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The Effect of Dissolution of Volcanic Glass on the Water Chemistry in a Tuffaceous Aquifer, Rainier Mesa, Nevada

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By ART F. WHITE, HANS C. CLAASSEN, *and* LARRY V. BENSOI˥

GEOCHEMISTRY OF WATER

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1535-Q

UNITED STATES DEPARTMENT OF THE INTERIOR

CECIL D. ANDRUS, *Secretary*

GEOLOGICAL SURVEY

H. William Menard, *Director*

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CONVERSION TABLE

The metric units in this report can be converted to inch-pound units by use of the multiplication factors given as follows:

To convert metric unit	Multiply by	To obtain U.S. inch-pound unit
kilometer (km)	0.622	mile (mi)
meter (m)	3.281	foot (ft)
square kilometer (km²)	.387	square mile (mi²)
meter per kilometer (m/km)	5.280	foot per mile (ft/mi)
liter per second (L/s)	15.850	gallon per minute (gal/min)
meter per second (m/s)	3.280	foot per second (ft/s)
cubic hectometer (hm³)	810.7	acre-feet (acre-ft)
cubic centimeter (cm³)	.06102	cubic inches (in³)
square meter per gram (m²/g)	4881.3	cubic feet per pound (ft³/lb)

GEOCHEMISTRY OF WATER

THE EFFECT OF DISSOLUTION OF VOLCANIC GLASS ON THE WATER CHEMISTRY IN A TUFFACEOUS AQUIFER, RAINIER MESA, NEVADA

By Art F. White[*], Hans C. Claassen, and Larry V. Benson[*]

ABSTRACT

Geochemistry of ground water associated with the Tertiary tuffs within Rainier Mesa, southern Nevada, was investigated to determine the relative importance of glass dissolution in controlling water chemistry. Water samples were obtained both from interstitial pores in core sections and from free-flowing fractures. Cation compositions showed that calcium and magnesium decreased as a function of depth in the mesa, as sodium increased. The maximum effect occurs within alteration zones containing clinoptilolite and montmorillonite, suggesting these minerals effectively remove bivalent cations from the system.

Comparisons are made between compositions of ground waters found within Rainier Mesa that apparently have not reacted with secondary minerals and compositions of waters produced by experimental dissolution of vitric and crystalline tuffs which comprise the principal aquifers in the area. The two tuff phases have the same bulk chemistry but produce aqueous solutions of different chemistry. Rapid parabolic dissolution of sodium and silica from, and the retention of, potassium within the vitric phase verify previous predictions concerning water compositions associated with vitric volcanic rocks. Parabolic dissolution of the crystalline phase results in solutions high in calcium and magnesium and low in silica. Extrapolation of the parabolic dissolution mechanism for the vitric tuff to long times successfully reproduces, at comparable pH, cation ratios existing in Rainier Mesa ground water. Comparison of mass-transfer rates of the vitric and crystalline tuffs indicates that the apparent higher glass-surface to aqueous-volume ratio associated with the vitric rocks may account for dominance of the glass reaction.

INTRODUCTION

Volcanic glasses are metastable supercooled liquids that exist due to an extreme reduction in nucleation, crystallization, and diffusion rates imposed by rapid increase in viscosity during initial rapid cooling. Rarity of natural glasses older than Cretaceous age tends to con-

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firm their metastable nature. Because of this relatively rapid reactivity, numerous researchers have suggested that volcanic glasses may contribute significantly to chemical composition of waters associated with volcanic rocks. The purpose of this study is to investigate the geochemical nature of ground waters contained in vitric and nonvitric tuffaceous aquifers of Rainier Mesa, Nev., and to ascertain the importance of glass dissolution and alteration on the water composition.

SETTING OF RAINIER MESA

Rainier Mesa, an eroded volcanic plateau, is in southern Nevada, approximately 160 km northwest of Las Vegas; it is within the north-central part of the Nevada Test Site operated by the U.S. Department of Energy. Rainier Mesa generally trends north-south and rises more than 750–1,000 m above neighboring basins; altitude of the mesa ranges between 2,250 and 2,340 m. The mesa is characterized by low precipitation, low relative humidity, and large daily variations in temperature. Average annual precipitation on Rainier Mesa is estimated to be 0.2 m per year.

PREVIOUS STUDIES

Chemical composition of water associated with vitric rocks can be inferred by comparison of weathered glasses with fresh glass or their crystalline counterparts. In comparing paired chemical analyses of weathered glass and crystalline rocks that had undergone primary crystallization, Lipman (1965) found that the glasses were deficient in silica and sodium and enriched in potassium. A number of rhyolitic tuffs from southern Nevada were included in these rock pairs. Lipman also presented several analyses of ground water from Rainier Mesa and other semiarid volcanic terrain in the Western United States; he pointed out that the main constituents in the ground water, sodium and silica, are those elements most deficient in weathered glasses.

In comparing a number of hydrated and nonhydrated glasses from rhyolites in southern Nevada, Noble (1965, 1967) concluded that the earlier stages of ground-water alteration of hydrated glass consist of loss of sodium and silica and gain of potassium. With continued alteration, potassium may also be leached. Aramaki and Lipman (1965) showed that loss of sodium in a number of rhyolitic glasses from Japan was directly related to the hydration state of the glass.

In investigating ion-exchange capacities of natural glasses, Truesdell (1962, 1966) concluded that glasses display an affinity for hydrogen, potassium, and calcium relative to sodium. Truesdell predicted that waters reflecting glass weathering will become sodium rich, similar to waters found in parts of the arid Southern United

States, where tuffs make up a considerable part of subsurface formations. White and Claassen (1976) and White (1979) also suggested that the high concentrations of dissolved sodium and silica in ground water in Oasis Valley, Nev., were related to glass dissolution in surrounding rhyolitic tuffs.

ACKNOWLEDGMENTS

GEOLOGY

Rocks comprising Rainier Mesa are primarily Tertiary (Miocene) volcanic tuffs overlying a Paleozoic basement composed principally of Devonian carbonate (Gibbons and others, 1963; Hanson and others, 1963; Thordarson, 1965). Figure 1 shows the general geology of the central portion of Rainier Mesa. Figure 2 shows a northwest-southeast trending cross section through the eastern side of Rainier Mesa, the position of which is also indicated in figure 1.

STRATIGRAPHY

In some locations within Rainier Mesa not included in figures 1 and 2, the tunnel beds, the oldest tuff formation shown, are underlain by and intertongued with the Redrock Valley Tuff, the Crater Flat Tuff, and the Tub Spring Member of the Belted Range Tuff. However, these Miocene formations generally lie below the hydrological and geochemical system investigated in this report. The reader is referred to Byers and others, 1976, for a discussion of their characteristics.

The tunnel beds (figs. 1 and 2) comprise a 1,000-m thickness of Miocene ash-fall tuff, reworked ash-fall tuff, tuffaceous sandstone, siltstone, and claystone. The tuff alternates between bedded and massive forms, and consists principally of nonwelded, partly-zeolitized and argillized vesicular pumice lapilli and glass shards in a porous ground mass of indurated-zeolitized volcanic ash (Diment and others, 1959; Hanson and others, 1963). The principal zeolite is clinoptilolite.
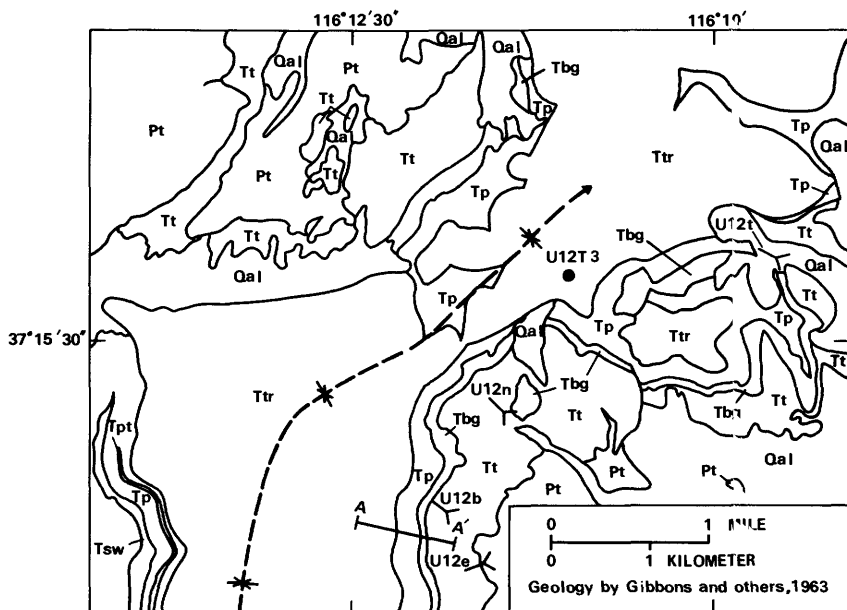
FIGURE 1.—Geologic map of Rainier Mesa and vicinity.

Also present are scattered phenocrysts of K-feldspar, plagioclase, quartz, biotite, and lithic volcanic fragments.

Overlying the tunnel beds in most of Rainier Mesa is an average 30-m thickness of the Grouse Canyon Member of the upper Miocene Belted Range Tuff. As discussed by Noble (1970), the majority of this rock is densely welded and soda-rich in which lime-poor sanidine-anorthoclase is the dominant phenocryst mineral, along with some quartz and less than 5 percent fayalite, an iron-rich clinopyroxene. The ground mass consists of fine-grained aggregates of alkali feldspar, cristobalite, and quartz. In some locations subhedral to anhedral grains of arfvedsonite, an iron-rich and sodium-rich clinopyroxene, are abundant. The source of the peralkaline Grouse Canyon Member is the Silent Canyon Caldera located northwest of Rainier Mesa (Byers and others, 1976).

The Miocene (12.5–13.2 million years before present (m.y. B.P.)) Paintbrush Tuff, erupted from Claim Canyon Caldera southwest of Rainier Mesa, generally lies unconformably on the Grouse Canyon Member of the Belted Range Tuff. On the western flank of Rainier Mesa, the undifferentiated bedded tuff of the Paintbrush is situated above the massive 120-m thickness of nonwelded to partly welded ash flow Stockade Wash Tuff, and intertongues with the partly welded to welded Topopah Spring Member of the Paintbrush Tuff

EXPLANATION

QUATERNARY { Qal ALLUVIUM

TERTIARY {
  Ttr RAINIER MESA MEMBER OF TIMBER MOUNTAIN TUFF

  Tpt>Tp Tp: PAINTBRUSH TUFF   Tpt : TOPOPAH SPRING. MEMBER OF PAINTBRUSH TUFF

  Tsw STOCKADE WASH TUFF

  Tbg GROUSE CANYON MEMBER OF BELTED RANGE TUFF

  Tt MIOCENE TUNNEL BEDS

PRE-TERTIARY { pT PRE-TERTIARY ROCKS UNDIFFERENTIATED

——— CONTACT

—✷—➤ APPROXIMATE TRACE OF RAINIER MESA SYNCLINE

〉U12t TUNNEL PORTAL AND NUMBER –– See table 1

A   A'
⊢———⊣ TRACE OF SECTION –– Section shown in figure 2

(maximum thickness 125 m). As shown in figures 1 and 2, the Stockade Wash Tuff and the Topopah Springs Member are missing from the section on the eastern flank of Rainier Mesa in the vicinity of the tunnel complex. The undifferentiated 220-m thickness of bedded Paintbrush Tuff consists principally of pumice lapilli and glass shards in a matrix of foliated volcanic ash. Minor phenocrysts consist of potassium feldspar, plagioclase, and biotite.

The Miocene (11.3 m.y. B.P.) Rainier Mesa Member of the Timber Mountain Tuff lies above the Paintbrush Tuff and comprises the cap rock of Rainier Mesa. The Rainier Mesa Member is a compositionally zoned, compound cooling unit consisting of a high-silica rhyolite tuff (120 m) overlain, with a partial cooling break, by a considerably thinner (30 m) thickness of quartz latite tuff. The Rainier Mesa Member of the Timber Mountain Tuff originated from the Timber Mountain Caldera west of Rainier Mesa. Except for a nonwelded shard tuff near the base, the partly welded to welded rocks of the Rainier Mesa Member are generally devitrified and phenocryst rich, containing abundant alkali feldspar, plagioclase, quartz, and sparse amounts of biotite, clinopyroxene, and magnetite.

STRUCTURE

As discussed by Hanson and others (1963) and Thordarson (1965), the major structure beneath Rainier Mesa is a broad north-east trending syncline that bisects the mesa into subequal northwest and
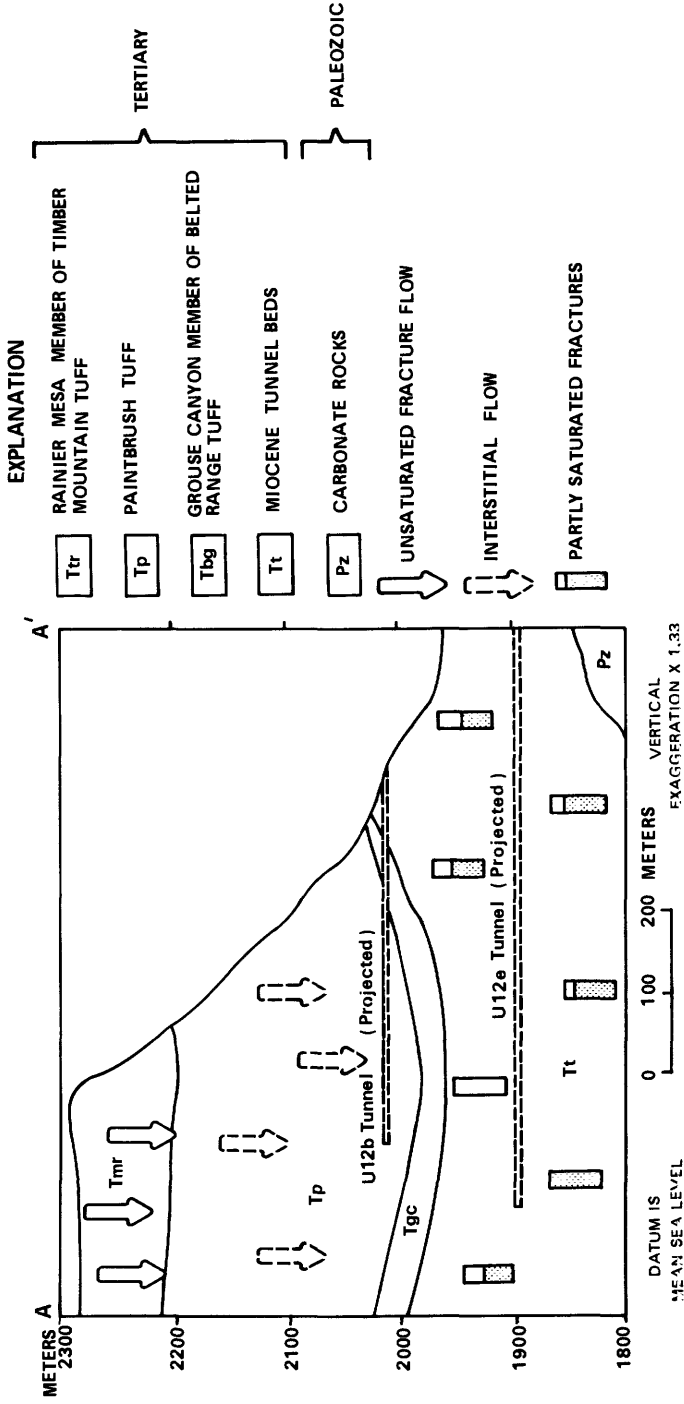
FIGURE 2.— Schematic cross section showing the stratigraphy and hydrology of Rainier Mesa.

southeast parts (fig. 1). The limbs of the syncline dip 2° to 12° and contain minor anticlinal and synclinal structures.

Joints and faults are generally inconspicuous, except locally in the nonwelded vitric, bedded Paintbrush Tuff, but are very conspicuous in the welded tuffs of the Rainier Mesa and Grouse Canyon Members. The lower rhyolitic tuff of the Rainier Mesa Member is characterized by large-scale well-formed columnar joints. These contractional joints terminate abruptly downward in the nonwelded vitric tuffs of the Paintbrush Tuff (Hanson and others, 1963).

Joints and faults also are observed in the tunnel beds, due to induration caused by extensive zeolitization. Thordarson (1965) described the width of some openings of faults and joints in the tunnel beds as being as much as 10 cm, whereas some faults and joints were completely sealed.

ALTERATION OF THE VOLCANIC ROCKS

Hoover (1968), in studying regional alteration of vitric tuffs in an area surrounding and including Rainier Mesa, described a vertical zonation of phases with clay minerals uppermost in the section followed sequentially by clinoptilolite, mordenite, and analcime. Similar zonations in vitric tuffs have also been noted elsewhere (Hay, 1963, 1968; Moila, 1970).

To investigate the specific alteration sequence of volcanic rocks within Rainier Mesa in more detail, cores were obtained from the U.S. Geological Survey core library at the Nevada Test Site. The stratigraphic sequence penetrated in core U12T 3 is shown in figure 3. The location of the core, which was recovered Feb. 8–25, 1973, is shown in figure 1.

Thin section petrography and scanning-electron microscopy (SEM) showed that glass in the tuffs of Rainier Mesa generally appeared in two forms: vesicular pumice fragments and nonvesicular glass shards. The alteration of nonvesicular glass is evidenced by the presence of etch pits in contrast to the vesicular glass that exhibits the effects of greater alteration. This is presumably due to greater surface area of the vesicular form, which enhances its rate of reaction.

X-ray diffraction analysis indicated that montmorillonite was present below 225 m in the tunnel beds of U12T 3. SEM showed that montmorillonite-coated glass surfaces appeared to form prior to and during precipitation of clinoptilolite. Above the upper zone of zeolitization, montmorillonite occurred as flakey aggregates in the form of spheres and three-dimensional "figure eights." Within the zone of zeolitization, the clay phase generally occurs as irregular aggregates that coat glass surfaces.
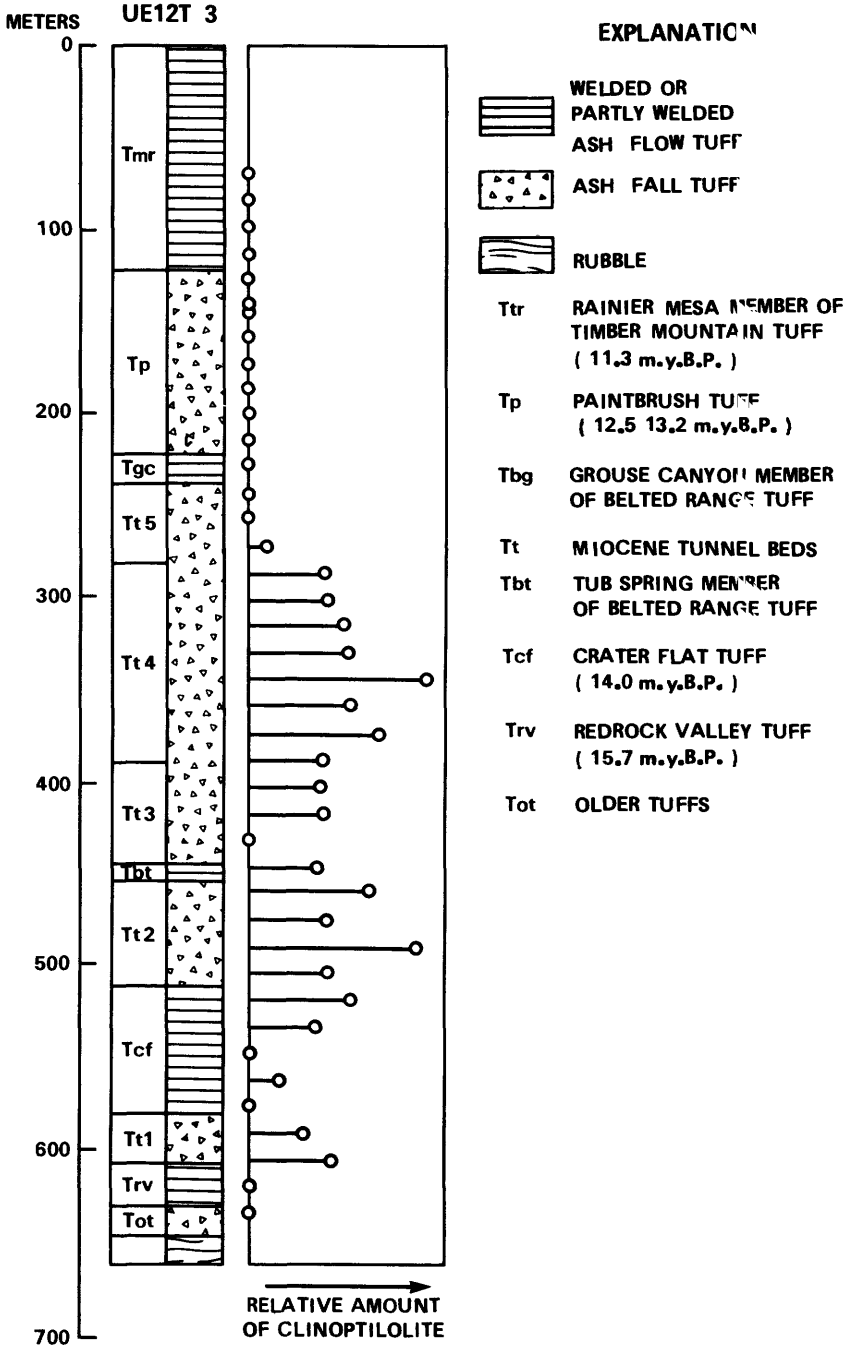
FIGURE 3.—Stratigraphy of core U12T 3.

Relative amounts of clinoptilolite present in core U12T 3, based on X-ray diffraction peak height for clinoptilolite (2.974 Å), are shown in figure 3. As indicated, although trace amounts of clinoptilolite occur throughout most of the section, extensive zeolitization is confined to the tunnel beds. SEM studies indicated that clinoptilolite appears as tabular crystals which show no features of surficial dissolution. The average of several partial chemical analyses of clinoptilolite performed by microprobe is presented in table 5. In a few core samples, a fibrous mineral tentatively identified as the zeolite mordenite, occurs as a diffuse mat coating clinoptilolite and montmorillonite. X-ray diffraction also indicated analcime was present in a few samples near the bottom of the core.

HYDROLOGY

Thordarson (1965) estimated that annual recharge from the top and sides of Rainier Mesa was approximately 4.2 cubic hectometers (hm^3). Based on hydraulic gradients, this water moves more or less vertically through the previously described sequence of tuffaceous rocks (fig. 2). These rocks can generally be grouped into three basic hydrologic units: (1) welded and partly welded tuffs of the Rainier Mesa Member of the Timber Mountain Tuff and the Grouse Canyon Member of the Belted Range Tuff; (2) friable vitric tuffs of the undifferentiated Paintbrush Tuff; and (3) zeolitized Miocene tunnel beds.

The Rainier Mesa Member and the Grouse Canyon Member possess average interstitial porosities of 14 and 19 percent, respectively; hydraulic conductivity of the Rainier Mesa Member is 4.7×10^{-9} m/s. These are the lowest values for porosity and interstitial conductivity measured in the tuffaceous strata beneath Rainier Mesa (Thordarson, 1965). However, due to extensive open joints and faults within these competent welded tuffs, fracture conductivity is generally high. The fractures in the Rainier Mesa and Grouse Canyon Members are unsaturated.

The friable vitric Paintbrush Tuff possesses an interstitial porosity of 40 percent and an average interstitial hydraulic conductivity of 1.9×10^{-6} m/s, both of which are relatively high (Emerick and Houser, 1962). The interstitial pore space is about 64 percent saturated. As discussed by Thordarson (1965), open fractures are rarely preserved in the Paintbrush Tuff due to the friable, incompetent nature of these rocks. Thus, interstitial conductivity would appear to be the dominant avenue of ground-water transport. See Claassen and White (1979), however, for a different point of view.

Winograd and Thordarson (1975) classified the tunnel beds within Rainier Mesa as a confining bed, which restricted fracture and inter-

stitial ground-water flow from the overlying tuffs from reaching the regional water table in the underlying Paleozoic carbonates. The average interstitial porosity of zeolitized Miocene tunnel beds ranges from about 25 to 38 percent and is close to 100 percent saturated (Byers, 1961). Most of this water is probably strongly held by capillary forces and is not available as free water. Interstitial hydraulic conductivity is low (9.4×10^{-8} m/s), due principally to a matrix of zeolites and clay minerals. Approximately 50–60 percent of the faults and 2 percent of the joints intersected by tunnels yielded water (Thordarson, 1965). The erratic distribution of perched fracture water is directly related to the extent, interconnection, and openness of the fracture system. However, the fact that ground water is perched more than 600 m above the regional water table indicates that the fractures are poorly connected. As suggested by Thordarson (1965), occurrences of open but empty fractures may mean either that they are open below to the regional water table or that they are poorly connected to sources of recharge in the overlying Paintbrush Tuff. Based on tritium concentrations, Clebsch (1961) estimated that waters contained in fractures in the tunnel beds ranged in age from 0.8 to 6 years.

GROUND-WATER CHEMISTRY

Ground-water samples were obtained both from fractures intercepted by drifts and adits driven into the tuffs of Rainier Mesa and from interstitial pores in core material previously described (fig. 3). Fracture-flow samples were collected over periods up to 48 hours in polyethylene containers. Alkalinity and pH measurements were obtained from samples as soon after collection as possible. Standard chemical analyses were performed by the National Water Quality Laboratory of the U.S. Geological Survey.

Interstitial water samples were obtained from selected sections of core sealed in beeswax at the time of recovery. Samples from the unzeolitized Paintbrush Tuff were generally extracted by centrifugation at 2,000 revolutions per minute (rpm) for 1 hour. Due to the lower permeability of the zeolitized tunnel beds, water samples in this tuff were generally squeezed by multiple-cycle triaxial compression (Dopek and Levinson, 1975). Fluid extraction yielded sample volumes ranging from 1 to 143 cm³. Chemical analyses were performed by the Desert Research Institute, Las Vegas, Nev.

INTERSTITIAL WATERS

Chemical analyses of waters from centrifuged and squeezed core segments, obtained at various depths, are presented in table 1. Figures 4 and 5 include plots of the relative mole percentages of major

cations and anions. As indicated, the cation composition varies between almost exclusively sodium to dominantly sodium with lesser amounts of calcium, magnesium, and potassium. The anion composition in figure 5 shows a much greater variation than the cation composition, varying between dominantly bicarbonate to dominantly chloride.

Figures 6, 7, and 8 are plots of concentrations of various chemical species as a function of depth in core U12T 3. Figure 6 indicates that interstitial silica concentrations generally increase with depth in the vitric Paintbrush Tuff to a maximum in the upper tunnel beds. Silica concentrations drop rapidly with depth in the lower half of the tunnel beds.

Although considerable scatter exists for the bicarbonate, chloride, and sulfate data, figure 7 suggests that bicarbonate concentrations increase with depth in the tunnel beds and that chloride concentrations decrease with depth. Cation data shown in figure 8 indicate that sodium concentrations increase with depth throughout the tuff sequence, with the sharpest increase in the lower tunnel beds. Calcium and magnesium exhibit sharp decreases in the lower tunnel beds.

FRACTURE WATERS

Chemical analyses of waters collected from fractures in various tunnels are presented in table 2. Data from U12b tunnel are reproduced from a report by Diment and others (1959). The relative mole fractions of cations and anions are plotted in figures 4 and 5. As is apparent from the figures, general ranges in cation compositions of fracture waters are very similar to interstitial waters. Comparisons of tables 1 and 2 also demonstrate that concentrations are also very similar. The total interstitial average cation milliequivalence per liter is 2.70, which is only slightly more than the 2.19 value for fracture waters.

In general, fracture waters plotting close to the sodium apex in figure 4 reflect ground-water flow paths which appear to have penetrated into the tunnel beds before discharging into the tunnels. For example, the average composition of U12e tunnel water plots much closer to the sodium apex in figure 4 than do U12b tunnel waters which are relatively high in bivalent cations. As shown in figure 2, U12e tunnel is generally confined to the tunnel beds, and water discharged into this tunnel must first penetrate the zeolitized tuffs. U12b tunnel is confined to the lower part of the Paintbrush Tuff, and waters discharging to this tunnel generally have not contacted the tunnel beds. However, as shown by data in table 2, considerable variations exist in the cation composition between samples in the same tunnel complex. For example, samples 29, 30, and 32 from the

TABLE 1.—*Chemical analysis of Rainier Mesa interstitial water from core U12T 3*

[Quantities are in millimoles per liter, except as indicated]

Sample No.	Depth (m)	Sodium	Potassium	Calcium	Magnesium	Bicarbonate	Sulfate	Chloride	Silica	pH
1	134.4	1.07	0.26	0.274	0.12	0.95	0.21	0.76	1.02	7.6
2	169.6	1.51	.36	.05	.29	2.25	.38	.90	.98	7.7
3	199.2	1.89	.26	.57	.26	2.25	.42	.76	.95	7.7
4	202.4	1.02	.11	.42	.17	.44	.42	1.07	1.16	7.6
5	257.6	1.30	.12	.40	.20	.43	.40	1.47	1.00	7.2
6	260.0	1.41	.14	.65	.30	.37	.74	1.75	1.25	7.5
7	441.4	2.00	.36	.22	.029	1.09	.54	.56	.82	7.6
8	442.4	2.42	.49	.27	.041	1.07	.87	.56	.88	7.6
9	291.4	1.11	.12	.20	.086	.79	.23	.59	1.25	7.8
10	320.3	1.36	.19	.23	.070	.84	.47	.85	1.25	7.7
11	320.6	1.37	.21	.45	.090	.57	-----	.99	.92	7.8
12	321.3	1.54	.21	.70	.18	1.29	.52	.82	1.28	8.2
13	350.8	1.01	.15	.32	.090	.97	.57	.85	1.25	7.9
14	411.2	1.34	.14	.14	.034	.61	.34	.45	.98	7.8
15	470.6	1.74	.038	<.005	<.002	.91	.22	.27	.75	7.9
16	472.4	2.27	.031	.005	.004	1.41	.34	.31	.72	7.9
17	501.7	2.62	.031	.055	.006	1.72	.32	.34	.64	8.1
18	503.2	2.83	.023	.045	.006	1.84	.31	.48	.66	8.1
19	532.8	3.09	.097	.025	.005	1.90	.38	.48	.69	8.0
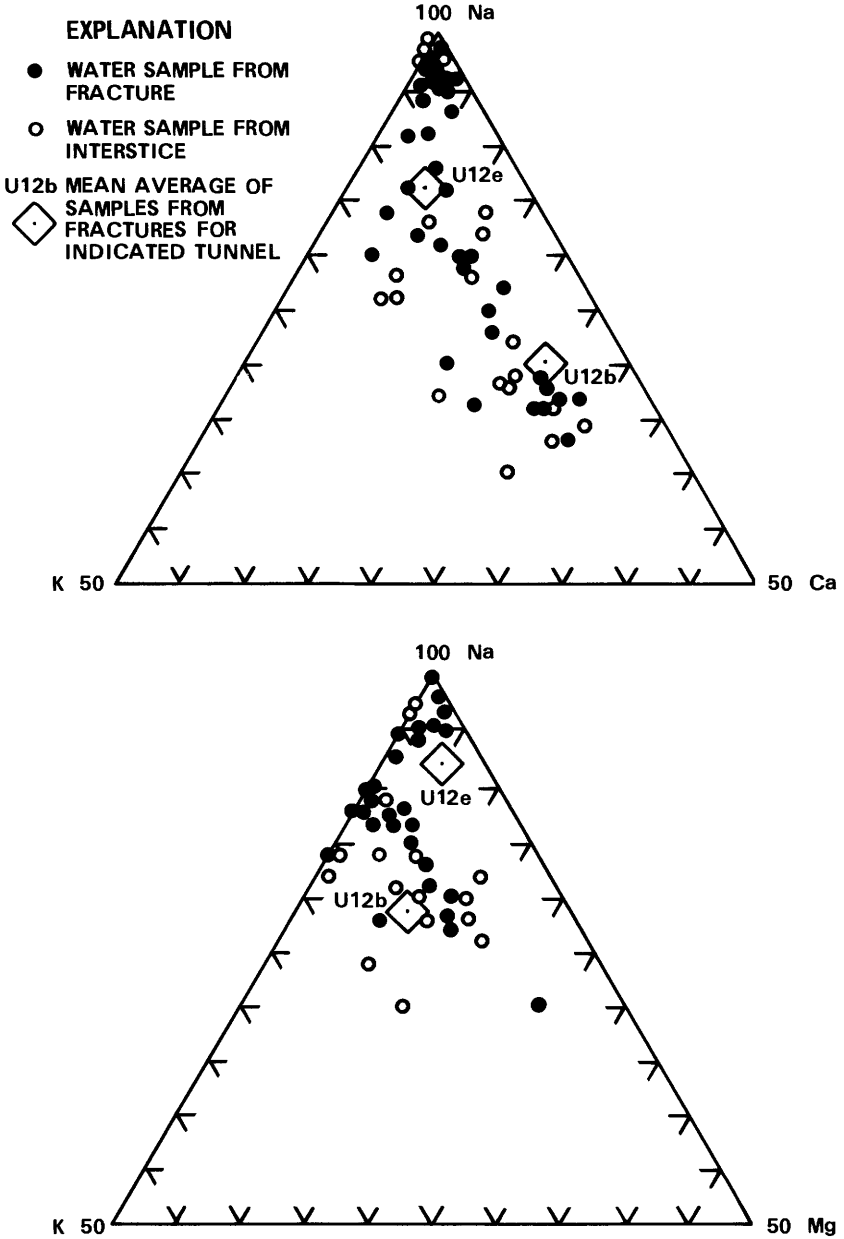
FIGURE 4.—Cation ratios of Rainier Mesa ground water.
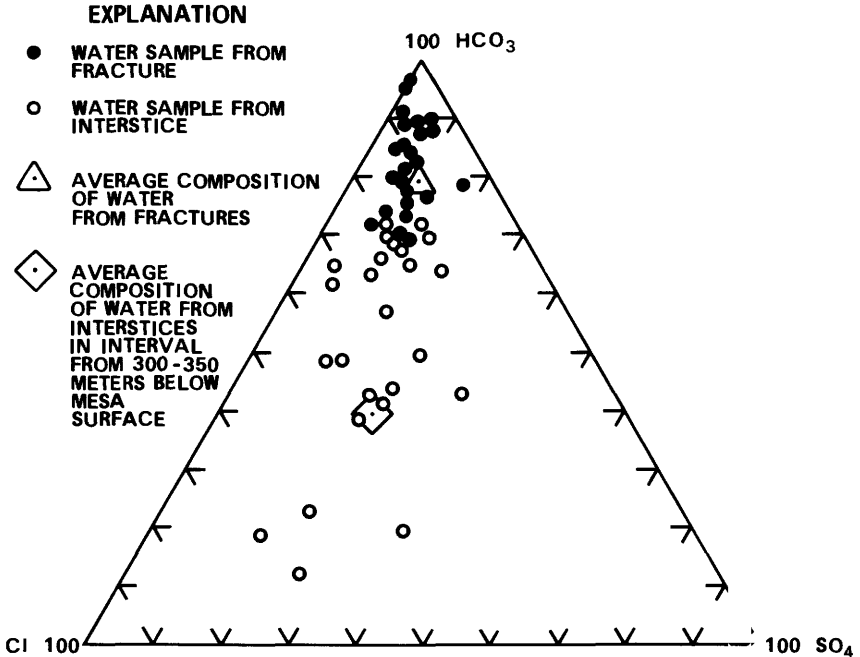
FIGURE 5.—Anion ratios of Rainier Mesa ground water.

U12e tunnel have cation compositions much higher in calcium and magnesium than the average shown in figure 4; yet, these samples were also collected from fractures in the tunnel beds. This discrepancy can at least partly be explained by structural controls on the tuffaceous rocks. Samples high in calcium and magnesium were generally collected from regions of the tunnel complex close to the axis of the Rainier Mesa syncline. Because the tunnels are dug horizontally into the mesa, segments closer to the synclinal axis generally possess a thinner overlying sequence of tunnel beds than tunnel segments on the limbs of the syncline (fig. 2). In addition, relatively-high calcium and magnesium waters in U12t tunnel (samples 11, 14, 16, and 17) were collected from fractures with flow rates greater than 6 L/s, as contrasted with the usual seeps of a few hundredths of a liter per second. This suggests that ground-water movement was relatively rapid, and residence times in the zeolitized tunnel beds may have been short.

Relative mole percentages of anions contained in the fracture waters are plotted in figure 5. As indicated, bicarbonate is the dominant anion in all the fracture water samples. This range in anion compositions is different from interstitial waters, which are generally higher in chloride and sulfate. Some overlap does occur between indi-

vidual fracture and interstitial water samples. As indicated by figure 7, interstitial waters generally increase in bicarbonate with depth, and the region of overlap corresponds to interstitial waters in the lower tunnel beds. Plotted in figure 5 are average interstitial water compositions, sampled at a depth interval between 300–350 m, which corresponds to the depth of fracture flow in the tunnels. Comparison of this average with the average composition of fracture waters indicates that the two types of waters coexisting at the same depth have different anion compositions.

GEOCHEMICAL CONTROLS

Dissolved chemical species in Rainier Mesa ground water reflect the interaction between ground water and the tuffaceous rock aquifer. These interactions consist principally of dissolution of primary silicate phases contained in volcanic rocks, precipitation of secondary mineral phases, and sorption and ion exchange with primary and secondary mineral surfaces.

FIGURE 6.—Concentration of silica as a function of depth.

FIGURE 7.—Concentrations of anions as a function of depth.
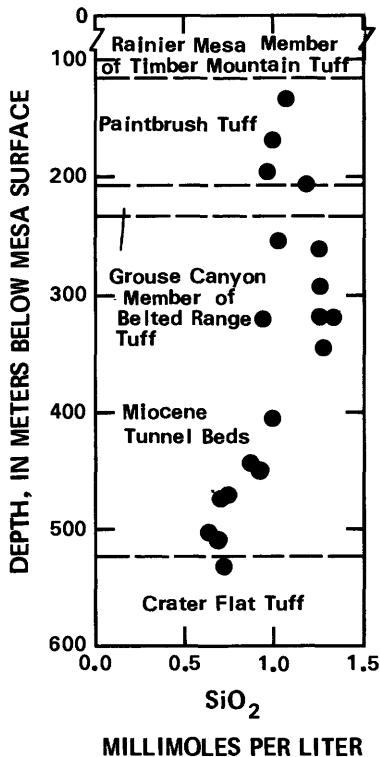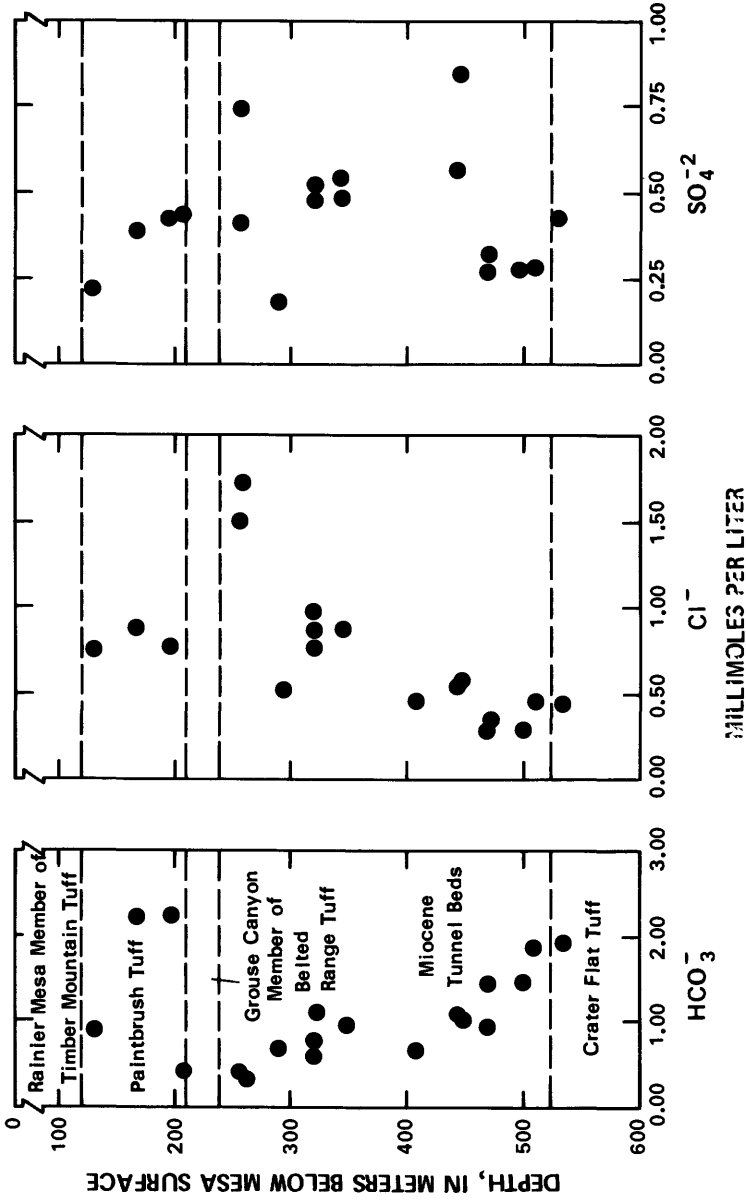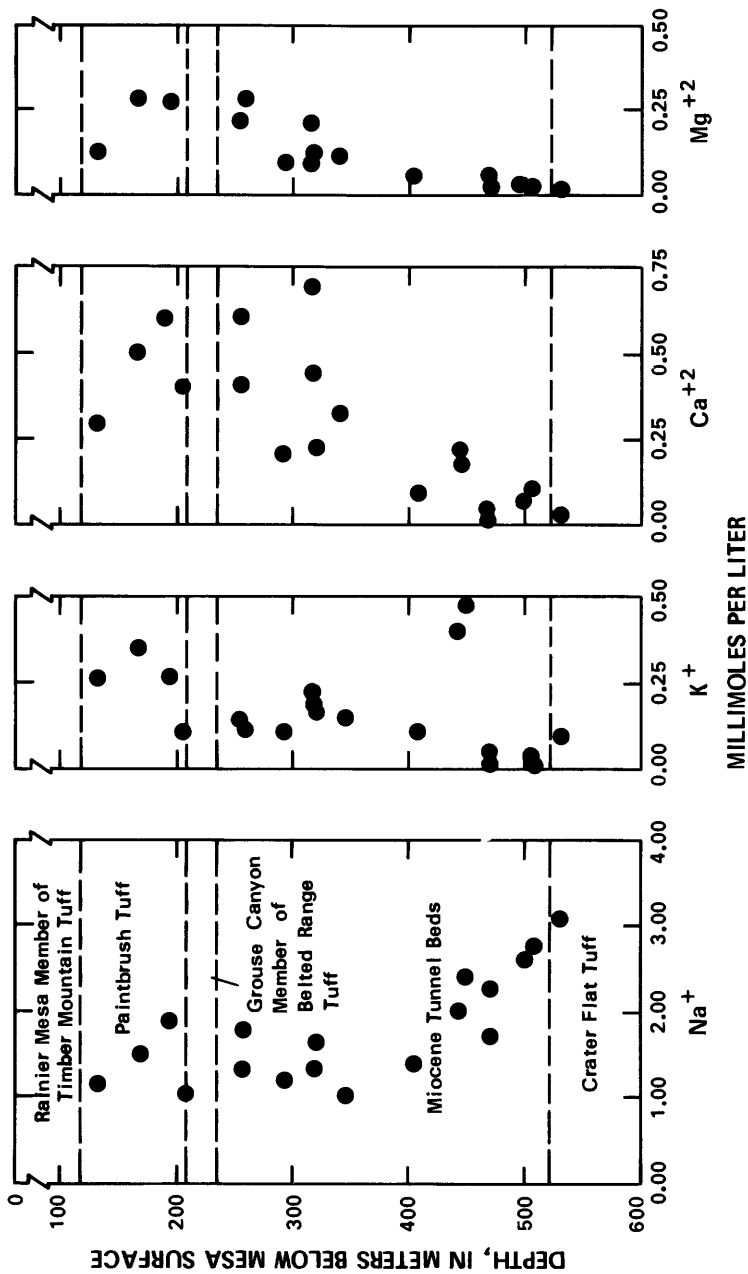
FIGURE 8.—Concentrations of cations as a function of depth.

TABLE 2.—*Chemical analysis of Rainier Mesa fracture water*

[Quantities are in millimoles per liter, except as indicated]

Sample No.	Tunnel designation	Sodium	Potassium	Calcium	Magnesium	Bicarbonate	Sulfate	Chloride	Fluoride	Silica	pH (units)	Date of collection
1	U12n.05 bypass	1.91	0.24	0.18	0.02	2.29	0.06	0.16	0.01	0.85	8.0	6-02-71
2	U12n.05	2.65	.28	.23	.02	2.85	.15	.37	.01	.72	7.6	9-21-71
3	U12n.05	3.04	.33	.40	.06	3.39	.28	.37	.01	.70	8.3	9-21-71
4	U12n main	2.70	.19	1.15	.28	3.62	.66	.90	.03	.68	8.2	8-03-72
5	U12n.07 bypass	.96	.01	.01	.00	.87	.05	.06	.02	.63	8.04	8-03-72
6	U12n.02	2.04	.14	.18	.01	2.25	.09	.20	.01	.88	7.31	11-14-72
7	U12t.02 bypass	.96	.00	.01	.00	.92	.00	.02	.02	.65	6.9	9-22-71
8	U12t.02	1.09	.01	.03	.01	1.08	.00	.05	.02	.65	7.0	9-22-71
9	U12t.02 bypass	1.13	.02	.07	.00	.82	.18	.05	.01	.63	7.5	9-22-71
10	U12t main	2.83	.09	.02	.01	2.44	.14	.28	.01	.65	7.5	9-22-71
11	U12t.03	1.44	.14	.50	.21	2.23	.18	.27	.02	1.35	—	2-15-73
12	U12t.03	1.39	.14	.22	.06	1.46	.19	.31	.01	.92	—	2-01-73
13	U12t.04	1.44	.13	.24	.08	1.61	.16	.28	.01	.88	—	8-22-73
14	U12t.03	1.30	.17	.50	.17	2.18	.16	.31	.02	1.00	—	3-19-73
15	U12t.03	1.65	.17	.23	.06	1.85	.16	.28	.01	.83	7.18	11-16-72
16	U12t.03	1.13	.14	.51	.19	2.15	.17	.26	.01	1.10	7.4	9-24-74
17	U12e.07	1.13	.15	.43	.17	2.00	.15	.06	.01	.90	7.4	3-11-60
18	U12e.04	1.04	.02	.01	.00	.79	.13	.10	.01	.60	7.3	6-02-59
19	U12e	1.13	.09	.06	.00	.87	.12	.17	.02	.90	7.6	11-22-59
20	U12e	1.04	.20	.06	.00	.93	.10	.11	.01	.87	7.0	11-29-59
21	U12e.04	1.26	.01	.04	.00	.88	.09	.17	.01	.60	6.9	1-07-60
22	U12e.03	1.35	.10	.04	.00	1.15	.09	.06	.02	.67	7.1	12-14-59
23	U12e	.87	.17	.20	.08	.92	.18	.23	.01	.92	7.8	1-29-59
24	U12e.02	1.39	.06	.00	.00	.98	.12	.27	.01	.78	7.4	10-11-58
25	U12e.05	1.44	.08	.06	.00	1.05	.12	.28	.01	1.23	7.4	9-12-58
26	U12e.03	1.74	.03	.06	.00	1.34	.12	.25	.02	.98	7.5	5-27-59
27	U12e.03	1.91	.04	.02	.00	1.34	.12	.28	.01	.63	8.0	5-20-59
28	U12e.03	1.74	.07	.04	.00	1.38	.12	.23	.02	.97	7.5	12-03-59
29	U12e.07	1.13	.15	.43	.12	2.00	.15	.11	.01	.90	7.4	3-18-66
30	U12e	1.48	.16	.33	.00	1.61	.15	.28	.01	1.02	8.0	1-22-59
31	U12e	2.04	.28	.10	.00	1.77	.15	.34	.01	.67	6.8	6-24-59
32	U12e	1.61	.20	.40	.04	2.00	.15	.34	.01	.87	7.9	7-18-59
33	U12e	3.04	.07	.08	.00	2.10	.33	.45	.02	2.10	7.0	7-21-58
34	U12b	.78	.07	.32	.04	1.21	.12	.14	.01	1.11	7.6	6-06-58
35	U12b.03	.65	.07	.24	.06	.79	.09	.21	.01	1.10	6.9	8-22-58
36	U12.04	.96	.08	.20	.34	.98	*	.34	*	*	7.5	9-29-58

*Not analyzed.

DISSOLUTION CONTROLS

The two primary reactive components within the rocks of Rainier Mesa are glass contained in vitric tuffs, and crystalline silicate minerals contained in devitrified tuffs. In the natural geochemical environment, the effect of silicate dissolution on ground-water chemistry is difficult to separate from coexisting influences of precipitation of secondary phases, in particular montmorillonite and clinoptilolite. Therefore, a controlled experimental study was undertaken to study the dissolution kinetics of the two principal rock types and to evaluate their importance in determining ground-water compositions.

A glass from the upper part of the Paintbrush Tuff was selected to represent the vitric rock type. Thin-section petrography and X-ray diffraction showed the tuff to be nearly pure glass with minor microlites of sanidine and magnetite, common constituents of silicic glassy rocks (Ross, 1962). Microprobe data indicated slight compositional differences between individual glass shards and fragments. The bulk chemical analysis is presented in table 3. A water content of 3.88 percent corresponds to that of a hydrated glass (Ross and Smith, 1955).

The crystalline phase was represented by a sample from the lower part of the Rainier Mesa Member of the Timber Mountain Tuff. This devitrified rock contained phenocrysts in order of decreasing abundance: sanidine, quartz, plagioclase, biotite, and clinopyroxene. Microprobe data revealed a potassium and silica-rich ground mass,

TABLE 3.—*Chemical composition of rocks used in kinetic experiments*

Constituent	Vitric Paintbrush Tuff (percent)	Crystalline Rainier Mesa Member of Timber Mountain Tuff (percent)
SiO_2	73	70
Al_2O_3...................	14	15
K_2O.....................	5.4	4.9
Na_2O....................	3.8	3.2
CaO......................	.44	.98
MgO.....................	.24	.29
TiO_2	.11	.30
Cl	.19	.13
F........................	.09	.09
CO_2....................	<.01	.04
H_2O....................	3.88	.43

probably corresponding to a sanidine-cristobalite assemblage common in rhyolitic tuffs (Lipman and others, 1966).

The bulk chemical analysis is also presented in table 3. A general chemical similarity exists between vitric and crystalline rock types. The glass is slightly higher in silica and monovalent cations and the crystalline rock is slightly higher in aluminum and bivalent cations.

<center>EXPERIMENTAL METHODS AND RESULTS</center>

Samples of the two rock types were crushed and the 60–200 mesh fraction retained. Brunauer, Emmett, Teller (B.E.T.) surface area measurements indicated respective surface areas for the glass and crystalline phases to be 3.6 m^2/g and 1.2 m^2/g.

Experimental dissolution methods were similar to those previously described by White and Claassen (1979). One hundred grams of rock were reacted with 2 L of deionized water at a fixed partial pressure of carbon dioxide (P_{CO_2}) in a constant-temperature water bath at 25 °C. The range in P_{CO_2} values was 1 atm (atmosphere) to 3×10^{-4} atm; it was obtained by mixing pure commercial grade CO_2 and compressed air; average pH range was between 4.5 and 7.5. The mixtures were agitated by stirring paddles at a rate just sufficient to keep the rock in suspension. During reaction, samples of the water-rock suspensions were removed and filtered, and the aqueous solution was analyzed for major constituents. The duration of an experiment was about 900 hours. Figure 9 is representative of dissolution data for the vitric tuff at average pHs of 4.82, 5.77, 6.38, and 7.12. Figure 10 shows data for the crystalline tuff at pH 4.83 and 6.93. The ordinate of the plots represent the flux of a species into solution per cubic centimeter of surface area of glass. The abscissa is the square root of time in seconds. The solid line represents the linear regression describing a parabolic fit to the data.

The data show that aqueous reaction of both phases can be described by an initial rapid nonparabolic mass transfer followed by parabolic mass transfer over longer times. Similar reaction sequences have been observed for silicate minerals (Luce and others, 1972, Busenberg and Clemency, 1976); artificial glasses (Rana and Douglas, 1961); and natural glasses (White and Claassen, 1979). Rapid initial concentration increases are attributed to surface exchange between aqueous hydrogen ions and cations at or near the solid-aqueous interface. As surface exchange approaches equilibrium with increasing time, kinetically slower parabolic rates of diffusion of ions into and out of the solid become the rate-controlling factor.

Concentration increases with time shown in figures 9 and 10 can be described by the empirical relation

$$Q = Q_o + kt^{1/2}, \tag{1}$$

where Q is the total mass transport, in moles per cubic centimeters, of a species into solution at any time, t, in seconds. Q_o is the parabolic intercept at $t = O$, which is taken to be the mass transported by the initial exchange reaction, and k is the parabolic rate constant. Q_o and k are determined by the regression fit of the data. Table 4 lists Q_o and k values for the six experiments shown in figures 9 and 10.

COMPARISON OF EXPERIMENTAL AND NATURAL WATER COMPOSITIONS

A quantitative prediction of species concentrations in Rainier Mesa can be made, based on the rate constants in table 4, if the residence time and aquifer surface-to-ground water volume ratio can be established (Claassen and White, 1979). However, relative elemental ratios, which to a first approximation are independent of the above parameters, provide a meaningful tool for gaging relative contributions of vitric and crystalline rocks to ground-water compositions.

Figure 11 shows trilinear diagrams similar to figure 4 describing the respective mole percent of Na-K-Mg and Na-K-Ca. The small squares in the upper third of the triangles correspond to the ground-water cation compositions associated with fracture waters in the rhyolitic tuffs (table 2).

Two large diamonds midway along the sodium-potassium axes in figure 11 represent composition of vitric and crystalline tuffs. As previously shown in table 3, the two compositions are very similar; however, note the dissimilarity between tuff compositions and compositions of the ground water.

Data points contained within the large arrows represent aqueous cation compositions at various times during dissolution experiments. Arrows labeled A through D represent the vitric-tuff experiments (table 4) at average pHs 4.82, 5.77, 6.38, and 7.12, respectively; E and F represent crystalline-tuff experiments at average pHs of 4.83 and 6.93, respectively.

Direction of the large arrows corresponds to changes in composition with increasing time. Note that aqueous composition trends generally move away from solid-state composition with time, reflecting continued retention of potassium. Compositions of solutions resulting from glass dissolution change with time toward the sodium-
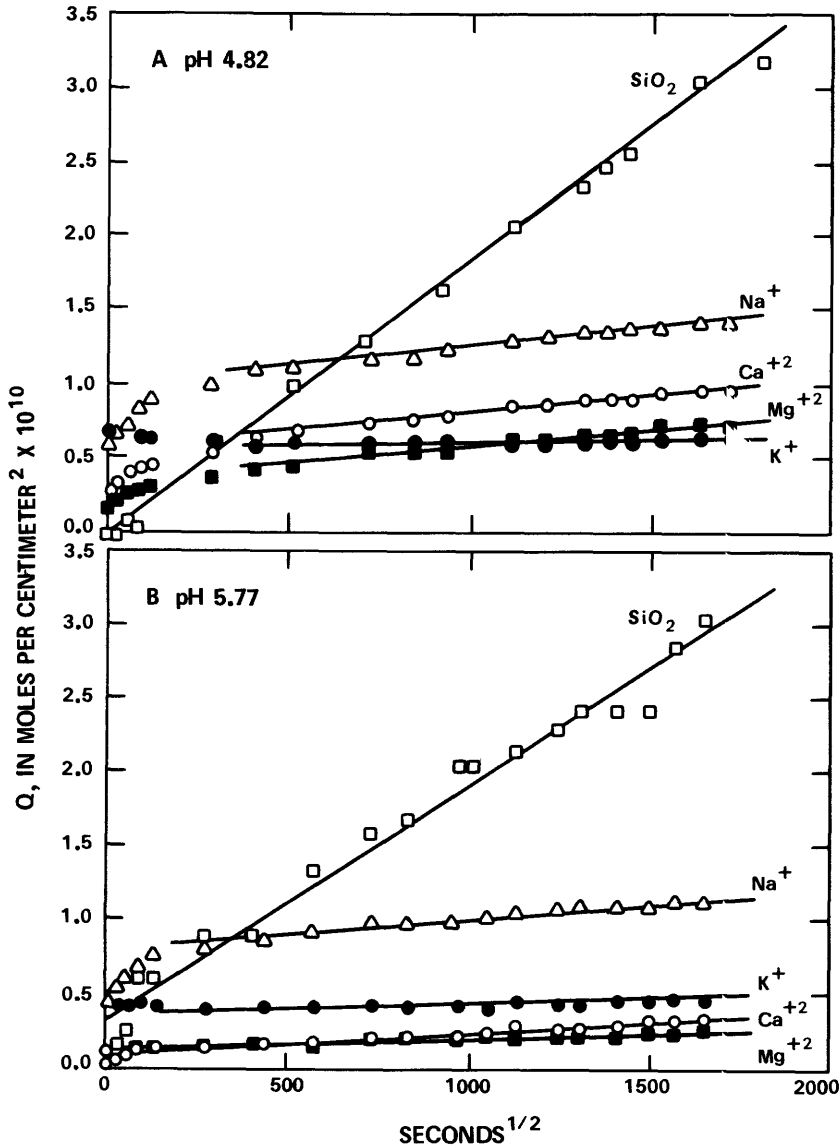
FIGURE 9.—Experimental dissolution of the vitric
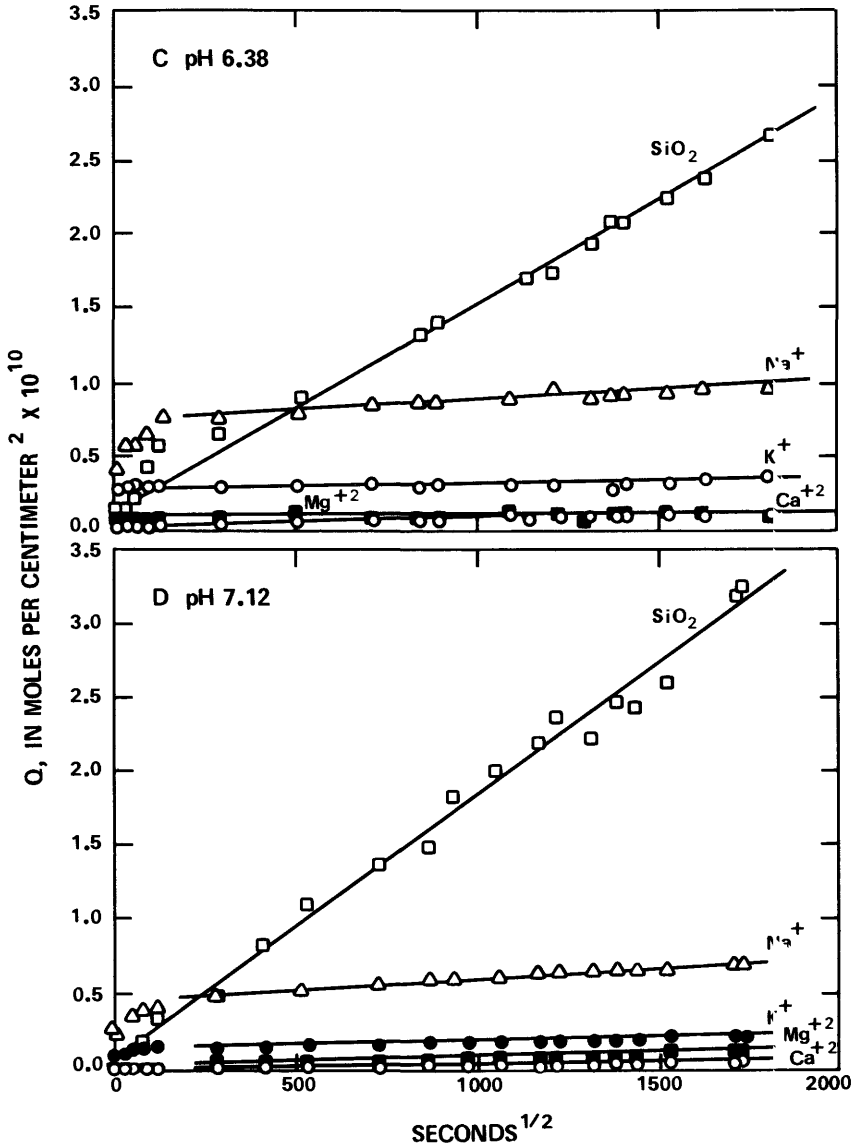
Paintbrush Tuff at 25°C and several average pHs.

TABLE 4.—*Kinetic rate constants and experimental-average pH*

$[Q_o = (moles/cm^3) \times 10^{16}; \quad k = (moles/cm^2 s^{1/2}) \times 10^{14}]$

Sample No.	Mean pH	Experimental pH range	Na		K		Ca		Mg		Si	
			Q_o	k	Q_o	k	Q_o	k	Q_o	k	Q_o	k
Vitric Tuff:												
17C A	4.82	4.67–4.97	1.02	2.41	0.590	0.278	0.592	2.33	0.399	2.02	0.0002	18.2
15C B	5.77	5.70–5.90	.807	2.04	.397	.422	.107	1.37	.141	.733	.330	15.8
21C C	6.38	6.21–6.58	.740	1.36	.290	.232	.0342	.550	.0707	.378	.0607	15.5
22C D	7.12	6.98–7.32	.517	1.29	.149	.220	.0203	.343	.0313	.203	.197	17.0
Crystalline Tuff:												
19B E	4.83	4.66–4.91	1.16	1.38	.979	.868	3.84	3.32	.431	1.18	.39	10.34
20A F	6.93	6.80–7.12	1.12	1.13	.755	.431	2.80	2.02	.361	1.00	.53	8.13
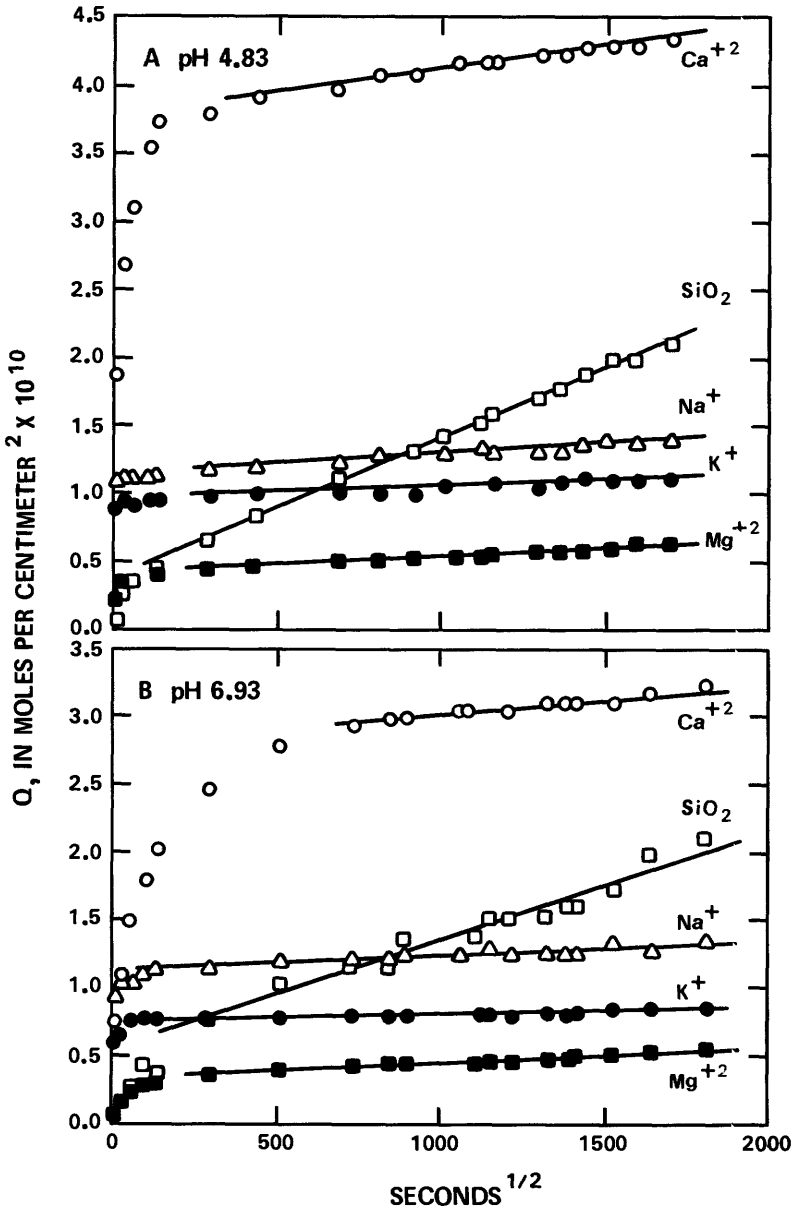
FIGURE 10.—Experimental dissolution of the crystalline Rainier Mesa Member of the Timber Mountain Tuff at 25 °C and two average pHs.

EXPLANATION

□ COMPOSITION OF WATER
   FROM FRACTURES IN
   RAINIER MESA MEMBER
   OF TIMBER MOUNTAIN TUFF

◇ COMPOSITION OF
   VITRIC PAINTBRUSH
   TUFF

⊕ COMPOSITION OF
   CRYSTALLINE
   RAINIER MESA
   MEMBER OF TIMBER
   MOUNTAIN TUFF

TREND OF DISSOLUTION
OF VITRIC TUFF WITH TIME

TREND OF DISSOLUTION
OF CRYSTALLINE TUFF
WITH TIME

EXTRAPOLATION TO
CONSTANT
COMPOSITION WITH
TIME BY USE OF
EQUATION 1

FIGURE 11.—Relative mole fractions of cations in the tuffaceous rocks, fracture
waters, and experimental solutions.

calcium and sodium-magnesium axes. Increases in pH cause compositions to shift toward the sodium apex. Solutions resulting from dissolution of the crystalline tuff trend with time directly toward the calcium and magnesium apexes.

As shown in figure 11, dissolution of the vitric phase, particularly under conditions of near-neutral pH, results in ion compositions that trend toward fracture-water compositions.

EXTRAPOLATION OF THE RATE EXPRESSION
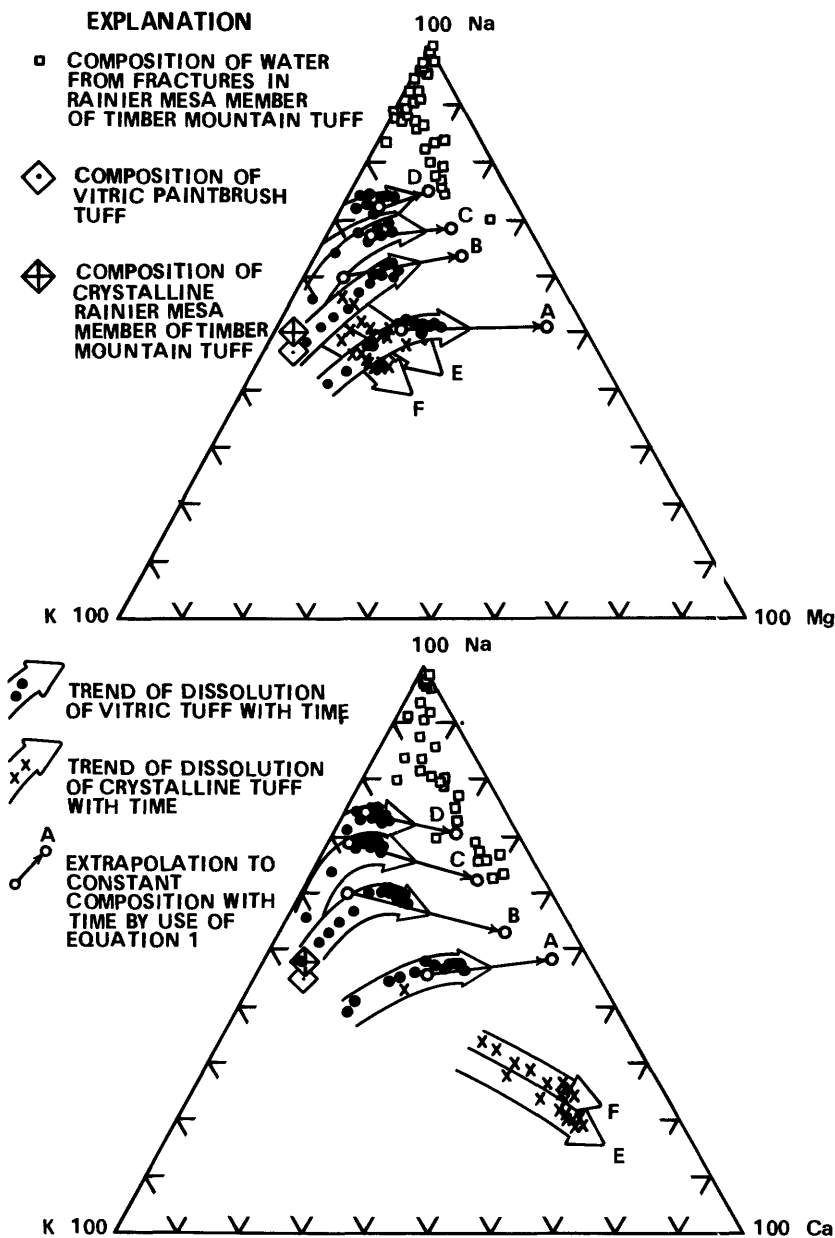
Extrapolation of the relatively short-term experimental data to much longer time intervals, representing the residence times of ground water within Rainier Mesa, is at best tenuous. Some experimental data for silicate minerals (Busenberg and Clemency, 1976) and artificial glasses (Rana and Douglas, 1961) suggest that cation diffusion represented by parabolic rates give way to surface dissolution of the silica-aluminum framework, resulting in linear kinetics at long times. However, as discussed by Paces (1973) and White and Claassen (1979), such bulk solution of the silicate phase results in congruent dissolution in which the ratios of species transferred in aqueous solution are equal to the ratio of species within the dissolving silicate phase.

Clearly, the cation ratios in the glass phase and the ground water within Rainier Mesa are very different. Figure 11 shows that fracture waters are deficient in potassium relative to glass composition, and enriched in calcium and magnesium in samples not exposed to the zeolitized tunnel beds. A possibility exists that all of the cation compositions are altered greatly by precipitation of mineral phases that would provide a sink for cations, in particular, potassium. However, principal alteration products found within Rainier Mesa, montmorillonite and clinoptilolite, do not concentrate potassium to any extent (table 5). In addition, the work of Lipman (1965) and Noble (1965, 1967) found that weathered glasses concentrate those ions which are found to be depleted in the Rainier Mesa ground water; again notably, potassium. From this evidence, glass dissolution appears incongruent. Therefore, probably the best method of extrapolating the experimental data to longer times is the use of equation 1, which describes incongruent dissolution.

Straight lines connecting open circles in figure 11 represent extrapolated changes in ion composition with time for four vitric tuff experiments (table 4) based on equation 1. The open circles at the ends of individual lines represent solutions to equation 1 at, from left

to right, 1.0×10^0 h, and 1×10^6 h. At short times, that is, 1×10^0 h, concentration of a species described by equation 1 will approximate the intercept concentration, Q_o. This value represents total ionic concentration attributed to initial-exchange reaction, and is not a good estimate of aqueous composition until exchange is essentially complete. This explains the discrepancy between data points at the base of the large arrows and the left-most open circles on the lines representing solutions to equation 1 for $t=1 \times 10^0$ h.

Once initial-exchange reaction is complete, the parabolic rate constant, k, accurately describes further mass-transfer increases. Aqueous composition changes are described by the straight lines connecting the open dots in figure 11. At long times (1.0×10^6 h), mass transfer due to parabolic reaction dominates total mass transfer, rendering initial-exchange reaction insignificant. The solution composition at this time is described in figure 11 by the right-most open circle on each of the straight-line plots. Cation mass-transfer ratios at this point will equal the ratio of the respective rate constants and will not change with additional increases in time.

As shown in figure 11, the predicted ion ratios to the right of the straight arrows for experiments C and D, at average pHs of 6.38 and 7.12, approach the Na-K-Ca ratios of the Rainier Mesa fracture waters, which presumably show least interaction with zeolites in the tunnel beds. The average pH of these samples is 7.6. However, this pH represents the maximum pH of reaction; the average pH of the reaction would be lower, assuming a closed system in which soil zone CO_2 is progressively depleted during silicate-dissolution reactions. The average pH of reaction is also predicted to be somewhat lower than 7.6 from the vitric-tuff dissolution data of figure 11.

Figure 11 also shows that Na-K-Mg composition of Rainier Mesa ground water resulting from vitric-tuff dissolution can be approximated by extrapolation of experiment D at an average pH of 7.12. This correlation occurs at a slightly higher pH than that predicted from figure 11, suggesting a possible loss of small amounts of magnesium from the ground water. Such a loss might be explained by precipitation of magnesium-rich montmorillonite, as discussed by Claassen and White (1979).

One result of experimental tuff dissolution is significant differences in solution-cation compositions associated with vitric and crystalline phases of a tuff of nearly identical bulk composition. Dissolution of the vitric phase produces a water that consists predominately of sodium and bicarbonate; whereas, dissolution of the crystalline phase results in a calcium-bicarbonate water. Both dissolution reactions are incongruent, displaying a strong retention of potassium in the solid phase. This is in agreement with data obtained from weathered glasses (Lipman, 1965; Noble, 1967).

In the case of a multiphase system such as crystalline tuff, observed rate constants may represent either the sum of comparable dissolution rates of individual minerals or the rate of a single very reactive phase. The relatively large rate constants for bivalent-cation release, coupled with low solid concentrations relative to sodium and potassium (table 3), suggest selective dissolution of a calcium-magnesium-rich mineral.

A possible source of calcium is plagioclase fledspar. Lipman and others (1966) indicated an oligoclase composition (An_{20-30}) for plagioclase found in tuffs in southern Nevada similar to those of Rainier Mesa. However, in studying dissolution rates of oligoclase, Busenberg and Clemency (1976) found that the ratio of sodium and calcium rate constants was approximately four to one. Dissolution of a comparable plagioclase in the crystalline tuff, therefore, cannot account for the relatively high calcium-to-sodium ratios in aqueous solution. A source of calcium and magnesium can be found in the limited amount of clinopyroxene found in Rainier Mesa crystalline tuff. Noble (1970) has previously suggested that calcium concentrations in related tuffs may be contained within clinopyroxene. Lipman and others (1966) found clinopyroxene compositions in a crystalline phase of the Paintbrush Tuff of $EN_{0.38}$ $FS_{0.13}$ $WO_{0.49}$. Selective dissolution of a similar clinopyroxene in the crystalline rocks of the Rainier Mesa Member of the Timber Mountain Tuff could account for relatively high calcium and magnesium concentrations in the experimental solutions.

ROLE OF SURFACE AREA ON COMPOSITION

Except in the case of silica dissolution, rate constants per square centimeter of surface, listed in table 4, are roughly similar for both vitric and crystalline tuffs. A much greater reactivity of the glass under experimental conditions cannot be invoked to explain its apparent dominance over the ground-water composition of Rainier Mesa. One possible explanation rests in differing aquifer characteristics of crystalline and vitric rock types. As previously mentioned, fracture flow is dominant in crystalline tuff of the Rainier Mesa Member of the Paintbrush Tuff and Grouse Canyon Member of the Belted Range Tuff; whereas, interstitial flow can occur in vitric tuffs of the Paintbrush Tuff. The solid-surface to aqueous-volume ratio would be expected to be much smaller in open fractures than in interstitial pore spaces. Consequently, total mass transfer per cubic centimeter of rock would be much higher for the glass phase. In addition, rate of ground-water movement through the unsaturated fracture system of the crystalline rock is expected to be more rapid than through the more tortuous pathways connecting partly saturated interstitial

pores within the vitric tuffs. The resulting greater retention time of ground water in the vitric tuff may also account for its dominance over the water composition.

Experimental dissolution of crystalline rock appears to be confined principally to a relatively reactive minor phase, probably clino-pyroxene. Prolonged weathering of fracture surfaces in the crystal-line cap rock could reduce or even eliminate such a phase, which, in turn, would also decrease mass transfer from the crystalline tuff.

MODIFICATION OF WATER COMPOSITIONS BY ALTERATION PRODUCTS

As shown in figure 11, fracture waters trend from cation composi-tions that can be reproduced by experimental glass dissolution at near-neutral pH to compositions almost totally depleted in calcium and magnesium. Figure 8 shows a similar depletion of bivalent cations as a function of depth. Most certainly, these trends are re-lated to formation of montmorillonite and clinoptilolite within the tuff sequence.

Table 5 lists the mole percentages of cations in ground water pre-dicted by experimental glass dissolution at pH 7.13 and average water compositions from U12b tunnel, which probably best repre-sents glass dissolution. Also included in table 5 are the compositions of montmorillonite given by Carr (1974) from the Grouse Canyon Member of the Belted Range Tuff from an area adjacent to Rainier Mesa and the average clinoptilolite composition from the 350-m level of core U12T 3 determined by microprobe analysis.

As indicated, the percentage of calcium is a factor of four greater than sodium in montmorillonite and an order of magnitude higher in clinoptilolite. Likewise, magnesium is a factor of seven greater in montmorillonite and a factor of five greater in clinoptilolite. There-fore, precipitation of either phase would deplete the bivalent cation composition relative to sodium in a water initially of a composition reflecting glass dissolution.

TABLE 5.—*Comparisons of cation mole fractions in waters produced by glass dissolution and in alteration minerals*

	Na	K	Ca	Mg
Compositions predicted by rate constants				
at pH 7.13	0.63	0.11	0.17	0.10
Compositions of fracture waters*	.63	.07	.22	.08
Montmorillonite	.08	.08	.23	.59
Clinoptilolite	.05	.20	.50	.25

*Included are U12b tunnel samples; 14 and 16, U12t tunnel samples; and 17, 29, and 30, U12e tunnel samples.

The onset of calcium and magnesium depletion at a depth coincident with the upper boundary of maximum montmorillonite and clinoptilolite formation also supports this removal mechanism. The corresponding rapid increases in sodium shown in figure 8 in the same depth interval may represent an increase in the reaction rate of glass relative to rates elsewhere in the sequence, or may be related to an exchange reaction between the relatively small amounts of sodium incorporated in the clinoptilolite or montmorillonite and aqueous calcium and magnesium ions.

Figure 6 shows that silica is saturated with cristobalite, $10^{-3.0}$ mol/L (Truesdell and Jones, 1974) in the lower part of the Paintbrush Tuff and decreases with depth in the tunnel beds. This decrease suggests that the rate at which silica is removed from ground water by clinoptilolite and montmorillonite precipitation is faster than the rate at which it is introduced by glass dissolution.

ANION COMPOSITIONS

The mechanism responsible for differences in anion composition between interstitial and fracture waters shown in figure 5 is not obvious. The relatively high bicarbonate percentages found in fracture waters is typical of ground waters associated with igneous rocks (Hem, 1970; White, 1979). Soil zone CO_2 is dissolved in ground water and contributes hydrogen ions during the acid attack of silicate rocks, resulting in formation of bicarbonate. Such a mechanism is analogous to the previously discussed experimental system.

Several possible conditions may explain the relatively high percentages of chloride and sulfate in interstitial waters. One possibility is that interstitial waters were contaminated by drilling fluid during coring. However, dye tests conducted by the Defense Nuclear Agency during drilling showed that contamination was negligible in zeolitized tunnel beds.

Another possibility is that interstitial-water composition reflects a relict water high in chloride and sulfate that was present at the time of deposition. The Paintbrush Tuff in particular shows strong cross bedding and reworking, indicative of a water-lain environment. The preservation of such waters over geologic time would require that large percentages of pore space be insulated from the presently active hydrologic system. Relatively high porosity but low interstitial conductivity found in zeolitized tunnel beds may be indicative of such an environment. A similar condition in the Paintbrush Tuff is less plausible due to relatively high interstitial conductivity. The relatively high bicarbonate waters found in the fractures within the tunnel beds must have moved by interstitial flow through the Paintbrush Tuff.

Another possibility is that the type and extent of chemical reactions between the tuffaceous rock and the interstitial and fracture waters are dissimilar. Noble (1967) showed that significant amounts of chloride are released during the reaction and hydration of glass in contact with ground water. However, no prior reason is evident as to why chloride produced by such a reaction is concentrated in interstitial waters relative to fracture waters. The fact that the total dissolved solid concentrations and cation ratios are similar tends to discount widely varying dissolution mechanisms. Some type of selective anion exchange, filtration, or incorporation within a precipitate could concentrate chloride relative to bicarbonate in interstitial waters. Unfortunately, no data exist that would substantiate or refute such a mechanism.

SUMMARY

Experimental results indicate that geochemistry of ground water within Rainier Mesa is the result of glass dissolution principally in the Paintbrush Tuff and Miocene tunnel beds. Glass dissolution is incongruent, with the preferential release of sodium, calcium, and magnesium, and the retention of potassium. This elemental selectivity is in agreement with the results of previous workers, based on comparisons between weathered and fresh glass and crystalline rocks. The dominance of glass dissolution is probably related to the porous nature of vitric tuff, which results in large surface areas and retention time. Based on similar water chemistries, glass dissolution can be inferred as the controlling factor in determining water quality in many aquifer systems associated with tuffaceous rocks in the western United States.

The cation composition of Rainier Mesa ground water is progressively modified as a function of depth in the mesa, with a depletion of calcium and magnesium relative to sodium. The depth at which this effect is maximum coincides with alteration zones containing clinoptilolite and montmorillonite in the tunnel beds. Based on composition ratios, ongoing precipitation of these minerals is an effective sink for removal of bivalent cations. Data show that although the range in cation compositions in interstitial and fracture waters are very similar, compositions of anions are different, with interstitial waters much higher in chloride and sulfate relative to bicarbonate.

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