATE THE SAMPLES
  90 READ (60, 10) NO,(RATIO(I),I=1,M)
  IF (999 - NO ) 102, 102, 500
  500 J = 0
  K = 0
  SUM = 0
  PROD = 0
  L = 0
  150 L = L + 1
  SUM=0
  DO 30 J = 1, M
  30 PROD(J) = COE(L,J) * RATIO(J)
  DO 190 K = 1, M
  190 SUM = SUM +(PROD(K))
  DISC(L) = SUM + CON(L)
  IF (L .NE. N ) GO TO 150
  WRITE (61,60) NO, DISC
  DISCX = 0
  IF (DISC(2) .GE. DISC(1)) 320, 330
  320 DISCA = DISC(2)
  GO TO 450
  330 DISCA = DISC(1)
  450 IF (DISC(4) .GE. DISC(3)) 340, 350
  340 DISCB = DISC(4)
  GO TO 460
  350 DISCB = DISC(3)
  460 IF (DISCA .GE. DISCB) 360, 370
  360 DISCX = DISCA
  GOTO 470
  370 DISCX = DISCB
  470 IF (N .GT. 4) 410, 430
  410 IF (DISC(5) .GE. DISCX ) 420, 430
  420 DISCX = DISC(5)
  430 RSUM = 0
  DO 300 J = 1, N
  300 RSUM = RSUM + EXPF(DISC(J) - DISCX )
  DO 310 J = 1, N
  310 P(J) = A(J)/RSUM
  WRITE (61, 390) NO, P
  GO TO 90
  102 STOP
  END

```

```

C
C
99 FORMAT (I3,1X,19F4.0)
33 FORMAT (4X,I4,I4)
150 FORMAT (1H0,I3,1X,19F4.0)
20 FORMAT (1H0,I3,1X,7F10.1)
22 FORMAT (    I3,1X,7F10.1)
160 FORMAT (1H0,I3,1X,19F4.2)
162 FORMAT (    I3,1X,19F4.2)
C
C
      DIMENSION RATIO(7,19), Z(7,19), Y(19), X(19), P(19), SUM(7),
1  SUMP(7), AMEAN(7), SUMSQ(7), STDV(7), CV(7)
C
C
      READ(60,33) K,L
      DO 10 I=1,K
10  READ(60,99) NC, (Z(I,J),J=1, L)
105 READ(60,99) NC, (Y(I),I=1,L)
      READ(60,99) NC,X
      IF(999-NC)102,102,500
500 DO 80 J=1, L
      IF (Y(J) .EQ.0.0) Y(J) = 0.1
      P(J)=1.00 - (X(J)/Y(J))/0.3333
80  IF (P(J).LE. 0.0) P(J)= 0.0
      DO 108 I=1,K
      DO 108 J=1, L
      RATIO(I,J) = (Y(J)/Z(I,J))*100.
      SUM(I) = SUM(I) + RATIO(I,J)* P(J)
      SUMSQ(I) = SUMSQ(I) +(RATIO(I,J)**2.) * P(J)
108 SUMP(I) = SUMP(I) + P(J)
      DO 90 I=1,K
      AMEAN(I) = SUM(I)/SUMP(I)
      STDV(I) = SQRT(SUMSQ(I)/SUMP(I)-AMEAN(I)**2.)
      CV(I) = STDV(I)/AMEAN(I)*100.
90  WRITE(61,150) NC, (RATIO(I,J),J=1, L)
      WRITE(61,160) NC, P
      WRITE(62,162) NC, P
      WRITE(61, 20) NC,(AMEAN(I),I=1,K)
      WRITE(62, 22) NC,(AMEAN(I),I=1,K)
      WRITE(61, 20) NC,(CV(I),I=1,K)
      WRITE(62, 22) NC,(CV(I),I=1,K)
      DO 50 I=1,K
      DO 50 J=1, L
50  RATIO(I,J) = 0.0
      DO 60 J=1, L
      P(J) = 0.0
      X(J) = 0.0
60  Y(J) = 0.0
      DO 70 I=1,K
      SUM(I) = 0.0
      SUMP(I) = 0.0
      AMEAN(I) = 0.0
      SUMSQ(I) = 0.0
      STDV(I) = 0.0
70  CV(I) = 0.0
      GO TO 105
102 STOP
      END

```

FORTRAN VERSION 2.1
PROGRAM MEANCV

08/14/69 1859

```

C
C
C   FORMAT SECTION
99  FORMAT (// I3, 1X,19F4.0)
100 FORMAT (4X, 19F4.0)
610 FORMAT (1H0, I3, 5X,3F15.1 )
620 FORMAT ( I3, 5X,3F15.1 )
710 FORMAT (6HAV.CV , 19F6.1)
C
   DIMENSION Y(19) , G(19), C(19)
   DIMENSION X(19), Z(19)
   J = 0
   G = 0
105 READ (60, 99) NO, Y
   IF (999-NO) 102, 102, 500
500 SUM = 0.
   J = J + 1
   DO 180 I = 1, 19
180 SUM = SUM + Y(I)
   AMEAN = SUM/19.
   SUMSQ = 0.
   DO 188 I = 1, 19
188 SUMSQ = SUMSQ + (Y(I))**2
   STDV = SQRTF(SUMSQ/19.- AMEAN**2)
   CV = (STDV/AMEAN) * 100.
   READ (60,100) X
   A = 0.
   B = 0.
   DO 600 I = 1, 19
   IF (Y(I) .EQ. 0.) Y(I) = 0.1
   Z(I) = X(I)/Y(I)
   G(I) = G(I) + Z(I)
600 A = A + Z(I)
   B = (A/19.) * 100.
   WRITE (61, 610) NO, AMEAN, CV, B
   WRITE (62, 620) NO, AMEAN, CV, B
   GO TO 105
102 DO 700 I = 1, 19
   AJ = J
700 C(I) = (G(I)/AJ) * 100.
   WRITE (61, 710) C
   STOP
   END

```

FORTRAN VERSION 2.0
PROGRAM RAT

05/26/69 1237

C
C

```

99 FORMAT (I3, 1X, 19F4.0)
100 FORMAT      (10X, BF7.6)
110 FORMAT      (1H0, I3, 2X, 6F6.2, 3F5.1, 2F6.2, 8F6.2)
112 FORMAT (I3, F5.2, F5.1, 4F5.2, 3F4.0, 2F5.2, F4.0, 7F3.0)
      DIMENSION Y(19), REE( 8), P(19), V( 8)
      DIMENSION Z(19)
      READ (60,100) (Z(I), I=5, 12 )
105 READ (60,99) NO, Y
      IF (999-NO) 102,102,500
500 READ (60,99) NO, P
      A =(Y(2)/Y(3) ) *14.745
      R =(Y(4)/Y(3) ) *182.037
      C =(Y(4)/Y(2) ) *12.345
      D =(Y(5)/Y(8) ) * 4.328
      E =(Y(18)/Y(17)) *4.273
      F =(Y(13)/Y(14)) *0.933
      DO 50 I=5,12
      SUM = SUM + Y(I)*P(I)
50 PSUM = PSUM + P(I)
      REAV = SUM/PSUM
      CP = P(5) + P(6) + P(8)
      YP = P(10) + P(11) + P(12)
      CAV = (Y(5)*P(5)+Y(6)*P(6)+Y(8)*P(8))/CP
      YAV = (Y(10)*P(10)+Y(11)*P(11)+Y(12)*P(12))/YP
      G =(CAV/YAV ) *13.965
      HP = P(13) + P(14) + P(15)
      H = ((Y(13)*P(13) + Y(14)*P(14) + Y(15)*P(15))/HP)/REAV
      IF (Y(11) .LE. 0.1) Y(11) = Y(12)
      DO 30 I=5,12
30 V(I) = Y(I)*Z(I)
      DO 40 I = 5, 12
40 REE(I) = V(I)/V(11)
      WRITE (61,110)NO,A,B,C,D,E,F,F,REAV,CAV,YAV,G,H,(REE(I),I=5,10),
1REE(12)
      DO 88 I=5,12
88 PEE(I) = REE(I)*100.
      WRITE (62,112)NO,A,B,C,D,E,F,F,REAV,CAV,YAV,G,H,(PEE(I),I=5,10),
1PEE(12)
      DO 35 I=1,19
      Y(I)=0.0
35 P(I) = 0.0
      DO 36 I=1,8
      V(I) = 0.0
36 REE(I) = 0.0
      REAV=0.0
      PSUM=0.0
      SUM =0.0
      CAV =0.0
      YAV =0.0
      CP =0.0
      HP =0.0
      YP =0.0
      A =0.0
      R =0.0
      C =0.0
      D =0.0
      E =0.0
      F =0.0
      G =0.0
      H =0.0
      GO TO 105
102 STOP
      END

```

FORTRAN VERSION 2.0
PROGRAM MARILYN

05/14/69 1241

```

C
C
C   FORMAT SECTION
40  FORMAT (1H0,I3,1X,19F4.0)
42  FORMAT (    I3,1X,19F4.0)
99  FORMAT (I3,1X,19F4.0)
100 FORMAT (4X, 19F4.0)
C
   DIMENSION Y(19), SUMSQ(19), SUM(19)
   DIMENSION X(19) , Z(19) , C(19), G(19)
   DIMENSION AMEAN(19), CV(19)
   DIMENSION STDV(19)
   J = 0
   C=0.0
   SUM =0.0
   SUMSQ=0.0
105  READ (60,99) NC, Y
      IF (NC .LT. 100) GO TO 30
      IF (999 - NC) 102, 102, 500
500  J=J+1
      READ (60,100) X
      DO 10 I=1, 19
         IF (Y(I) .EQ. 0) Y(I) = 0.1
         Z(I) = X(I)/Y(I)
         G(I) = G(I) + Z(I)
         SUM(I) = SUM(I) + Y(I)
10   SUMSQ(I) = SUMSQ(I) + (Y(I))**2.0
      GO TO 105
30   AJ = J
      DO 80 I=1, 19
         C(I) = (G(I)/AJ) * 100.
         AMEAN(I) = SUM(I)/AJ
         STDV(I) = SQRT(SUMSQ(I)/AJ - AMEAN(I)**2.0)
80   CV(I) = (STDV(I)/AMEAN(I)) * 100.
      WRITE (61, 40) NC, AMEAN
      WRITE (62, 42) NC, AMEAN
      WRITE (61, 40) NC, CV
      WRITE (62, 42) NC, CV
      WRITE (61, 40) NC, C
      WRITE (62, 42) NC, C
      DO 600 I=1, 19
         Y(I)=0.0
         SUMSQ(I) =0.0
         SUM(I)=0.0
         Z(I)=0.0
         C(I)=0.0
         G(I)=0.0
         AMEAN(I)=0.0
         CV(I)=0.0
         STDV(I)=0.0
600  X(I)=0.0
      J = 0
      GO TO 105
102  STOP
      FND

```

FORTRAN VERSION 2.1
PROGRAM MARILYN2

08/14/69 1859

```

C
C
C   FORMAT SECTION
40  FORMAT (1H0,I3,1X,19F4.0)
42  FORMAT (      I3,1X,19F4.0)
99  FORMAT (I3,1X,19F4.0)
C
   DIMENSION Y(19), SUMSQ(19), SUM(19)
   DIMENSION AMEAN(19), CV(19)
   DIMENSION STDV(19)
   J = 0
   C=0.0
   SUM =0.0
   SUMSQ=0.0
105  READ (60,99) NC, Y
   IF (NC .LT. 100) GO TO 30
   IF (999 - NC) 102, 102, 500
500  J=J+1
   DO 10 I=1, 19
   SUM(I) = SUM(I) + Y(I)
10  SUMSQ(I) = SUMSQ(I) + (Y(I))**2.0
   GO TO 105
30  AJ = J
   DO 80 I=1, 19
   AMEAN(I) = SUM(I)/AJ
   STDV(I) = SQRTF(SUMSQ(I)/AJ - AMEAN(I)**2.0)
80  CV(I) = (STDV(I)/AMEAN(I)) * 100.
   WRITE (61, 40) NC, AMEAN
   WRITE (62, 42) NC, AMEAN
   WRITE (61, 40) NC, CV
   WRITE (62, 42) NC, CV
   DO 600 I=1, 19
   Y(I)=0.0
   SUMSQ(I) =0.0
   SUM(I)=0.0
   AMEAN(I)=0.0
   CV(I)=0.0
600  STDV(I)=0.0
   J = 0
   GO TO 105
102  STOP
   END

```

FORTRAN VERSION 2.1
PROGRAM GENESIS

OR/14/69 1859

C
C

```

9 FORMAT (I8)
10 FORMAT (4X, 19I4)
101 FORMAT (I3, 1X, 19F4.0)
201 FORMAT (1H0, I4, 19F6.2)
202 FORMAT (      I4, 19F4.0)
      DIMENSION Y(19), J(57), K(57), R(57),      Q(57)
      READ (60, 9) L
      READ (60, 10) (J(I), I=1, L)
      READ (60, 10) (K(I), I=1, L)
105 READ (60,101) NC, Y
      Y(4) = Y(4)/10.
      IF (NC .GT. 200) Y(7) = Y(7)*3.0
      IF (999-NC) 102, 102, 500
500 DO 503 I=1, L
      M = J(I)
      N = K(I)
      R(I) = Y(M)/Y(N)
      M=0.0
      N=0.0
503 Q(I) = R(I)*100.
      R(4) = R(4)/10.
      Q(4) = Q(4)/10.
      Y(6) = (Y(6)/42.4) *100.
      Y(14) = (Y(14)/6.3)*100.
      NC = NC*10 + 1
      WRITE (61,201) NC, (R(I), I=1,L),Y(6), Y(14)
      WRITE (62,202) NC, (Q(I), I=1,L),Y(6), Y(14)
      NC = 0
      DO 33 I=1,19
33 Y(I) = 0.0
      DO 34 I=1,57
      R(I) = 0.0
34 Q(I) = 0.0
      M=0.0
      N=0.0
      GO TO 105
102 STOP
      END

```

FORTRAN VERSION 2.1
PROGRAM CLAY

08/14/69 1859

```

C
10 FORMAT (1H0, 4X, 19F4.0)
11 FORMAT (3F4.2)
12 FORMAT (4X, 19F4.0)
   DIMENSION X(5,19), A(19), AC(19), B(19), BC(19), C(19), CC(19),
13(19), DC(19), P(19), Q(19), R(19), S(19), E(19)
40 READ (60,11) V, Y, Z
   IF (V .EQ. 9.99) GO TO 102
   DO 20 I=1,5
20 READ (60,12) (X(I,J), J=1,19)
   DO 30 J=1,19
   A(J) = (X(1,J) + X(2,J))/2.
   R(J) = X(3,J) / V
   C(J) = X(4,J) / Y
30 D(J) = X(5,J) / Z
   DO 80 J=1,19
   AC(J) = A(J) - R(J)
   BC(J) = B(J) - C(J)
   CC(J) = C(J) - D(J)
80 DC(J) = D(J)
   WRITE (61,10) AC
   WRITE (61,10) BC
   WRITE (61,10) CC
   WRITE (61,10) DC
   DO 70 J=1,19
   IF (AC(J) .LT. 0.0) AC(J) = 0.0
   IF (BC(J) .LT. 0.0) BC(J) = 0.0
   IF (CC(J) .LT. 0.0) CC(J) = 0.0
   IF (DC(J) .LT. 0.0) DC(J) = 0.0
   E(J) = AC(J) + BC(J) + CC(J) + DC(J)
   P(J) = (AC(J)/E(J)) * 100.
   Q(J) = (BC(J)/E(J)) * 100.
   R(J) = (CC(J)/E(J)) * 100.
70 S(J) = (DC(J)/E(J)) * 100.
   WRITE (61,10) P
   WRITE (61,10) Q
   WRITE (61,10) R
   WRITE (61,10) S
   DO 60 J=1,19
   DO 50 I=1,5
50 X(I,J)=0.0
   AC(J)=0.0
   BC(J)=0.0
   CC(J)=0.0
   DC(J)=0.0
   P(J)=0.0
   Q(J)=0.0
   R(J)=0.0
   S(J)=0.0
60 E(J)=0.0
   V=0.0
   Y=0.0
   Z=0.0
   GO TO 40
102 STOP
   END

```

APPENDIX XIII

SUGGESTIONS FOR FURTHER STUDY

1. Determine the statistical distribution of the coefficient of variation used for correlation in the variation analysis method.
2. Assess the contribution of volcanic ash to agricultural soils of both western and eastern Oregon. Chemical pretreatments probably will be needed to quantitatively separate small amounts of volcanic glass from whole soil samples.
3. Investigate INAAC of heavy mineral fractions and mono-mineral fractions.
4. Use the dithionite-citrate-bicarbonate iron removal treatment and other differential solubility treatments to remove weathering products from volcanic glass or heavy minerals separated from upper horizons of soils developed from Mazama ash.
5. Determine the depth and quantity of St. Helens Y contamination at the Dick Spring soil location.
6. Investigate the possible use of other elemental ratios such as Al/Ga for correlating weathered materials.
7. Evaluate volcanic ash weathering in the bog environment in relation to the thickness and location of peat above and below the ash.
8. Evaluate the possibility of presence of high Co and Cr

content in Fe interlayered clays.

9. Compare the elemental content of crystalline minerals of clays from Mazama transect soils with each other and with Parkdale clay minerals. Investigate the possible correlation of residues from the buried subsoils to the residues from Mazama and Parkdale clays.

10. Use INAA to determine if $< 2\mu$ glass prepared by grinding pumiceous lapilli or ash has the same trace element composition as sand size glass. Other experiments could be performed by comparing $< 2\mu$ glass to "allophane" and by determining its solubility during various chemical treatments.