

James G. Bockheim
A. Kenneth Schlichte
College of Forestry

Erich A. Crecelius
John T. Kummer
Department of Oceanography

Wasant Pongsapich
Norman W. Tenbrink
William M. Weber
Randall L. Gresens
Department of Geological Sciences

University of Washington
Seattle, Washington

Compositional Variations of the Mazama Ash as Related to Variation in the Weathering Environment¹

The Mazama ash is a layer of pyroclastic material widely distributed throughout the Pacific Northwestern states and adjoining parts of British Columbia and Alberta. The source of this material was the cataclysmic eruption of Mount Mazama in southwestern Oregon, which produced the basin now holding Crater Lake. The eruption threw large quantities of pumice and ash material high into the air where the prevailing winds transported it hundreds of miles to the north and northeast.

Radiocarbon dates obtained from organic material associated with the Mazama ash place its age at approximately 6,600 years (Fryxell, 1965). Powers and Wilcox (1964) and Wilcox (1965) have described the refractive indices of the various mineral components (clino- and orthopyroxene, hornblende, plagioclase, and glass) of the Mazama ash and contrasted these with the values obtained from other pyroclastic deposits. Czamanske and Porter (1965) have shown that elemental composition, TiO_2 content in particular, can be used to distinguish the Mazama ash from other pyroclastic deposits. The Mazama ash has been widely used as a stratigraphic marker horizon in the dating of archeological, geological, and biological events in the Pacific Northwest.

At approximately equal distances from the vent, the Mazama ash should have an essentially uniform chemical composition, although the composition is subject to variation caused by the mechanisms stated by Czamanske and Porter (1965). The Mazama ash was deposited in a broad range of weathering environments. On sites where the ash has remained undisturbed and uncontaminated since the time of deposition, the differences in chemical composition can largely be ascribed to the differences in the type and intensity of the weathering processes which have taken place over the last 6,600 years. The purpose of this study is to examine the variation in the chemical composition in samples of the Mazama ash which have been exposed to a wide range of weathering conditions and to relate this variation in chemical composition to the types and intensities of weathering processes which have taken place.

¹This paper is the result of a class project in a one-quarter geochemistry course at the University of Washington.

The characteristics of the material resulting from the weathering of a surficial deposit have been related to the various factors which affect them by the equation of Jenny (1941):

$$s = f(p, t, c, o, r, \dots)$$

in which s represents the sum of the characteristics exhibited by the deposit after weathering, p parent material, t time, c climate, o organisms, and r topographic relief. In the case of the Mazama ash, the first two variables can be considered to be constant, leaving climate, organisms, and relief to be the variables which will produce the major differences between the ash located at the various locations. Climate, as represented by annual precipitation, was selected as the most important single variable in this study because of the close relationship between vegetation and zonal soil patterns and rainfall distribution.

Experimental Procedure

Sampling. As shown in Figure 1, samples of the Mazama ash were collected from a variety of environments in the state of Washington. A range of 15 to 115 inches of precipitation is represented by 10 sample stations.

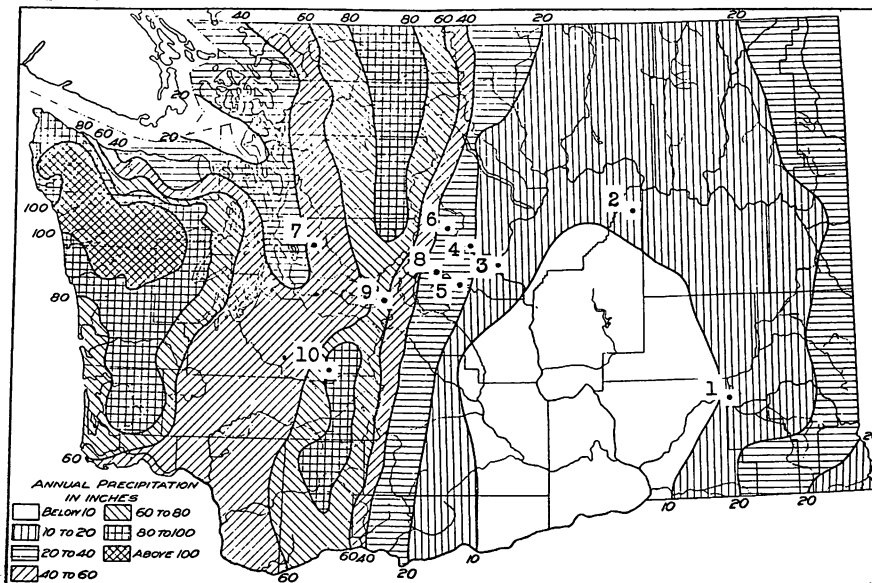


Figure 1. Distribution of sites from which samples of Mazama ash were collected and belts of average annual precipitation in inches throughout the state of Washington (from Landes, 1917).

The Mount Mazama ash was identified in the field by its color and stratigraphic location. In the laboratory, sample identification was verified by refractive index.

At five of the stations, ash was collected from three laterally separated sample sites. Two samples were used for chemical analysis; the third sample was used for determination of color and of refractive index. Single samples from the remaining five stations were provided by Dr. S. C. Porter of the Department of Geological Sciences,

University of Washington. An attempt to avoid contamination was made on all sites. All samples were collected from B or C soil horizons.

Sample Preparation. Ash samples were oven-dried at 100°C for 10 hours; then 0.500 g of each sample was weighed into a teflon beaker. Twenty-five ml of 48% hydrofluoric acid were added to each beaker and evaporated to dryness three times. Eight ml of 70% perchloric acid and 25 ml of 48% hydrofluoric acid were then added and evaporated to dryness. The residue was dissolved in 40 ml of 5% hydrochloric acid and brought up to a volume of 50.00 ml.

Analysis. Chemical analyses were run on a Perkin-Elmer Model 303 Atomic Absorption Spectrometer. Chemical data from Powers and Wilcox (1964) and Czamanske and Porter (1965) were used to estimate the optimum working range to which the samples were diluted.

Standards were prepared to cover the working range of the samples according to the Perkin-Elmer manual. Procedures given in Angino and Billings (1967) were followed to minimize interference. Calibration curves for each element were drawn by plotting a best-fit straight line for standards covering the working range.

Experimental Error. Estimates of the maximum instrumental error and error in dilution of samples and standards are given for each element in Table 1. These estimates equal the greatest deviation of any standard from the best-fit absorbance-ppm curve used for calibration.

Results and Discussion

As shown in Tables 1 and 2, the various elements behave differently with an increase

TABLE 1. Quantitative chemical analyses of Mazama ash and average annual precipitation at sample locations shown in Figure 1. Analyses were made on dissolved rock powders by atomic absorption.

Sample	Precipitation (inches/year)	Composition (percentage by weight)										Munsell color index
		TiO ₂ ±.03	Total iron* ±.05	Al ₂ O ₃ ±3.7	CaO ±.03	MgO ±.17	K ₂ O ±.01	Na ₂ O ±.14				
1a	10-15	0.40	2.46	14.0	1.52	0.53	2.55	6.12			5YR	8/1
1b	10-15	0.47	2.43	15.0	1.57	0.53	2.65	6.25				
2	10-15	0.52	2.96	15.0	2.24	0.86	2.53	5.41			10YR	8/1
3a	10-15	0.55	2.73	15.0	1.93	0.70	2.65	5.72			7.5YR	8/1
3b	10-15	0.50	2.70	13.0	2.67	0.81	2.59	5.28				
4a	25	0.50	2.86	14.0	1.75	0.90	2.34	5.23			10YR	8/1
4b	25	0.52	2.83	15.0	1.89	0.81	2.59	5.54				
5a	25-30	0.53	3.16	16.0	2.00	0.78	2.11	4.98			10YR	8/2
5b	25-30	0.60	3.40	17.0	2.06	0.86	2.20	5.01				
6	35	0.75	4.29	19.0	2.24	1.40	1.73	4.25			10YR	7/3
7	45-50	0.67	3.60	20.2	1.72	0.85	1.89	4.60			10YR	6/4
8	70	0.62	3.59	19.8	1.71	0.83	1.89	4.62			7.5YR	6/4
9a	85	0.63	4.25	18.0	1.01	0.60	1.42	3.18			7.5YR	6/3
9b	85	0.63	4.31	24.0	1.27	0.65	1.45	3.26				
10	115	0.62	4.12	21.0	1.75	0.80	1.60	4.10			10YR	7/4
11**	—	0.48	2.40	15.0	1.90	0.73	2.67	5.93			10YR	8/1

*As Fe₂O₃

** Subaqueous core sample, Chase Lake, Washington

in annual precipitation and a corresponding increase in the degree of chemical alteration. Titanium, iron, and aluminum increase with precipitation (Fig. 2); magnesium does not show a noticeable trend, and calcium, potassium and sodium decrease as precipitation increases (Fig. 3). These relative changes in elemental composition are in agreement with the weathering trends found in volcanic ash deposits in Japan by Aomine and Wada (1962). The trends in elemental composition with increasing rainfall, found by Czamanske and Porter (1965) in studying the Glacier Peak and Mazama ashes, are in agreement with the results of this report with the exception of calcium, which they found to increase with increasing rainfall.

Solubility is one of the major factors affecting the accumulation or removal of an element during weathering. Ionic potential (defined as the ionic charge of an element divided by its ionic radius) controls the solubility through its effect on the complex that the element will form in water. Cations with ionic potentials less than 3.0 tend to form soluble cations in water; cations with ionic potentials between 3.0 and 12 tend to form insoluble hydroxides; and cations with ionic potentials greater than 12 tend to form soluble complex anions (Keller, 1957).

TABLE 2. Matrix of correlation coefficients between inches of precipitation per year and weight percent of selected oxides in fifteen samples of Mazama ash.

	Precipitation	TiO ₂	Total iron*	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
Precipitation	1							
TiO ₂	.56	1						
Total iron*	.82	.88	1					
Al ₂ O ₃	.82	.76	.86	1				
CaO	-.53	-.06	-.33	-.44	1			
MgO	-.06	.62	.37	.14	.56	1		
Na ₂ O	-.83	-.76	-.95	-.80	.41	-.20	1	
K ₂ O	-.87	-.77	-.96	-.87	.49	-.20	-.95	1

* As Fe₂O₃

The elements which show the greatest removal with increasing rainfall, potassium, sodium, and calcium have ionic potentials of 0.75, 1.0, and 2.0, respectively. These are all within the range of soluble cations. The negative correlations between rainfall and elemental percentage for these three elements shown in Table 2 decrease as the ionic potentials increase toward 3.0. Magnesium has an ionic potential of 3.0, a value located directly on the boundary between soluble cations and insoluble hydroxides. This may account for the extreme variation of magnesium over wide ranges of precipitation. Variation in the micro-environments of the various sampling sites may have caused magnesium to behave as a soluble cation in one case, while, in another case, it behaved as an insoluble hydroxide. The elements which showed a relative increase during the weathering of the ash, iron, aluminum, and titanium have ionic potential values of 4.7, 5.9, and 5.9, respectively. These values are well within the range of the insoluble hydroxides. The data suggests that these elements were relatively immobile.

The weathering of silicates is primarily a process of hydrolysis (Krauskopf, 1967), i.e., the reaction between H⁺ and OH⁻ ions of water and the elements or ions of a rock or mineral. The correlation between availability of water (precipitation) and chemical alteration is given in Table 2. The presence of large quantities of water, however, is not always indicative of a high degree of chemical alteration. This is

Figure 2. Relationship between percent by weight of Al_2O_3 , Fe_2O_3 and FeO , and TiO_2 in the Mazama ash and average annual precipitation in inches.

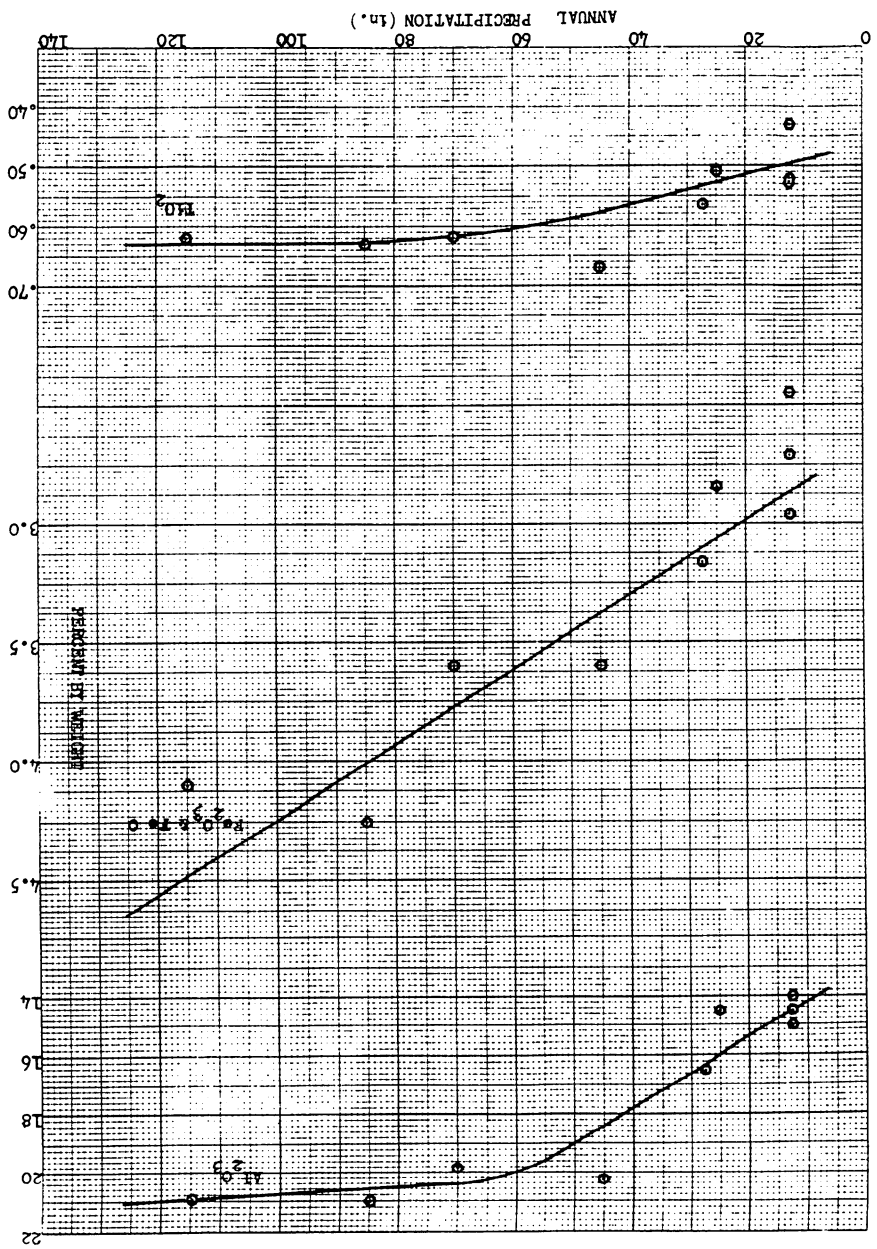
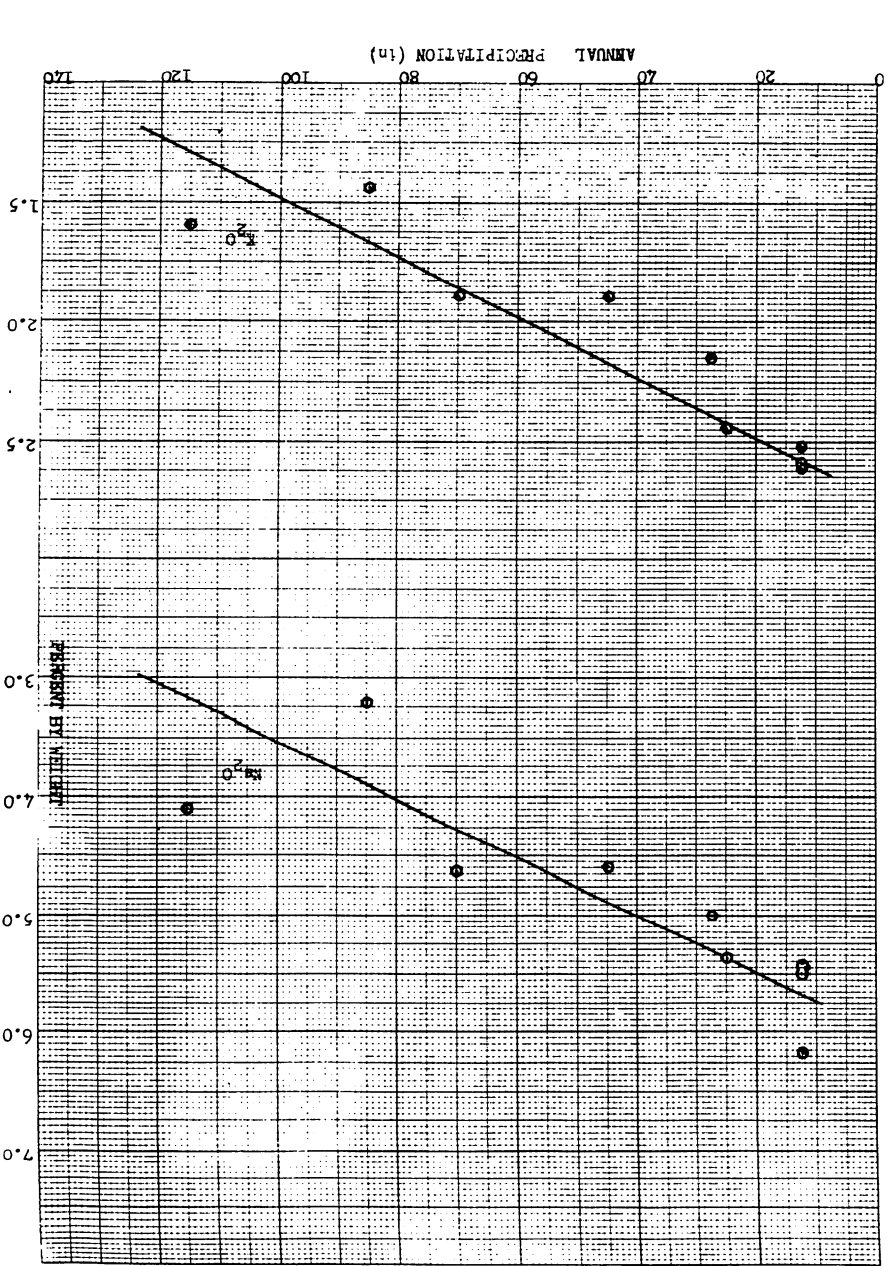


Figure 3. Relationship between percent by weight of Na_2O and K_2O in the Mazama ash and average annual precipitation in inches.



illustrated by sample 11 from Chase Lake. The composition of this subaqueous sample is similar to samples from low rainfall regions, indicating very little chemical alteration of the ash in that environment.

The degree of alteration of the subaqueous sample was probably slight because leaching was negligible in such an environment. The decomposition products of hydrolysis and other weathering reactions were not removed, as little "fresh" water was brought into contact with the ash. An equilibrium was thereby produced between the ash and the surrounding solution. Thus, very little weathering of the ash occurred.

The percentages listed in Table 1 represent only the relative amounts of the various elements in the samples. They do not indicate the absolute loss or gain of the constituent oxides relative to the original composition of the unaltered ash. The magnitude of such loss or gain can be approximated by a method described by Krauskopf (pp. 100-104, 1967) in which it is assumed that the Al_2O_3 content of the ash layer does not change with degree of weathering. This assumption appears valid in that Al_2O_3 shows a relative increase as precipitation increases (*i.e.*, while the other elements were leached out of the ash layer, Al_2O_3 increased in percentage because it was not removed). By assuming immobility of Al_2O_3 , the loss or gain of each oxide relative to constant Al_2O_3 can be calculated.

The relative percent of loss or gain for the various oxides is graphed versus precipitation on Figures 4 and 5 and summarized on Figure 6. Two reference standards were employed: one a jump pumice from near the crater on Mount Mazama, the other on what is considered an essentially unweathered sample from the Marmes Site of this report (sample #1). The composition of either standard might be considered similar to the original ash composition. Because of slight differences in the composition of the samples, the plots of percentage change do not pass through the origin of the graph. However, the trends determined using the two "unweathered" samples show the relative changes in composition which take place between the different precipitation conditions. The trends shown in Figures 4-6 reinforce and clarify the conclusions based on Figures 2 and 3. That is, the alkali elements sodium and potassium show an increase in amount of removal with increasing precipitation. The more resistant titanium, while it is actually depleted as precipitation increases, shows a relative increase only because it is not removed as readily as either K_2O or Na_2O .

Total iron (Fe_2O_3 and FeO) increases with increasing precipitation. This finding can be interpreted in two ways: (1) Soluble ferrous iron (Fe^{2+}) may have been introduced into the ash layer by leaching of upper soil horizons. Following oxidation the iron is precipitated in the ash layer as Fe^{3+} . (2) If iron is mobile, aluminum could also be expected to be translocated from above (Crompton, 1967). The latter alternative would imply that constant Al_2O_3 composition is erroneous.

Neither explanation can be refuted or supported by the data made available through this study.

Figure 4 also suggests that the rate of decrease of Na_2O and K_2O is not strictly linear with increasing precipitation when all values are "normalized" to constant Al_2O_3 content. Rather, for both elements their rate of decrease lessens abruptly at nearly 60 inches of annual precipitation. Thus, it appears that the influence of precipitation alone upon relative depletion of these elements may be overshadowed by other controlling factors at sufficiently high levels of precipitation.

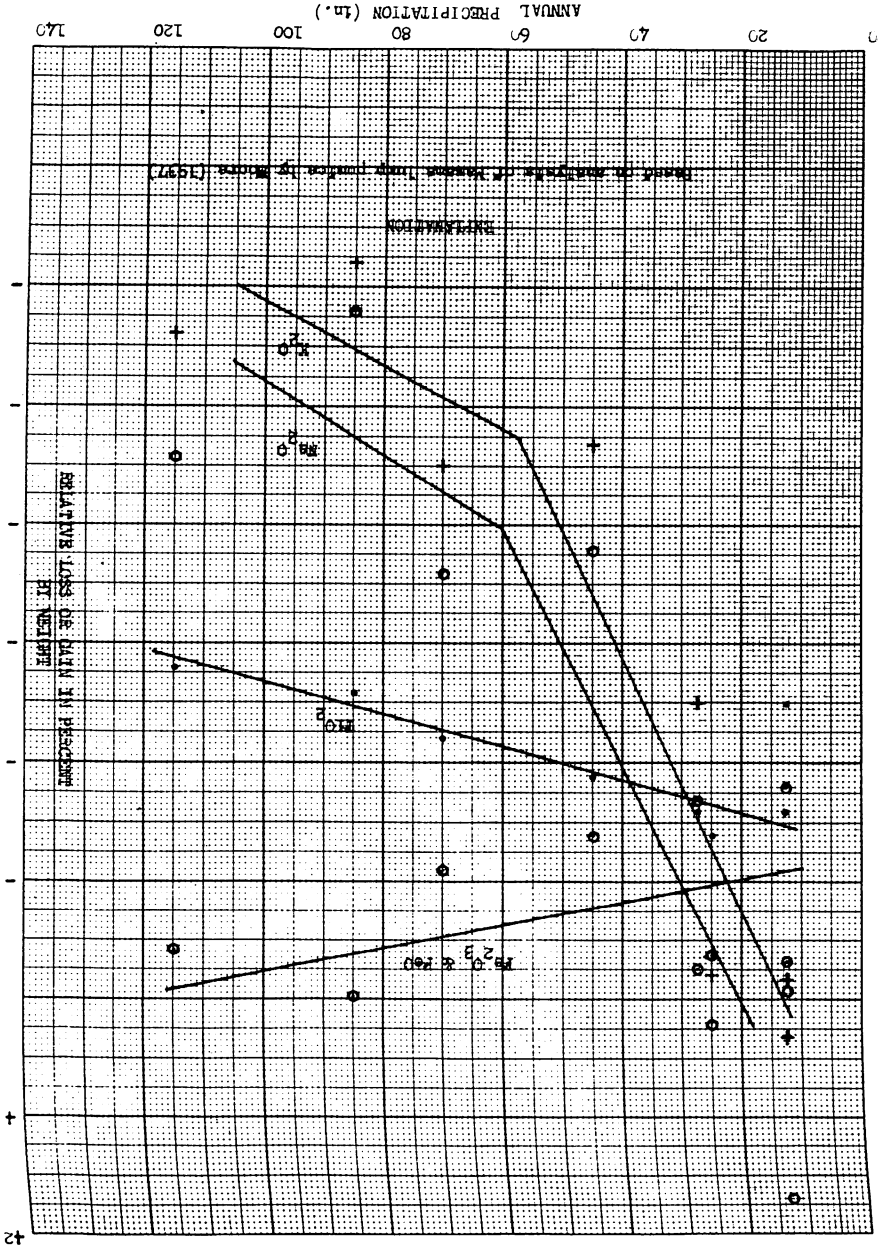


Figure 4. Relative loss or gain in percent by weight of Fe_2O_3 and FeO , TiO_2 , Na_2O and K_2O with Al_2O_3 held constant as a function of average annual precipitation in inches, based on analysis of Mazama jump pumice by Moore (1937).

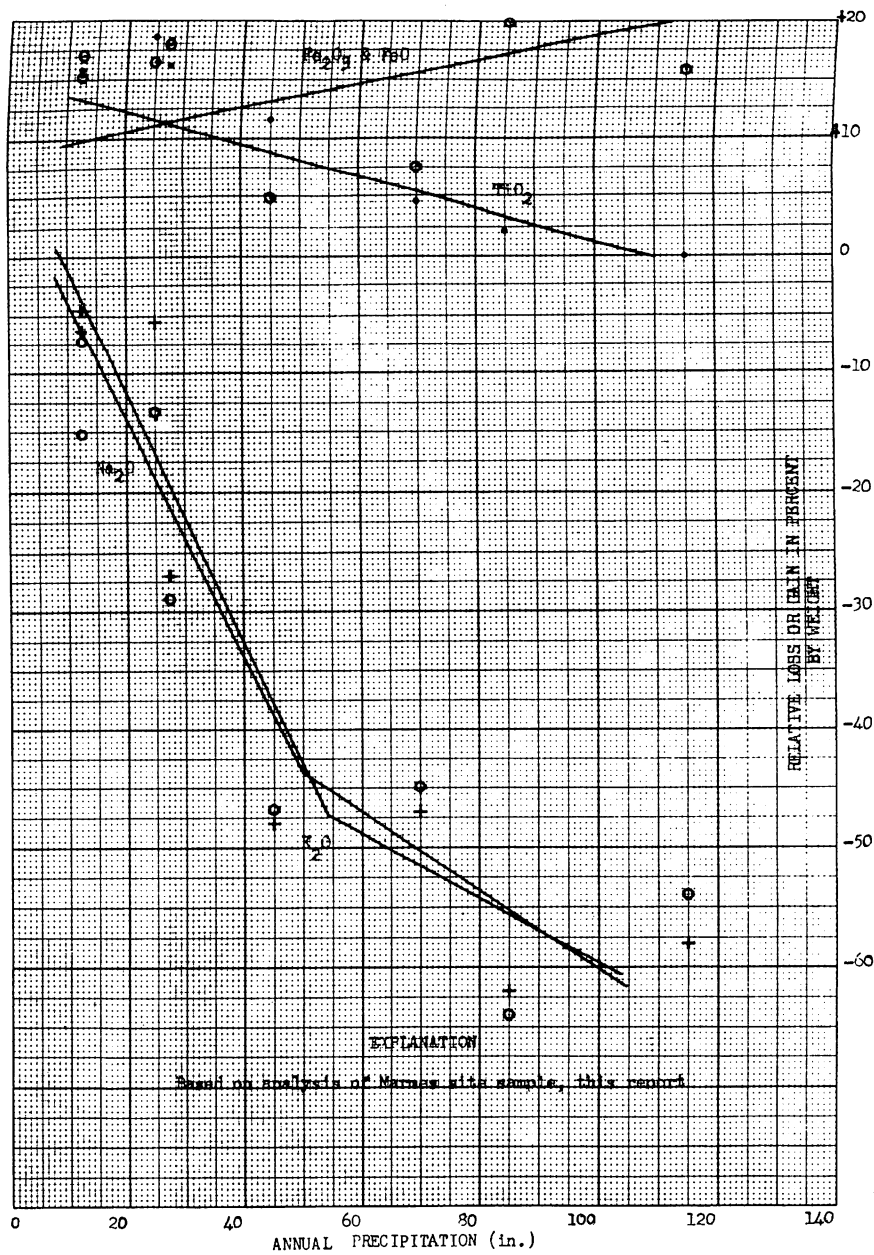


Figure 5. Relative loss or gain in percent by weight of Fe_2O_3 and FeO , TiO_2 , Na_2O and K_2O with Al_2O_3 held constant as a function of average annual precipitation in inches, based on analysis of Marmes site sample.

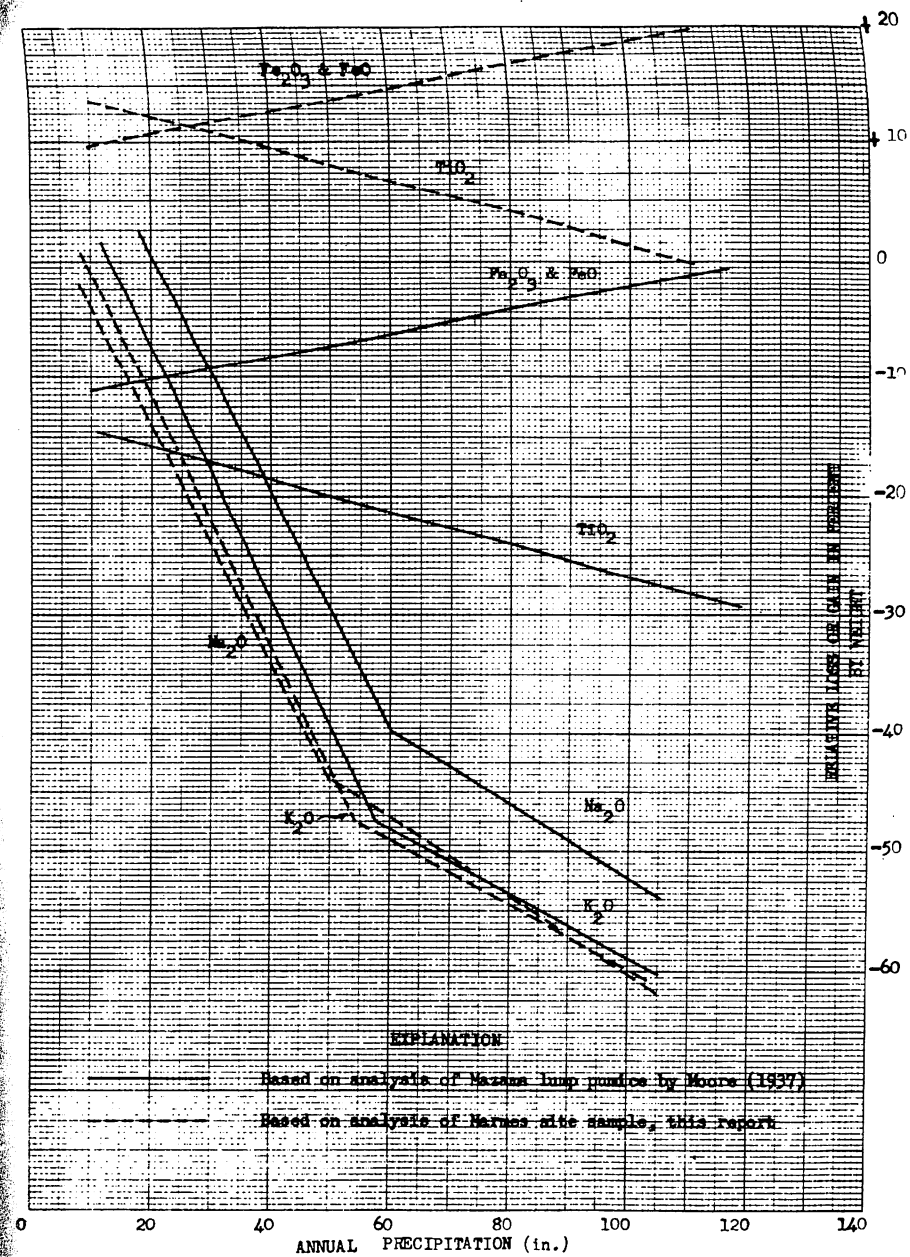


Figure 6. Relative loss or gain in percent by weight of Fe_2O_3 and FeO , TiO_2 , Na_2O and K_2O with Al_2O_3 held constant as a function of average annual precipitation in inches, based on analysis of Mazama lump pumice by Moore (1937) and analysis of Marmes site sample.

Summary and Conclusions

If original composition of Mazama ash was reasonably uniform, then the following definitive trends of compositional variation within the ash are related to differences in annual precipitation between present environments of weathering: (1) Fe, Al, and Ti increase markedly in relative abundance with increasing annual precipitation. (2) Na and K decrease markedly with increasing precipitation, with Ca demonstrating a similar but less conclusive trend. (3) Mg exhibits no conclusive relationship to annual precipitation, but appears to decrease slightly with increasing precipitation.

The above conclusions are compatible with chemical predictions for the behavior of the respective elements in a hydrolyzing, weathering environment based on a consideration of their respective ionic potentials. That is, elements of (1) above are expected to form insoluble hydroxides; elements under (2) to form soluble cations, and Mg is expected to form either an insoluble hydroxide or soluble cation dependent on local environmental factors. Thus, Na, K and Ca are mobile or soluble components relative to Fe, Al and Ti, are more rapidly removed from the ash, and thereby produce a relative enrichment in Fe, Al and Ti.

Strong positive correlations between changes in the amount of any element within one of the above two groups and changes in the amount of the other elements in the same group also suggest similar chemical behavior of the elements within each group.

If the compositions of all ash samples are "normalized" to an "unweathered" reference standard by assuming that Al content remains unchanged during weathering, the following approximations of percent change between conditions of 20 inches of annual precipitation and 100 inches annual precipitation have taken place over 6,600 years of weathering:

$$\text{K}_2\text{O} = -49\%$$

$$\text{Na}_2\text{O} = -46\%$$

$$\text{TiO}_2 = -11\%$$

$$\text{FeO} + \text{Fe}_2\text{O}_3 = +8\%$$

It should be emphasized that these figures are only crude approximations based on the assumptions of "normalization" described in connection with Figure 4. Nonetheless, these results illustrate rather dramatically the approximate magnitude of the absolute compositional changes effected by the relative trends described above.

Strong correlations exist between variation in annual precipitation and variation in percent by weight of Al_2O_3 , Fe_2O_3 , TiO_2 , K_2O and Na_2O in Mazama ash. Annual precipitation thus appears to be a very satisfactory index of the effective chemical weathering environment of the ash for these elements. It must be remembered, however, that weathering is controlled by many factors and locally these can modify the overall effect of precipitation.

By increasing the number of samples throughout the range of annual precipitation, it may be possible to develop an equation which would predict the ranges of composition values for selected elements in the Mazama ash using annual precipitation as the single independent variable. Such an equation could provide a "climatic correction" which would project the weathered composition of an ash deposit back to a dry environment, "unweathered" composition. Such a "climatic correction" would increase the validity of using elemental percentages as a basis for differentiating between different pyroclastic units.

Czaminske and Porter (1965) recognized that the use of the titanium content of an ash as a stratigraphic indicator requires unweathered samples. Our study confirms this, and our Figures 4-6 suggest that the $\text{TiO}_2:\text{Al}_2\text{O}_3$ ratio of an ash may be a useful indicator, even on weathered samples, because the titanium content shows only a small change relative to the aluminum content.

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