Reports

Titanium Dioxide in Pyroclastic Layers from Volcanoes in the Cascade Range

Abstract. *Rapid determinations of titanium dioxide have been made by x-ray emission techniques to evaluate the potentiality of using the* TiO_2 *content of samples for checking field correlations and assisting in identification of pyroclastic units from Cascade volcanoes. Preliminary data suggest that the two most widespread units have characteristic ranges of* TiO_2 *content and that other, less extensive layers have ranges which, though characteristic, often overlap the ranges of the more widespread layers. Relative to fresh samples, weathered samples from B and C soil horizons are enriched in* TiO_2.

The usefulness of widespread layers of volcanic ash as markers of stratigraphic horizons in Pleistocene sediments of the Pacific Northwest is widely recognized, and recent work has served to differentiate several of the most important layers on the basis of stratigraphic position and petrographic characteristics (*1–3*). The Glacier Peak ash, recently dated at close to 12,000 years old (*3*), and the 6600-year-old Mazama ash (ash layer O of Crandell and others, *1*) are of particular value in stratigraphic studies of late-Wisconsin events, while two widespread layers of ash from Mount St. Helens (ash layer Y, 3200 years old, and ash layer W, 400 to 500 years old) are important in studies of post-Hypsithermal (Neoglacial) events. In many areas, these pyroclastic layers can be easily distinguished from one another by stratigraphic position, degree of weathering, thickness, and grain size. In certain instances, however, especially at a distance from the source where grain size and thickness are minimal, two or more ashes may exhibit similar gross characteristics that make field identification difficult. Petrographic methods serve to identify ash layers but entail time-consuming laboratory techniques and considerable experience. Our study was begun in hope of discovering a fairly rapid analytic method that might serve, independently or in conjunction with other work, to differentiate ash layers with minimum effort.

Titanium was chosen as a potentially useful element for distinguishing between pyroclastic layers because of its geochemical characteristics, because TiO_2 content is relatively easy to measure, and because available analyses show an appreciable difference between the TiO_2 content of whole pumices from Glacier Peak and Mount Mazama, as well as the respective glass fractions (Table 1). Although its behavior during chemical weathering is not well known, the Ti^{4+} ion should be relatively immobile. Titanium freed from glass or crystals is likely to be precipitated as an oxide or to be effectively tied up in a residual clay-mineral fraction. In fact, geochemical studies of weathering (*4–6*) suggest that the TiO_2 content of weathered rock and pumice, and of residual soils, generally remains more nearly constant, relative to Al_2O_3, than the contents of other major oxides.

Samples of fine ash were separated from coarse organic debris and exotic pebbles by sieving with a 115-mesh screen; coarse samples were sieved and hand-picked to obtain the larger fragments of clean ash for analysis. Large fragments of pumice were washed when necessary, and the outer portions were cut away to obtain clean pieces. Three-gram portions of each sample were ground 20 to 40 minutes with a motor-driven Fischer grinder. Ash samples were cleaned only by megascopic mechanical sorting because a rapid and simple analytical procedure was desired. Our data (Fig. 1) suggest that the lack of "rigorous" cleaning did not appreciably extend the measured ranges of TiO_2 content for Glacier Peak and Mazama ejecta.

For analysis by x-ray emission techniques, 1 g of each ground sample was compressed at 2720 atm into a 35-mm pellet with boric acid backing (*7*). The Cr-target of a General Electric EA-75 x-ray tube was used with an SPG-7 flow-type proportional counter tube. We used 40 kv and 70 ma for excitation, a vacuum path with a 0.005 by 1¼-inch (0.1 by 32 mm) collimator, and a 1.5-volt baseline with a 2-volt window. Under these conditions a precision of 0.0015 percent TiO_2 (by weight) was obtained. Samples G-1, W-1, and 56P24, containing 0.26, 1.07, and 0.43 percent TiO_2, respectively, were used as comparison standards to establish a linear calibration. Excluding sieving and grinding time, which need not be attended, a sample can be prepared as a briquette and analyzed in less than 10 minutes, even by a relatively inexperienced operator.

Analyses for TiO_2 in Glacier Peak and Mazama ejecta are summarized in Fig. 1 (*8*). Nearly all samples were collected from B and C soil horizons. For each eruption, three classes of sample material are distinguished. One class, shown by shaded symbols, consists of fairly coarse (3 to 25 mm) fragments of pumice from sites in Washington (Glacier Peak) and Oregon (Mazama), within 110 and 160 km of the respective vents. Most of these were collected and identified by Virginia Steen and Roald Fryxell of the Laboratory of Anthropology, Washington State University, and are of certain origin because of their size, refractive index, and proximity to one of the two vents. Two fresh samples of pumice from each eruption also were furnished by R. E. Wilcox of the U.S. Geological Survey. A second class of samples, shown by half-shaded symbols, consists of fine ash (often <115 mesh) identified as from either Glacier Peak or Mazama by optical methods (by Wilcox or Steen) or by consideration of field relationships (by Fryxell), or both. Samples collected by D. R. Mullineaux and ourselves from previously described localities, or from stratigraphic positions which allow little doubt as to age, are represented by unshaded symbols.

Examination of Fig. 1 shows that

all TiO_2 values for Glacier Peak ash lie below 0.60 percent and all those for Mazama ash lie above 0.51 percent. Most of the overlap results from analyses of three fine ashes from the Snake River Canyon. Hence the established overlap is only 0.02 percent TiO_2 for most localities in Washington. The typical difference between TiO_2 contents of ash from the two eruptions is displayed by a pair of samples from the same section, collected from a single auger hole in the southern part of Creston Bog in east-central Washington (*2, 3*). Sample 63W17, recovered from a depth of 118 to 142 cm, is fine Mazama ash with a TiO_2 content of 0.60 percent; sample 63W19, recovered from a depth of 195 to 206 cm, contains sand-size Glacier Peak ash having a TiO_2 content of 0.45 percent.

The spread in TiO_2 content for samples from each source appears to be related largely to the degree of weathering, for which the megascopic appearance of the sample is generally a good indicator. Dry samples of relatively unaltered, powdered pumice from Glacier Peak and Mount Mazama are white (2.5Y 8/0 and 10YR 8/1, respectively; see *9*). Samples of fine Mazama ash collected along U.S. Highway 97 in central Washington, which have TiO_2 contents similar to those of unaltered Mazama pumice, also are whitish (10YR 8/1 or 10YR 8/2). In contrast, TiO_2-rich samples from each family show distinct evidences of alteration. With increase in TiO_2 content, lump pumices tend to be much softer, owing to decomposition, and both pumice and ash samples tend to have yellower hues suggestive of alteration and oxidation. For example, pumice samples GP-1, GP-2-B3, and M-4 (Fig. 1) are light gray (2.5Y 8/2, 2.5Y 7/2, and 2.5Y 7/2, respectively) while ash samples with TiO_2 content greater than 0.75 percent are light gray to very pale brown (10YR 7/2 to 10YR 7/3 or darker).

The semiquantitative analyses shown in Table 2 disclose chemical changes which accompany megascopic changes in ash character and color. Fresh lump pumice samples 56P24 from Trinity, Washington, and 63W23 from Diamond Lake, Oregon, may be used as standards of comparison. Weathered lump pumice samples GP-2-B3 from Holden, Washington, and M-4 from Walker Mountain, Oregon, represent the highest degree of chemical alteration.

Table 1. Chemical analyses of Glacier Peak and Mazama whole pumices and glass fractions. The analyses for Mazama pumice and glass have not been made on the same sample, and the chemical differences between the Glacier Peak pumice and glass are more closely paralleled if our semiquantitative analysis for lump pumice (sample 63W23 from Diamond Lake, Oregon; see Table 2) is used for comparison with the glass fraction.

Oxide	Glacier Peak		Mazama	
	Pumice*	Glass†	Pumice‡	Glass†
SiO_2	65.49	69.22	68.56	70.58
Al_2O_3	16.01	14.30	14.22	14.42
TiO_2	0.43	0.28	0.58	0.42
Fe_2O_3	1.16	0.62	1.42	0.57
FeO	1.88	1.08	1.49	1.24
MnO	0.07	0.05	0.03	0.06
MgO	1.67	0.69	0.83	0.51
CaO	3.64	2.19	2.35	1.83
Na_2O	3.87	3.53	5.18	5.08
K_2O	2.20	2.74	2.47	2.70
P_2O_5	0.12	0.12	0.10	0.09
H_2O+	2.69	3.49	>3.32	2.01
H_2O-	0.79	1.23		0.10

* Lump pumice, Chiwawa River at Phelps Creek, Trinity, Wash., sample 56P24, collected by H. A. Powers, 1956. U.S. Geological Survey analysis C970. † Analyses I and III of Powers and Wilcox (*2*). ‡ Analysis of younger lump pumice from Chemult, Oregon (Moore, *15*).

Approximately the same chemical changes have taken place in the Glacier Peak and Mazama ejecta we have analyzed; relative increases in TiO_2 content are accompanied by apparent increases in Al_2O_3, CaO, and total iron, and by relative decreases in SiO_2, K_2O, and Na_2O. Aomine and Wada (*5*) have noted similar changes in elemental composition within differentially weathered layers of pumice and ash in Japan. In general, TiO_2 contents of samples from B and C horizons of well-drained soils are progressively greater for localities with higher precipitation. This relationship confirms the expectation that relatively more weathering, and hence apparent TiO_2 concentration, should take place in the B and C horizons in more humid regions.

Depletion in TiO_2-rich mafic crystals could bring the TiO_2 content for fine Mazama ash into the range typical for Glacier Peak ejecta (Table 1 and Fig. 1). The apparent correlation between amount of precipitation and TiO_2 content of samples makes it difficult to evaluate the extent of crystal segregation with distance or direction from the vents because a decrease in concentration of crystals produces changes in ash composition essentially opposite to those produced by weathering. The bulk chemical data given in Table 2 for samples 65W3 from Manyberries, Alberta, 65-S-36 from Steptoe Canyon, Washington, and 65-S-45 from Lewiston, Idaho, suggest that some samples may be deficient in crystals. If true, the "normal" TiO_2 contents of many relatively unaltered samples—for example, 65-S-35, 63722-9, 8-14-63-1, and 65418-1 (Table 2)—probably result from slight crystal fractionation plus incipient weathering.

Three samples of Mazama ash (65-S-30, 65-S-36, 65-S-45) from the Snake River Canyon, collected by Roald Fryxell from basal layers of massive ash deposits 30 to 90 cm thick, contain only 0.52 to 0.53 percent TiO_2. The basal ash is thought by Fryxell to represent initial fallout. Aside from reworking in situ, at least two mechanisms are possible for pro-

Table 2. Semiquantitative chemical analyses for pumices and ashes. Analyses were made on undiluted rock powders by x-ray emission (*16*). Collection sites are given in the text.

Sample	SiO_2	Composition (percentage by weight)			CaO	K_2O	Na_2O
		Al_2O_3	TiO_2	Total iron*			
			Glacier Peak				
56P24†	65.49	16.01	0.42	3.25	3.64	2.20	3.87
65W3	68.1	13.7	.42	3.2	3.1	2.6	
GP-2-B3	59.1	18.8	.59	5.0	3.8	1.7	3.3
			Mazama				
63W23	65.4	15.9	0.60	3.4	2.6	2.2	4.5
65-S-36	68.3	14.1	.52	3.0	1.8	2.6	
65-S-45	68.0	14.1	.53	3.2	1.8	2.5	
65-S-35	67.4	14.4	.58	3.7	2.1	2.5	
63722-9	64.9	15.1	.60	3.7	2.3	2.3	
8-14-63-1	63.7	16.2	.58	2.9	2.4	2.2	
65418-1	61.2	16.1	.61	3.1	2.3	2.1	
8-14-62-6	58.2	18.8	.76	4.5	2.5	1.9	
M-4	54.7	22.3	.74	5.0	3.3	1.5	3.2

* As Fe_2O_3. † Analysis from Table 1.

Table 3. Titanium dioxide contents of some Mount St. Helens and Mount Rainier pumices.

Pyroclastic layer	Sample number	Color*	TiO_2 (% by wt.)
W	63724-1	2.5Y8/0	0.46
W	12-7-62-8	7.5YR8/0	0.51
W	8-15-64-9	7.5YR8/0	0.55
Y	8-18-63-7	7.5YR8/0	0.53
Y	8-22-61-5	2.5Y7/2	0.62
Y	8-14-61-1	2.5Y8/0	0.62
T	63724-2	2.5Y8/0	0.66
T	8-15-64-8	5Y8/1	0.69
T	12-7-62-9	.....	0.72
C	8-16-63-9	10YR7/1	1.05
C	64925-1	2.5Y7/2	1.08
C	8-31-64-5	10YR6/1	1.26
R	8-5-63-2	2.5Y7/2	1.16

* Munsell notation (*9*).

duction of glass-rich ash. (i) Crystal content (composition) of ash may change during the course of an eruption, with ashes of different compositions encountering different wind patterns. (ii) Local differences in ash composition may be caused by shifting winds during an eruption, by "layering" of ash in winds at different altitudes, or by distance from the vent. If the basal ash represents initial fallout which was crystal-deficient, preservation of low TiO_2 values and a glass-rich bulk chemistry at these localities is probably due to unusual ash thickness and low precipitation. Five additional samples from Steptoe Canyon, collected from upper, apparently reworked portions of the ash beds and from a talus, have TiO_2 contents of 0.58 or 0.59 percent (of these samples only 65-S-35 is plotted on Fig. 1). Comparison of the analyses for samples 65-S-36 and 65-S-35 in Table 2 shows that the latter sample has undergone slight chemical changes here considered typical of weathering.

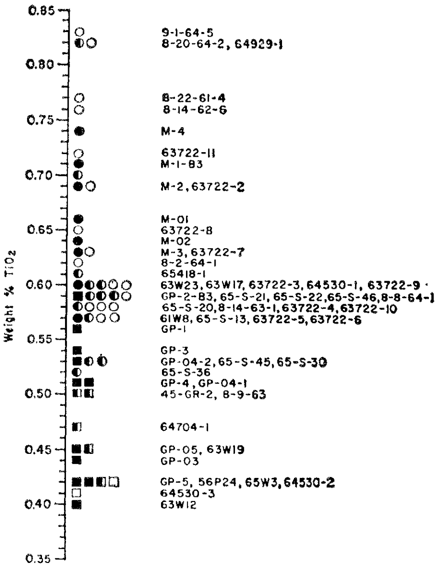

Fig. 1. Titanium dioxide contents of Mazama (circles) and Glacier Peak (squares) ejecta. Shaded symbols represent pumice; half-shaded, ash (corroborated); open, ash (uncorroborated).

Sample 63722-9, from 2.4 km north of Swauk Pass on Route 97, is representative of a suite of ten fine, white samples of Mazama ash collected from the east-central Cascades. Its composition is remarkably similar to that of 63W23 but, as noted, thin layers of crystal-deficient ash could achieve a composition similar to that of the fresh lump pumice as a result of incipient weathering.

Color appears to be a good indicator of alteration for samples collected from B and C soil horizons at sites which lie above the water table. Samples taken from bogs have undergone relatively little chemical change (Table 2) but may have misleading appearances. Sample 65418-1, from the Tri Lakes Bog in the Puget Lowland, is pale brown (10YR 6/3) but has a TiO_2 content (0.61) near that of fresh Mazama pumice. Its color is most probably due to organic stains from the bog environment. Sample 8-14-63-1, from a bog near Mystic Lake in Mount Rainier National Park, is indistinguishable in TiO_2 content (0.58) and color (white; 10YR 8/1) from fresh Mazama ash. Specimen 8-14-63-1, differs markedly in appearance and composition (compare 8-14-62-6, Table 2) from five samples of Mazama ash, collected from well-drained sites in the park, which have colors ranging from light gray to pale brown (10YR 7/2 to 10YR 6/3) and show a relatively narrow range in TiO_2 content from 0.76 to 0.83 percent.

Table 3 presents data for several other pyroclastic layers important to Pleistocene studies in western Washington, namely, layers T, W, and Y from Mount St. Helens and layers C and R from Mount Rainier (*1, 10*). Samples were collected as coarse sands and pumice fragments. The TiO_2 contents of St. Helens pumices are similar to those of Glacier Peak and Mazama ejecta, but the more restricted distribution of the St. Helens ash falls (*1*) and their relatively recent age and corresponding stratigraphic position prevent this overlap from negating the potential usefulness of the TiO_2 method for characterizing the two older, more widespread pyroclastic layers. The method could prove useful in distinguishing between layers T and W and between the W and Mazama or T and Glacier Peak layers.

The Mount Rainier pumices, as expected from the more mafic nature of ejecta from that volcano, are much richer in TiO_2 and distinctly darker than the other pumices studied (Table 3). D. R. Mullineaux (*11*) has noted that the C layer is not homogeneous and that darker layers of pumice of the aspect of 8-31-64-5 contain fragments of lighter C pumice (probably the less TiO_2-rich variety). The TiO_2 data support the conclusion, evident from field relationships, that layer C is of complex origin.

Particular interest has centered on an extensive layer of "fresh", pale-yellow ash and pumice within Mount Rainier National Park. Although the layer has been described as a young ash fall from Mount Rainier (*12*), Crandell and others (*1*) believe it represents the Y layer from Mount St. Helens. Analyzed samples, including 8-14-61-1 from the Kautz Creek exposure (*12*, plate 4, B), show TiO_2 contents characteristic of Mount St. Helens eruptions.

Titanium dioxide contents of the ashes reflect chemical differences in the magmas associated with individual volcanoes and appear to show a correlation with mafic mineral assemblages and glass refractive indices of the ashes (*1, 2*). Determination of TiO_2 content may prove useful in identifying pyroclastic layers (*13*). Layers within a particular field area should be identified initially by a combination of known methods, including stratigraphic position, refractive indices and composition of the glasses, relative abundance and refractive indices of the heavy minerals, and TiO_2 content. Once an identity has been established, rapid, routine determination of TiO_2 content should facilitate correlations within local areas. The narrow ranges in TiO_2 content for Mazama ash from well-drained localities within Mount Rainier National Park and along 80 km of U.S. Highway 97 between Swauk Prairie and Rocky Reach Dam in the east-central Cascades of Washington are typical examples (*14*).

While our attention has been directed toward one element, it is possible that pyroclastic layers could be more definitely characterized chemically by measuring suitable trace-element ratios. Such measurements might prevent confusion of the effects of enrichment by alteration with inherent elemental abundances; this confusion affects the use of TiO_2 as an identifying parameter.

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Radiation Sintering of Lunar Dust

Abstract. *Protons in the solar wind displace atoms in the grains of lunar dust. These atoms may, through diffusion, sinter the dust layer into a partly coherent but still highly porous structure.*

It has been variously suggested (*1*) that nearly all the moon's surface is covered by a layer of fine dust. Optical evidence seems to indicate that this layer is exceedingly porous and that the micron-size particles cast shadows whenever the angle of the incident light is not normal. The exceedingly low thermal inertia of the surface can also be explained by means of this model, although the conclusions are less direct. These factors, which are related to the basic question of the mechanical strength and rigidity of the surface, are critical for the landing of a moon probe.

Several authors have suggested that corpuscular radiation from the sun, which consists primarily of protons, may produce coloration (*2*) of lunar dust and even sputtering, which could explain the polarization behavior (*3*) and perhaps could increase cohesion between dust particles (*4*). Increase of cohesion seems unlikely because very high doses, corresponding to about 10^5 years of unperturbed exposure to solar protons, would be necessary to obtain it. I wish to draw attention to the possibility that the protons may lead to gradual sintering of the particles of lunar dust into a relatively rigid but open—that is, not dense—structure, without sputtering. By sintering I mean gradual transition from a local mechanical contact to a rigid local bond between two grains without formation of a solid mass. Recent experiments done at the Brookhaven National Laboratory show that 80-μ diamond dust sinters near 50°C when exposed to a fast (about 1 Mev) neutron flux of about 10^{20} neutrons per square centimeter (*5*). Similarly, 40-μ Al_2O_3 dust is sintered at approximately the same temperature after irradiation of 6×10^{18} neutrons per square centimeter (*6*). Unfortunately the lowest total neutron flux at which these phenomena occur is not known.

Essentially all solid-state reactions take place because of the availability and motion of crystal lattice defects such as vacancies or interstitial atoms. Dienes and Damask (*7*) and others (*8*) have shown that neutron or proton irradiation can accelerate these reactions by a factor of 10^6 or more because it increases the concentration of vacancies and interstitial atoms above that normally present. It is essential, however, that there be enough thermal agitation to provide for the motion of these defects. It is well known that interstitial atoms in ionic solids (*9*) and metals (*10*) can move at temperatures as low as 10°K. Inasmuch as the temperature of the lunar surface varies between about 150° and 350°K one can safely assume that at least the interstitial atoms have enough mobility, especially when the sun is high in the lunar sky. The rather immobile vacancies may lead to formation of color centers or to luminescence.

In making quantitative estimates it is important to note that neutrons displace atoms in all kinds of solids only by direct elastic collisions. On the other hand, charged particles such as protons can loose energy and produce displacements not only by elastic collisions but also by double-ionization (*11*) processes in insulating crystals. The exact composition of the lunar surface is not known, but one suspects the presence of various hard oxides such as quartz and magnesium oxide (*2, 3, 12*). Inasmuch as Al_2O_3 resembles these rocks more than diamond does, the data from Brookhaven on Al_2O_3 are of primary significance. The Debye temperature, melting point, and type of bonding suggest that the mobility of defects in these oxides is comparable. One expects also that the rate-controlling process is the motion of the interstitial oxygen. The results obtained at Brookhaven on sintering of Al_2O_3 indicate that the number of displaced atoms in each grain is about 20 times greater than the number of atoms on its surface. A large fraction of the atoms will reach the surface because of the outward strain gradient. One can thus expect that, under these conditions, local sintering will occur when the number of displaced atoms reaching the surface is perhaps 10 times as great as the number of atoms on the surface.

The average proton flux impinging upon the lunar surface can be divided into: (i) solar wind (*13*), or expanding solar corona, of a mean energy of about 4 kev and a flux of 10^8 particles per square centimeter per second; (ii) the newly discovered, high-energy, continual flux (*14*) of high-energy protons which varies from perhaps 1 to 10 particles cm^{-2} sec^{-1} at 2 Mev to 1/10 particle cm^{-2} sec^{-1} at 10 Mev; and (iii) protons associated with solar flares (*15*) which can reach 10^3 particles cm^{-2} sec^{-1} at 1 Mev and a rapidly decreasing flux at higher energies. While theoretical and experimental information about the production of defects and the range of high-energy protons is fairly good, the situation with 4-kev protons is rather uncertain. From various con-