Geochemistry of Outcrop Samples from the Raven Canyon and Paintbrush Canyon Reference Sections, Yucca Mountain, Nevada

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CONTENTS

Abstract 1
Introduction 1
  Purpose and scope of report 1
  Geologic framework 1
  Acknowledgments 3
Data collection 3
Geochemistry of outcrop samples 7
Conclusions 14
References cited 17

FIGURES

1. Map showing generalized geology of the Yucca Mountain area and the locations of the Raven Canyon and Paintbrush Canyon reference sections 2

2–8. Graphs showing:

2. Concentrations of zirconium and titanium in samples from the Raven Canyon reference section 9
3. Concentrations of calcium, strontium, and barium in samples from the Raven Canyon reference section 10
4. Concentrations of yttrium, lanthanum, and cerium in samples from the Raven Canyon reference section 11
5. Concentrations of potassium, niobium, and rubidium in samples from the Raven Canyon reference section 12
6. Ratios of rubidium to strontium (Rb/Sr), calcium to strontium (Ca/Sr), and potassium to rubidium (K/Rb) in samples from the Raven Canyon reference section 13
7. Present-day and initial $^{87}Sr/^{86}Sr$ values for samples from the Raven Canyon and Paintbrush Canyon reference sections 15
8. IR(Sr) values versus reciprocal strontium concentrations for samples from the Raven Canyon and Paintbrush Canyon reference sections 16

TABLES

1. Geochemical data for samples from the Raven Canyon reference section, Yucca Mountain, Nevada 4
2. Geochemical data for samples of the Calico Hills Formation from the Paintbrush Canyon reference section, Yucca Mountain, Nevada 6
3. Strontium-isotope data for samples from the Raven Canyon and Paintbrush Canyon reference sections 7

CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
foot (ft)	0.3048	meter (m)
gram (g)	0.03527	ounce (oz)
kilometer (km)	0.6214	mile (mi)
meter (m)	3.281	feet (ft)
millimeter (mm)	0.03937	inch (in)

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5\ (°C) + 32.$$

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

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Abstract

As part of the site characterization studies being conducted by the U.S. Geological Survey at Yucca Mountain, Nevada, reference stratigraphic sections were established in outcrop areas where the volcanic rocks of Miocene age have been minimally altered. Beneath most of Yucca Mountain tuffs of the Calico Hills Formation, tuffs of the Crater Flat Group, and older tuffs, recognized only in drill core, have been pervasively altered to zeolites and other low-temperature, secondary minerals. Previous studies have indicated that open-system (nonisochemical) conditions prevailed during this alteration largely obscuring the original compositions and textures of these units. The reference sections were sampled to obtain critical geochemical and isotopic baseline data for characterizing the primary compositions of the rock units and for assessing the degree and extent of element mobility attendant with the past alteration of the rock mass. The open-system alteration of the pre-Paintbrush Group units may serve as a useful analogue for alteration that could occur in the Topopah Spring Tuff in the near field of the potential repository due to thermal loading.

INTRODUCTION

The Yucca Mountain area in southern Nevada (fig. 1) is being evaluated for its suitability as a potential site for the construction of an underground, high-level nuclear waste repository (U.S. Department of Energy, 1988). With support from the Department of Energy Yucca Mountain Site Characterization Project under Interagency Agreement No. DE-AI08-92NV10874, the U.S. Geological Survey (USGS) is conducting detailed petrographic, geochemical, and isotopic analyses of samples collected from drill cores and from outcrops. The geochemical and isotopic compositions of the volcanic rocks of Yucca Mountain derive from those of their parental magmas, from changes resulting from the eruptive processes and from post-depositional alteration. In this study, geochemical and isotopic data were acquired on samples from reference sections selected in areas where the effects of the post-depositional alteration has been minimal. These data will be used as baseline information for delineating and correlating zonal features in the volcanic rock units, and for assessing possible future open-system alteration (chemical changes) that may occur in the thermal aureole of the potential repository after it has been loaded with nuclear waste.

Purpose and Scope of Report

Geochemical and isotopic data are reported for 76 rock samples from the Raven Canyon and Paintbrush Canyon reference sections. A major goal of this study is to establish baseline geochemical and isotopic data for relatively unaltered, nonwelded to densely welded zones of the various rock units that compose the volcanic stratigraphy at Yucca Mountain. These data are acquired by locating and sampling outcrops where the rocks have been minimally affected by the regional alteration described by Broxton and others (1987). Unaltered vitric and devitrified tuffs in the Prow Pass and Bullfrog Tuffs of the Crater Flat Group and in younger units are present in Raven Canyon at the southernmost end of Yucca Mountain near Highway 95 (fig. 1), and vitric tuffs in Calico Hills Formation crop out in Paintbrush Canyon (fig. 1). The data in this report were previously compared with data for core samples from UE-25a #1 and UE-25b #1 to assess the degree and extent of element mobility during alteration of the volcanic units (Peterman and others, 1993).

Geologic Framework

The rock mass at Yucca Mountain (fig. 1) consists of a thick sequence of rhyolitic tuffs and lavas of Miocene age (Spengler and Fox, 1989). These units range in numerical age from about 11.5 to 14.0 Ma

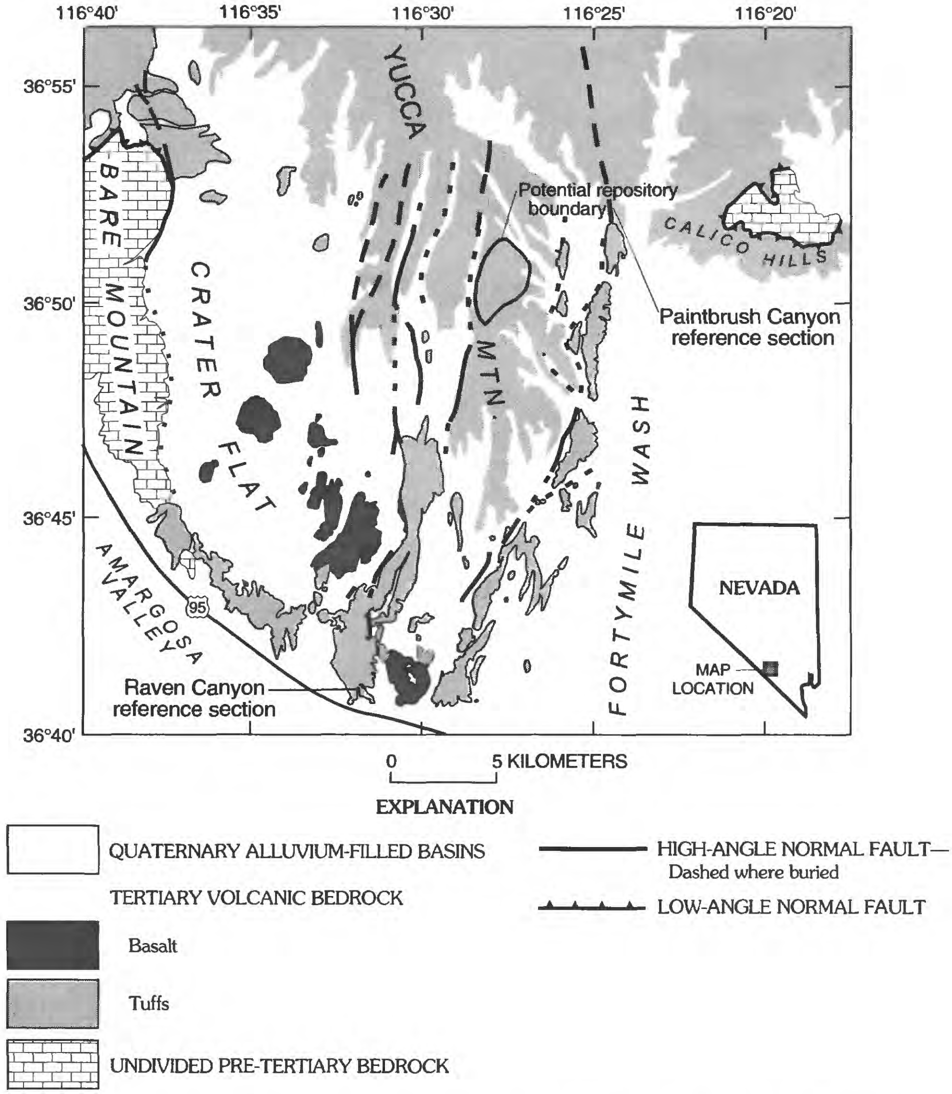

Figure 1. Generalized geology of the Yucca Mountain area and the locations of the Raven Canyon and Paintbrush Canyon reference sections.

(million years before the present). As much as 3 km of the volcanic section may exist beneath the potential repository level, which is in the Topopah Spring Tuff. The upper 500 m of the sequence is above the water table and generally consists of a thick zone of welded tuff underlain by nonwelded to partially welded tuff. Much of the nonwelded to partially welded tuffs in the unsaturated zone, including the Calico Hills Formation and part of the Prow Pass and Bullfrog Tuffs of the Crater Flat Group, has been extensively altered to zeolites (Broxton and others, 1987). All of the units below the water table are severely altered. The mineralogic and geochemical effects associated with this past alteration are being studied at the Los Alamos National Laboratory (Broxton and others, 1987; Broxton, 1992). The USGS (Peterman and others, 1991; Peterman and others, 1993; Spengler and Peterman, 1991) is using isotope and trace element geochemistry to characterize the vertical and lateral variability of the rock units including the degree and extent of element mobility in the past.

Potassium-argon ages of authigenic illite and stratigraphic relationships indicate that the regional alteration occurred within a few million years of the time of eruption and deposition of the volcanic rocks (Broxton and others, 1987). However, K-Ar dating of zeolites (WoldeGabriel and others, 1992) yielded a wide spectrum of ages. The conditions under which zeolites retain argon are not known although zeolites clearly are less retentive than illite. Nonetheless, the spectrum of K-Ar zeolite ages may be reflecting susceptibility of the rock mass to low-temperature modification long after the main episode of alteration.

An understanding of the isotopic and chemical changes that occurred during diagenesis could be useful for predicting possible future changes that may occur in the near field of the potential repository if pore or perched water is mobilized during heating of the rock mass by the nuclear waste. Rock intervals that are rich in zeolites, such as the Calico Hills Formation, may function as important natural barriers to the migration of certain radionuclides between the potential repository level and the water table (Herbst and Canepa, 1989). However, the presence of zeolites also may complicate the performance of the natural system which is the final barrier to the release of radionuclides to the environment. The zeolitized rocks contain substantial amounts of water that can be released at temperatures greater than 80°C (Bish, 1990). During loading of the potential repository and heating of the surrounding rocks, water could be released from the Calico Hills Formation and from zeolitized zones in the Topopah Spring Tuff. This dehydration would be accompanied by a volume decrease of a given mass of rock which could potentially lead to increased permeability (Bish, 1990). If the heated water resulting from dehydration were to move into the previously unaltered Topopah Spring Tuff in the near field of the potential repository, secondary minerals could form. Presumably, the lower vitrophyre of the Topopah Spring Tuff would be especially vulnerable to such alteration (Levy and O'Neil, 1989; Peterman and others, 1991). This process could be important to the performance of the potential repository because the increase in specific rock volume associated with the formation of lower density secondary minerals would tend to seal fractures and decrease permeability. Furthermore, zeolites formed within this alteration halo could be an additional barrier to the migration of radionuclides, particularly ^{90}Sr and ^{137}Cs.

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DATA COLLECTION

At the Raven Canyon reference section (fig. 1) samples were collected along three traverses that collectively intercepted a stratigraphic thickness of approximately 1,100 ft of the Tram, Bullfrog, Prow Pass, Wahmonie, and Topopah Spring Tuffs. The lower part of the reference section (bedded tuff and Tram Tuff) was measured using a Jacob's staff and was designated traverse A. The middle part of the reference section (bedded tuff and Bullfrog Tuff), in Raven Canyon proper, was measured by tape and compass traverse and was designated traverse B. The upper part of the reference section (bedded tuff, Prow Pass, Wahmonie, and Topopah Spring Tuff) was measured using a Jacob's staff and by tape and compass and was designated traverse C. Coordinates of the starting points (lowest stratigraphic positions) of the Raven Canyon traverses were estimated from the Big Dune 7.5 minute quadrangle relative to the 1927 North American Datum: traverse A, 38°41.2' N and 116°32.7' W; traverse B, 38°41.1' N and 116°32.3' W; and traverse C, 38°41.4' N and 116°32.1' W. At the Paintbrush Canyon reference section, samples of the Calico Hills Formation were collected along a single traverse that intercepted approximately 600 ft of section. Coordinates of the starting point (base) of the Paintbrush Canyon section were estimated from the Topopah Spring NW 7.5 minute quadrangle: 116°24.8' W and 36°54.7' N. The Paintbrush Canyon section was measured using a Jacob's staff.

Soil and bedrock surfaces and near-surface fractures in this region are permeated by pedogenic calcite that contains both Ca and Sr. To remove the calcite, samples were coarsely crushed to fragments approximately 5 mm or smaller, treated with 0.1N hydrochloric acid until reaction with calcite ceased, repeatedly rinsed with deionized water, and then dried before pulverization to approximately 200 mesh in a Spex shatterbox mill. This mild acid leaching removes the calcite but does not have an appreciable effect on the silicate minerals. Major and trace elements were determined by energy-dispersive, X-ray fluorescence on 3- to 5-gram splits of the 200-mesh bulk-rock samples. Multiple secondary targets and USGS rock standards were used to analyze for K, Ca, Ti, Rb, Sr, Y, Zr, Nb, Ba, La, and Ce concentrations in the samples (tables 1 and 2). Replicate analyses of USGS rock standard GSP-1 yield the following coefficients of variation: K, ±1.2 percent; Ca, ±3.7 percent; Ti, ±2.4 percent; Rb, ±1.4 percent; Sr, ±1.3 percent; Y, ±8.3 percent; Zr, ±3.6 percent; Nb, ±3.7 percent; Ba, ±2.9 percent; La, ±7.1 percent; and Ce, ±3.9 percent.

Table 1. Geochemical data for samples from the Raven Canyon reference section, Yucca Mountain, Nevada

[Strat. pos. refers to the stratigraphic position of the samples measured in feet. Sample H95C-24+10 is arbitrarily taken as the reference for denoting the position of the other samples; ppm, parts per million]

Sample	Strat. pos. (ft)	Unit[1]	K (percent)	Ca (percent)	Ti (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Nb (ppm)	Ba (ppm)	La (ppm)	Ce (ppm)
H95C-24+10	0	Tpt-vit	4.22	0.630	1,459	156	30	28	249	21	257	111	165
H95C-24B+0	5	Tpt-devit	4.92	0.747	2,296	130	48	34	447	16	419	181	278
H95C-24+0	5	Tpt-devit	4.15	0.653	1,335	148	37	31	245	21	224	108	169
H95C-23+0	25	Tpt-devit	3.79	0.560	851	190	18	31	131	25	83	58	92
H95C-22+0	45	Tpt-devit	3.72	0.569	875	183	16	31	134	24	88	60	88
H95C-21+0	65	Tpt-devit	3.72	0.600	830	188	18	30	129	24	82	66	98
H95C-20+12	79	Tpt-devit	3.74	0.544	825	182	18	31	128	21	78	60	90
H95C-19+14	98	Tpt-devit	3.84	0.546	802	179	18	31	132	24	77	57	93
H95C-19+7	101	Tpt-mw-v	2.87	0.650	808	175	27	31	132	24	87	61	91
H95C-19+0	105	Tpt-mw-v	3.79	0.565	831	183	19	29	138	23	85	63	100
H95C-18+7	118	Tpt-nw-v	3.44	0.533	862	173	20	29	134	23	74	63	96
H95C-18C+0	122	Tpt-nw-v	3.75	0.561	1,127	176	22	33	198	22	89	77	133
H95C-18B+0	123	Bt-v	3.60	0.552	688	183	21	31	116	23	80	74	115
H95C-18A+0	125	Bt-v	3.04	0.647	1,004	163	101	29	131	22	195	67	107
H95C-16+0	165	Bt-v	2.87	1.972	2,943	115	716	20	275	13	1,603	51	100
H95C-14+6	192	Tcp-nw-v	3.61	0.578	660	160	59	37	159	29	279	59	104
H95C-12+0	235	Tcp-pw-vp	3.77	0.688	669	173	66	33	156	30	277	68	104
H95C-10+16	267	Tcp-pw-vp	3.92	0.517	614	169	58	34	150	30	283	62	107
H95C-9+3	293	Tcp-pw-vp	3.98	0.504	681	169	54	33	151	29	283	65	97
H95C-8+0	315	Tcp-pw-vp	3.93	0.510	691	172	54	34	149	28	290	62	100
H95C-7+10	326	Tcp-pw-vp	3.98	0.513	706	174	58	31	155	29	289	45	84
H95C-6+10	346	Tcp-pw-vp	3.92	0.520	733	168	57	34	155	29	291	69	109
H95C-4+4	389	Tcp-pw-vp	3.86	0.568	712	167	59	32	156	30	290	69	115
H95C-3+9	406	Tcp-pw-vp	3.89	0.629	721	155	65	37	158	30	291	58	108
H95C-2+5	428	Tcp-nw-v	3.17	0.537	663	189	50	39	159	32	278	74	116
H95C-1+0	451	Tcp-nw-v	3.23	0.529	700	189	59	39	160	30	291	65	100
H95C-0+10	466	Tcp-nw-v	3.22	0.526	688	194	54	38	174	30	277	62	108
H95C-0+1	470	Af-v	3.06	0.644	778	153	103	33	183	25	394	81	136
H95B-26+0	481	Tcb-nw-v	3.23	0.697	915	176	156	32	156	26	562	61	113
H95B-24+0	501	Tcb-nw-v	3.15	0.696	982	160	172	33	162	28	573	58	111
H95B-20+9	545	Tcb-nw-v	3.32	0.698	1,035	168	178	34	162	27	603	70	133
H95B-18+0	581	Tcb-pw-vp	4.39	0.689	1,003	166	178	32	160	25	615	63	104
H95B-17+0	603	Tcb-mw-vp	4.42	0.714	1,068	168	178	33	168	27	617	51	100
H95B-16+0	622	Tcb-mw-vp	3.85	0.740	1,117	163	184	29	170	26	614	50	102
H95B-14+35	644	Tcb-dw-devit	3.86	0.762	1,067	159	173	34	176	27	596	63	118

Table 1. Geochemical data for samples from the Raven Canyon reference section, Yucca Mountain, Nevada--Continued

Sample	Strat. pos. (ft)	Unit[1]	K (percent)	Ca (percent)	Ti (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Nb (ppm)	Ba (ppm)	La (ppm)	Ce (ppm)
H95B-13+10	672	Tcb-dw-devit	3.67	0.783	1,054	156	183	31	170	26	612	66	99
H95B-12+5	689	Tcb-dw-devit	3.63	0.817	1,243	141	206	33	189	27	607	59	105
H95B-11+5	711	Tcb-dw-vit	3.71	0.813	1,244	140	213	32	191	26	645	52	97
H95B-10+0	728	Tcb-vit	3.13	0.906	1,116	160	234	32	188	26	628	60	108
H95B-8+0	762	Tcb-vit	3.11	0.941	1,399	160	335	30	255	26	792	75	139
H95B-4+26	809	Tcb-vit	3.40	1.061	1,546	150	388	32	247	24	886	79	147
H95B-4+16	813	Tcb-vit	3.38	1.044	1,627	150	476	30	271	23	1,010	85	163
H95B-3+3	831	Tcb-nw-v	3.19	0.663	926	153	179	32	171	26	622	75	130
H95-26+5	838	Tcb-nw-v	2.93	0.775	940	133	219	24	184	23	633	63	111
H95B-0C+0	846	Tcb-nw-v	3.37	0.650	976	178	160	31	160	26	554	71	131
H95-25+7	846	Bt-v	2.90	0.574	934	145	172	29	172	26	610	67	124
H95B-0B+0	852	Bt-v	3.38	0.789	955	184	252	23	136	19	1,000	62	116
H95-24+9	854	Bt-v	3.35	0.693	846	211	206	30	131	22	777	57	95
H95B-0A+0	862	Bt-v	3.46	0.831	1,281	151	170	33	184	26	520	73	117
H95-24+0	863	Bt-v	3.83	1.016	1,420	135	219	27	182	25	560	73	131
H95-22+0	883	Bt-v	3.50	0.994	1,480	139	247	25	182	22	710	85	137
H95-21+1	892	Bt-v	3.44	0.864	1,375	146	223	27	161	22	658	86	146
H95-20+0	903	Bt-v	3.34	0.692	1,145	178	139	31	157	25	463	54	98
H95-18+0	923	Bt-v	3.47	0.820	1,295	147	188	34	304	30	478	65	120
H95-16C+9	934	Tct-dw-devit	2.99	0.639	883	116	91	22	117	19	505	51	73
H95-16A+9	934	Tct-dw-devit	3.18	0.754	1,082	117	121	24	125	19	524	49	85
H95-16+5	938	lith tuff	4.19	0.784	1,447	134	133	40	339	30	491	76	124
H95-14+9	953	lith tuff	4.36	0.580	1,455	148	122	41	341	31	475	67	124
H95-13+0	973	lith tuff	3.94	0.805	1,473	152	119	43	341	33	447	69	131
H95-12+1	982	Bt-v	3.53	0.660	1,295	157	124	33	254	28	515	66	113
H95-10+6	997	Bt-v	3.19	0.668	1,038	156	130	43	321	34	439	59	104
H95-8+7	1,016	Bt-v	3.66	0.737	1,180	142	154	32	208	27	617	64	112
H95-7+0	1,033	Bt-v	3.74	0.701	1,058	155	142	32	195	26	555	73	132
H95-5+7	1,046	Bt-v	3.60	0.661	1,064	155	134	31	194	25	548	61	96
H95-4+4	1,059	Bt-v	3.74	0.724	1,134	157	140	33	194	24	548	63	108
H95-2+1	1,082	Bt-v	3.68	0.738	1,162	145	146	30	189	26	578	69	127
H95-0+7	1,096	Bt-v	3.72	0.677	1,039	162	116	31	165	28	482	55	99

[1]Unit designations: Tpt, Topopah Spring Tuff; Tac, Calico Hills Formation; Tcp, Prow Pass Tuff; Tcb, Bullfrog Tuff; Tct, Tram Tuff. Rock types and modifiers: dw, densely welded; mw, moderately welded; pw, partially welded; nw, nonwelded; vit, vitrophyre; devit, devitrified; v, vitric; vp, vapor phase mineralization; Bt, bedded tuff; Af, air fall; lith tuff, lithic-rich tuff. Stratigraphic terminology and unit symbols are from Sawyer and others, 1994.

Table 2. Geochemical data for samples of the Calico Hills Formation from the Paintbrush Canyon reference section, Yucca Mountain, Nevada

[Strat. pos. refers to the stratigraphic position of the samples measured in feet. The positions of the upper and lower contacts of this section are shown for reference; ppm, parts per million]

Sample	Strat. pos. (ft)	Lithology	K (percent)	Ca (percent)	Ti (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Nb (ppm)	Ba (ppm)	La (ppm)	Ce (ppm)
Upper contact	598	--	--	--	--	--	--	--	--	--	--	--	--
DH-9	317	Vitrophyre	4.53	0.559	537	204	15	32	70	22	71	48	65
DH-8	279	Vitrophyre	3.75	0.564	526	212	17	33	73	23	71	47	72
DH-7	217	Vitrophyre	4.11	0.578	583	226	26	31	76	22	93	48	78
DH-6	183	Breccia	3.63	0.818	580	189	19	25	79	22	82	45	68
DH-5	130	Vitrophyre	3.93	0.795	580	212	31	33	75	22	88	43	65
DH-4	76	Vitrophyre	4.26	0.568	581	235	23	31	77	22	101	49	71
DH-3	62	Breccia	3.59	0.820	543	208	18	29	74	22	75	41	63
DH-2	39	Breccia	3.00	1.217	542	181	26	24	68	22	56	37	63
DH-1	12	Breccia	3.88	0.422	414	146	13	25	56	19	70	39	52
Lower contact	0	--	--	--	--	--	--	--	--	--	--	--	--

Strontium-isotope compositions were determined by thermal ionization mass spectrometry on representative samples from the Raven Canyon and Paintbrush Canyon reference sections (table 3) using conventional dissolution and mass spectrometric procedures described previously (Peterman and others, 1985). All $^{87}Sr/^{86}Sr$ values were adjusted to a scale on which the value for modern sea water is 0.70920 as determined by analyses of standard EN-1 which was prepared from the shell of a modern tridacna collected from Enewetok Atoll in the western Pacific Ocean. Relative to the standard, the $^{87}Sr/^{86}Sr$ values are accurate to better than ±0.01 percent (95-percent confidence level) of the value reported.

GEOCHEMISTRY OF OUTCROP SAMPLES

The geochemical data (table 1) for samples from the Raven Canyon reference section are presented in graphs showing element concentrations and ratios as a function of stratigraphic position of the samples. Geochemical data for samples from the Calico Hills Formation (table 2) are presented in tabular form only, and isotopic data for samples from both sections (table 3) are presented as a composite section.

Geochemical variations within the Topopah Spring Tuff reflect the first-order lithologic variations described by Lipman and others (1966). The lower two-thirds to three-quarters of the unit is devitrified, densely welded, crystal-poor, high-silica rhyolite

Table 3. Strontium-isotope data for samples from the Raven Canyon and Paintbrush Canyon reference sections

[The Calico Hills Formation of the Paintbrush Canyon section is shown in its appropriate stratigraphic position (strat. pos.) relative to the Raven Canyon section]

Sample	Unit[1]	Strat. pos. (ft)	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	IR(Sr)
H95C-18-7	Tpt-nw-v	118	25.05	0.71649	0.71194
DH-9	Tac-vit	125	38.87	0.71764	0.71052
DH-8	Tac-vit	171	35.29	0.71782	0.71136
DH-5	Tac-vit	584	19.99	0.71493	0.71127
DH-4	Tac-vit	814	29.59	0.71689	0.71147
DH-3	Tac-breccia	869	33.46	0.71686	0.71073
H95C-14+6	Tcp-nw-v	1,014	7.85	0.71199	0.71054
H95C-10-16	Tcp-pw-vp	1,089	8.43	0.71207	0.71051
H95C-7+10	Tcp-nw-vp	1,148	8.68	0.71218	0.71058
H95C-4+4	Tcp-nw-vp	1,211	8.19	0.71214	0.71063
H95C-1+0	Tcp-nw-v	1,273	9.27	0.71116	0.70945
H95C-0-10	Tcp-nw-v	1,289	10.40	0.71208	0.71016
H95C-0-1	AF-v	1,293	4.30	0.71134	0.71055
H95B-24+0	Tcb-nw-v	1,322	2.69	0.70924	0.70874
H95B-18-0	Tcb-pw-vp	1,404	2.70	0.70920	0.70870
H95B-14-35	Tcb-dw-d	1,467	2.66	0.70909	0.70860
H95B-11-5	Tcb-dw-v	1,532	1.90	0.70872	0.70837
H95B-4+26	Tcb-v	1,631	1.12	0.70828	0.70807
H95B-0C+0	Tcb-nw-v	1,667	3.22	0.70933	0.70873
H95-22+0	Bt-v-m	1,706	1.63	0.70942	0.70911
H95-18+0	Bt-v-m	1,745	2.26	0.71270	0.71227
H95-16+5	lith tuff	1,759	2.80	0.71013	0.70959
H95-10+6	Bt-v	1,818	3.47	0.70993	0.70926
H95-5+7	Bt-v	1,867	3.35	0.71025	0.70961

[1]Unit abbreviations are the same as in table 1.

consisting largely of microcrystalline quartz and feldspar. The high-silica rhyolite is overlain by quartz latite separated by an interval that is transitional in composition upward due to mixing of high-silica rhyolite and quartz latite (Schuraytz and Vogel, 1989). The upper three samples of the Topopah Spring Tuff at the Raven Canyon reference section are from the quartz latitic caprock and vitrophyre (table 1). The increase in Zr and Ti (fig. 2), Ca, Sr, and Ba (fig. 3), La and Ce (fig. 4), and decrease in Rb and Nb (fig. 5) upward in the unit are characteristic features of the quartz latite (Peterman and others, 1991). In contrast, the subjacent high-silica rhyolite is remarkably uniform in composition. These internal geochemical features are characteristic of the Topopah Spring Tuff throughout its extent at Yucca Mountain. The younger Tiva Canyon Tuff has a similar internal compositional zonation (Peterman and Futa, *in press*). These first-order geochemical and lithologic features of the Topopah Spring and Tiva Canyon Tuffs are the inverse reflection of compositional gradients in their source magmas. Locally, the Topopah Spring Tuff has been altered to zeolites and clay in a zone at the top of the lower vitrophyre (Levy and O'Neil, 1989; Peterman and others, 1991). In drill hole UE-25a #1, this altered zone is marked by substantial increases in Sr and Ca contents. Corresponding increases in Ti and Zr in this zone indicate that these elements can be mobilized during intense alteration of glassy rock where they are not securely sequestered in discrete minerals (Peterman and others, 1991). This localized alteration in the Topopah Spring Tuff is not present at the Raven Canyon reference section (figs. 2 and 3).

The Wahmonie Formation in the Raven Canyon reference section is represented by nonwelded to partially welded bedded tuffs, and the three samples collected show large variations in the concentrations of Zr, Ti, Ca, Sr, and Ba, (figs. 2 and 3). Detailed sampling and analyses are needed to characterize this unit.

The Prow Pass Tuff at Raven Canyon consists of a central zone of partially welded tuffs displaying vapor-phase mineralization overlain and underlain by nonwelded vitric zones. The concentrations of Ca, Sr, and Ba (fig. 3) are remarkably uniform throughout the unit irrespective of the zonal variations. For example, the total range in Ba of 277 to 291 ppm (micrograms of element/gram of sample) throughout the unit is well within analytical error. The minor variations in Sr (50 to 66 ppm) and Ca (0.52 to 0.68 percent) are correlative (figs. 3 and 6). Zirconium ranges from 149 to 194 ppm with the highest value in a nonwelded vitric sample at the base, and Ti, ranging from 614 to 713 ppm, may increase slightly with depth. A step increase in K upward is accompanied by a step decrease in Rb between samples to 406 and 428 ft (fig. 5) resulting in a step increase upward in K/Rb ratios (fig. 6).

The Bullfrog Tuff consists of nonwelded vitric tuffs that are underlain by partially to moderately welded tuffs containing vapor-phase mineralization and by densely welded, devitrified tuffs. The lower part of the unit consists of vitrophyre underlain by nonwelded vitric tuff. These zonal variations in welding and crystallization are accompanied by systematic downward increases in Ti, Zr, Ca, Sr, Ba, La, and Ce followed by marked decreases in these elements in the nonwelded, vitric tuffs at the base (figs. 2, 3, and 4). In contrast, K, Nb, Rb, and Y are relatively uniform throughout the unit (figs. 4 and 5). These variations may be primary or may indicate incipient alteration of the vitrophyre perhaps similar to that which occurs in the lower part of the Topopah Spring Tuff (Peterman and others, 1991).

The relatively thin Tram Tuff at Raven Canyon consists of densely welded, devitrified tuff underlain by lithic-rich tuff. The densely welded, devitrified tuff has much smaller concentrations of Zr, Ti, K, Rb, Nb, Y, La, and Ce (figs. 2, 4, and 5) than the underlying lithic-rich tuff. The densely welded and lithic-rich tuffs are similar in alkaline-earth element concentrations (fig. 3). Most of the element concentrations scatter considerably in the bedded vitric tuffs that overlie and underlie the Tram Tuff (figs. 2–5).

The Calico Hills Formation, although not present at Raven Canyon, is extensive beneath most of Yucca Mountain where it has been zeolitized (Broxton and others, 1987). However, vitric tuffs of the Calico Hills Formation occur in an area between Yucca Wash and Fortymile Wash (Dickerson and Hunter, 1994), and a well-exposed sequence in Paintbrush Canyon was selected as a geochemical reference section (fig. 1). In this area, the Calico Hills Formation is composed of an alternating tuff breccia, bedded tuff, and vitrophyric rhyolite.

Nine samples of the Calico Hills Formation were collected from a stratigraphic interval of approximately 300 ft; these samples are limited in their compositional range (table 2). Peterman and others (1993) compared these vitric tuffs with samples of the zeolitized tuffs of the Calico Hills Formation penetrated by drill holes UE-25a #1 and UE-25b #1. Zeolitization was accompanied by large-scale open-system behavior in Ca and Sr whereas Zr and Ti were relatively immobile. The composition of the vitric Calico Hills Formation is similar in many respects to that of the high-silica rhyolite of the Topopah Spring Tuff at Raven Canyon and to the high-silica rhyolite of the Tiva Canyon Tuff in drill hole UE-NRG#3 (Peterman and Futa, *in press*). The

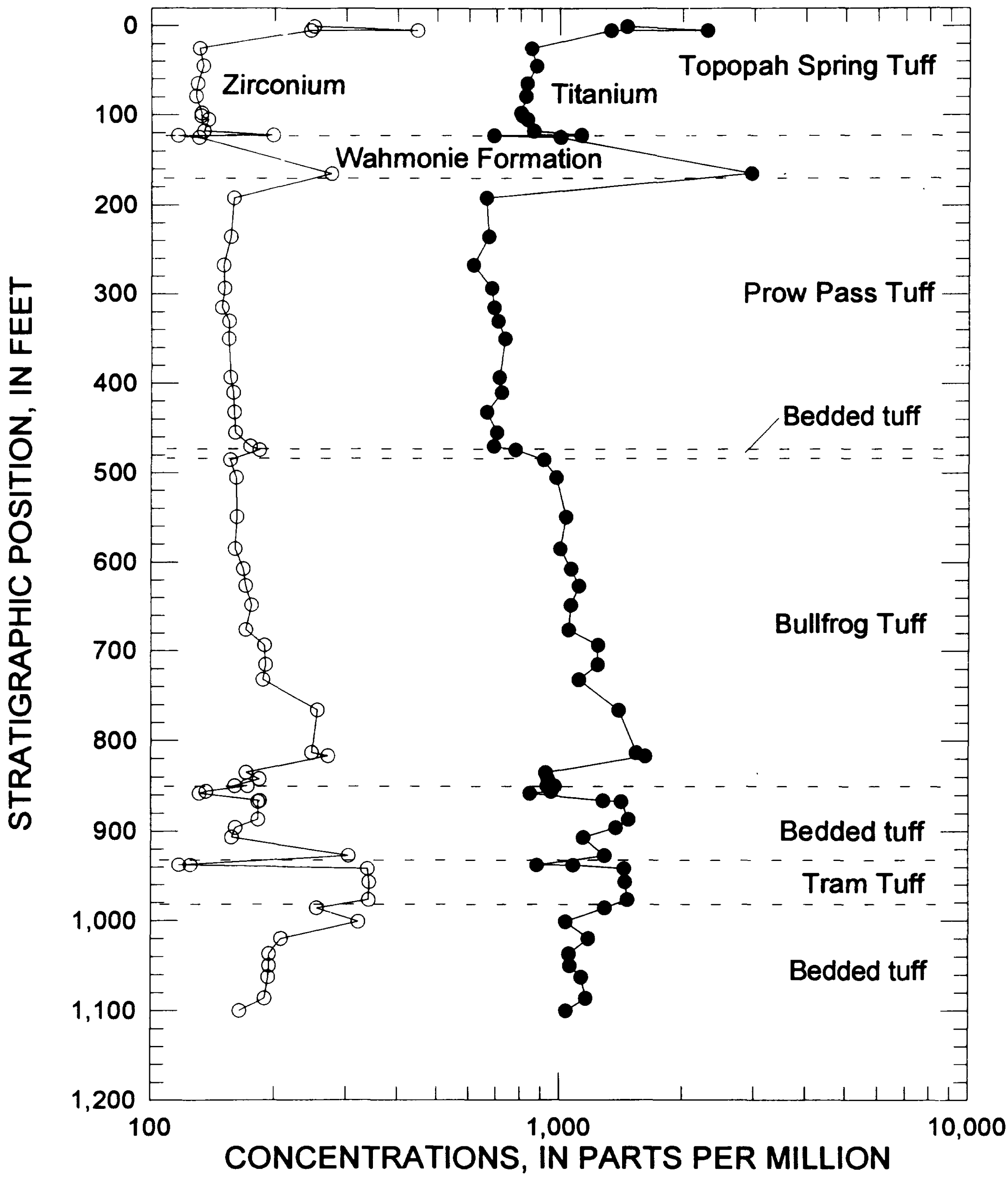

Figure 2. Concentrations of zirconium and titanium in samples from the Raven Canyon reference section.

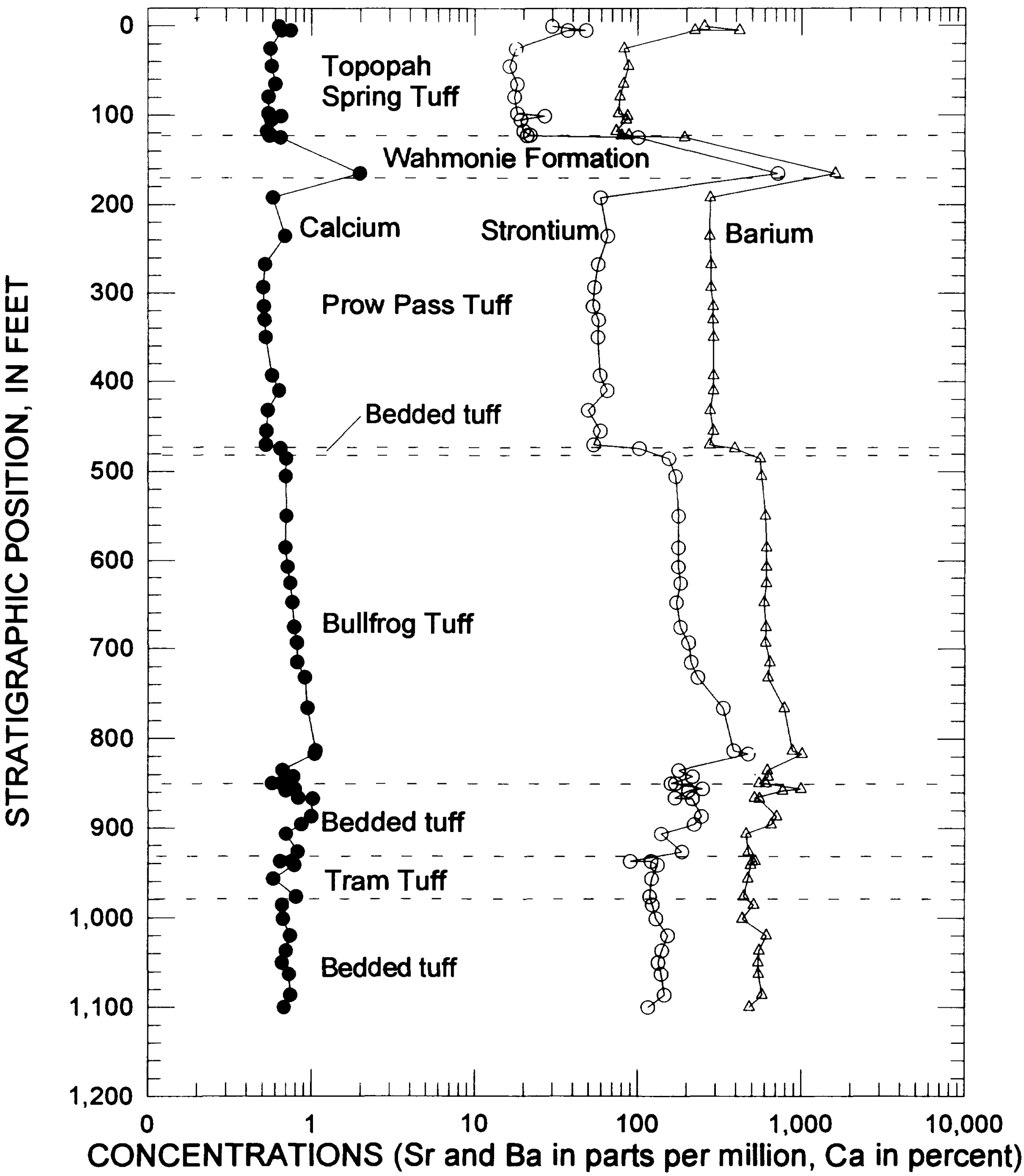

Figure 3. Concentrations of calcium, strontium, and barium in samples from the Raven Canyon reference section.

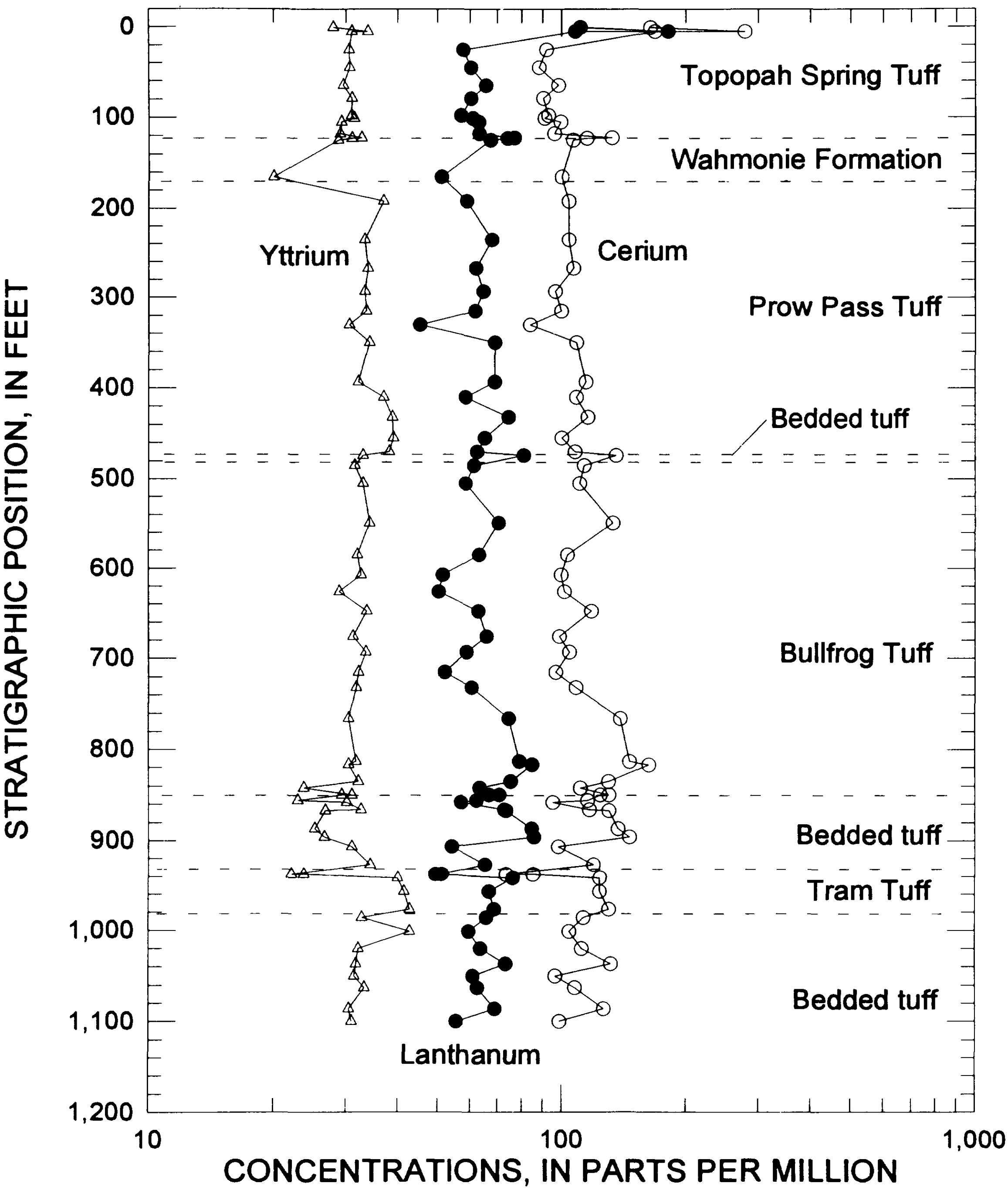

Figure 4. Concentrations of yttrium, lanthanum, and cerium in samples from the Raven Canyon reference section.

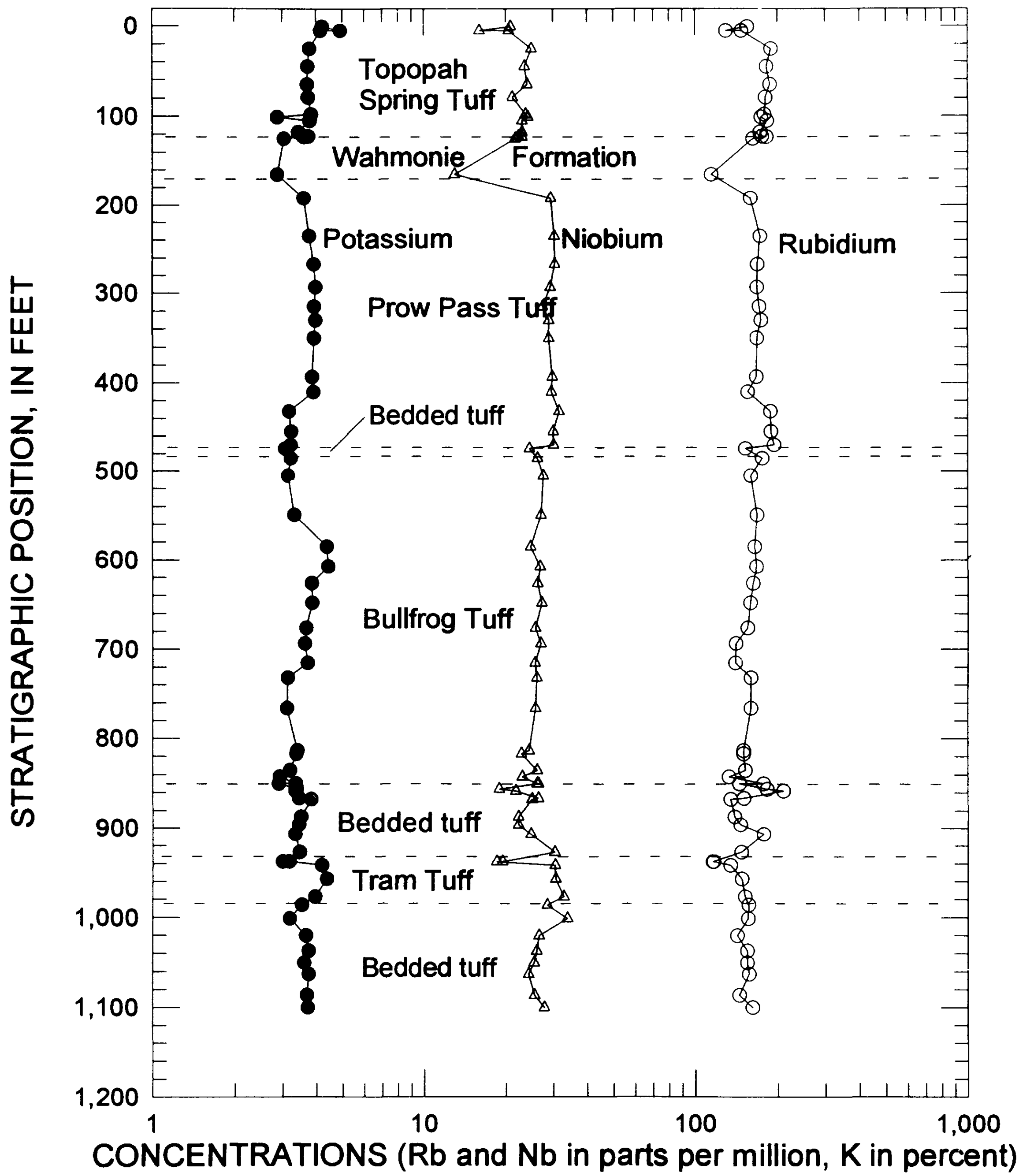

Figure 5. Concentrations of potassium, niobium, and rubidium in samples from the Raven Canyon reference section.

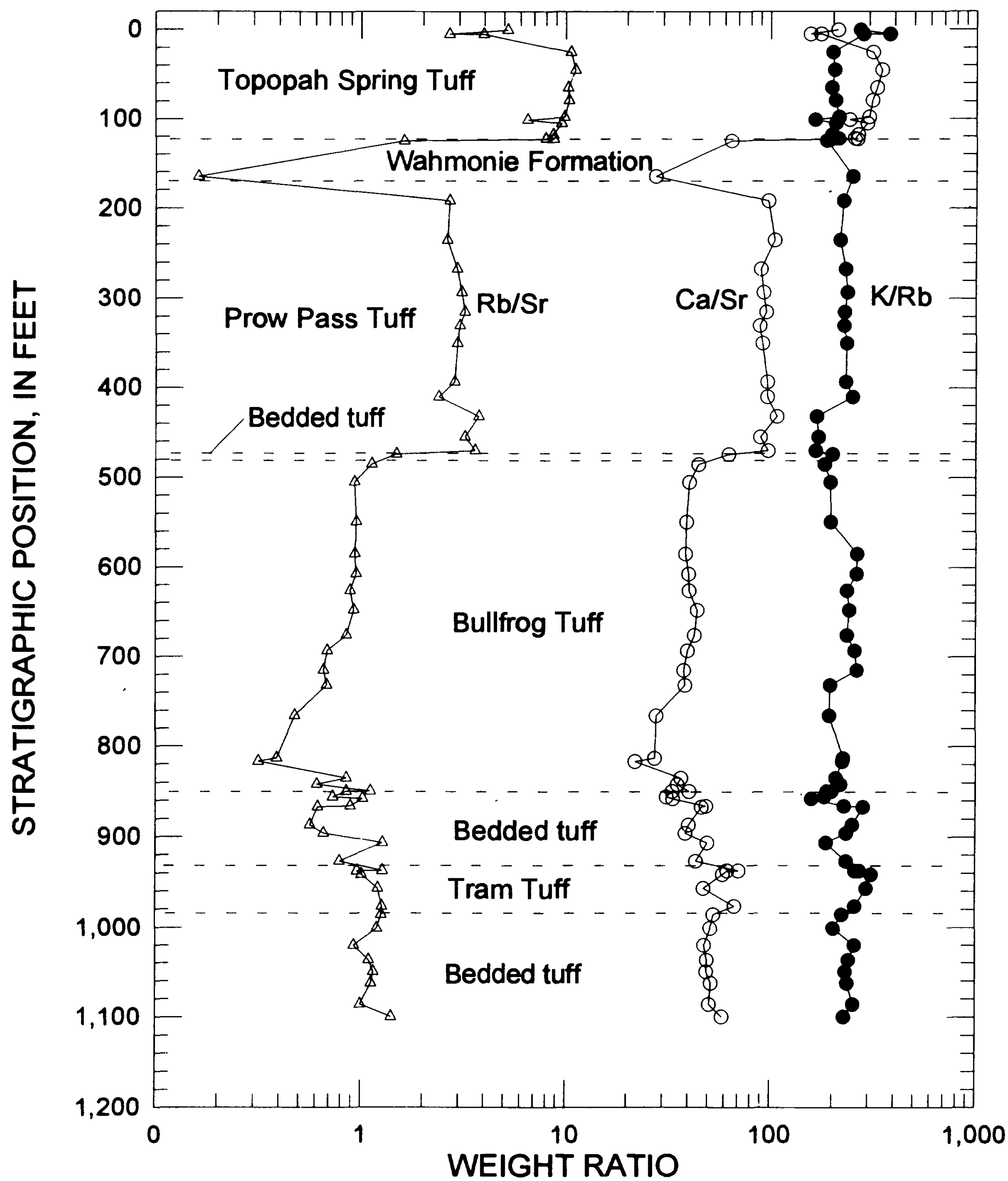

Figure 6. Ratios of rubidium to strontium (Rb/Sr), calcium to strontium (Ca/Sr), and potassium to rubidium (K/Rb) in samples from the Raven Canyon reference section.

most important difference is in the much lower Zr concentration (56 to 79 ppm) of the Calico Hills Formation (table 2) compared with the high-silica rhyolites of the younger units (approximately 130 ppm for the Topopah Spring Tuff and 200 ppm for the Tiva Canyon Tuff).

Strontium isotope measurements were completed on selected samples from the Raven Canyon and Paintbrush Canyon reference sections. Data for the Calico Hills Formation have been integrated with data for samples from Raven Canyon to form a composite section for illustrative purposes (fig. 7). The nonwelded vitric zones near the contacts of the Prow Pass and Bullfrog Tuffs show considerable isotopic variation (fig. 7) which may indicate alteration related to localized fluid flow along these more conductive zones.

The general decrease down section in measured present-day and calculated initial $^{87}Sr/^{86}Sr$ values (fig. 7) is consistent with results obtained on composite samples prepared from USW G-1 core (Spengler and Peterman, 1991). The high initial $^{87}Sr/^{86}Sr$ ratio, designated IR(Sr), for the sample of high-silica rhyolite from the Topopah Spring Tuff is characteristic of this unit where it is relatively unaltered. For example, 16 samples of the Topopah Spring high-silica rhyolite from drill hole USW G-4 have a narrow range in IR(Sr) values and a mean and standard deviation of 0.71284±0.00019 (Z.E. Peterman, unpub. data, 1994). The range in Sr contents and mean IR(Sr) values ($\pm 1\sigma$) for the units in the Raven Canyon and Paintbrush Canyon reference sections are: Calico Hills Formation, 15 to 31 ppm, 0.71107±0.00037; Prow Pass Tuff, 54 to 59 ppm, 0.71031±0.00044; and Bullfrog Tuff, 156 to 476 ppm, 0.70853±0.00024. These systematic geochemical and isotopic variations are features that relate to the origin and crustal contamination of the source magmas. The IR(Sr) values for all samples are plotted against the reciprocal of the Sr concentrations in figure 8. Disregarding the point in the upper left-hand corner of the graph, which represents a bedded tuff, the data clearly indicate two trends. Linear arrays of data on a plot of this type commonly indicate mixing of two end members. Samples that have 1/Sr values of less than 0.01 (Sr concentrations greater than 100 ppm) plot close to a steep line that is labeled "Mixing (Assimilation)." This array probably indicates mixing (through assimilation) of primitive, mantle-derived magma (high Sr concentrations and low $^{87}Sr/^{86}Sr$) with Precambrian crustal material (lower Sr concentrations with higher $^{87}Sr/^{86}Sr$). The data to the right of the steep mixing line in figure 8 are largely data for samples of the Prow Pass Tuff and the Calico Hills Formation. Fractional crystallization without assimilation would result in migration of the liquid composition away from a point on the steep curve to lower Sr concentration values with no change in the IR(Sr) values. The horizontal line labeled "Differentiation" is the locus of one possible path that could result from fractional crystallization involving plagioclase or sanidine removal, or both, and concomitant depletion of the residual liquid in Sr.

CONCLUSIONS

- Samples of densely welded, devitrified tuff from relatively unaltered intervals of the Raven Canyon and Paintbrush Canyon reference sections have trace element concentrations and Sr isotope ratios showing only slight variability or reflecting internal lithologic variations that are primary features inherited from compositionally and isotopically zoned magmas.

- At the Raven Canyon reference section, the greatest degree of element variability is within nonwelded tuffs between the major units. This variability probably indicates water-rock interaction along these more transmissive units.

- The thick lower vitrophyre of the Bullfrog Tuff at Raven Canyon displays systematic increases in Ti, Zr, Ca, Sr, Ba, La, and Ce concentrations downward compared with concentrations in the overlying densely welded, devitrified portion of the unit. These variations may be primary or may indicate incipient alteration of the vitrophyre perhaps similar to the localized alteration in the lower part of the Topopah Spring Tuff.

- Data in this report for unaltered tuffs at reference sections at Raven Canyon and Paintbrush Canyon can be used as baseline information for geochemical and isotopic studies of the rock mass at Yucca Mountain. Such data can be of value in correlating zonal features within the volcanic units in drill holes and in the Experimental Studies Facility (ESF). This baseline data can also contribute significantly to developing an understanding of the degree and extent of element mobility in the past. By analogy, this information can be useful in assessing possible future alteration in the Topopah Spring Tuff that might be induced by heating and mobilization of water liberated from nearby zeolitized zones.

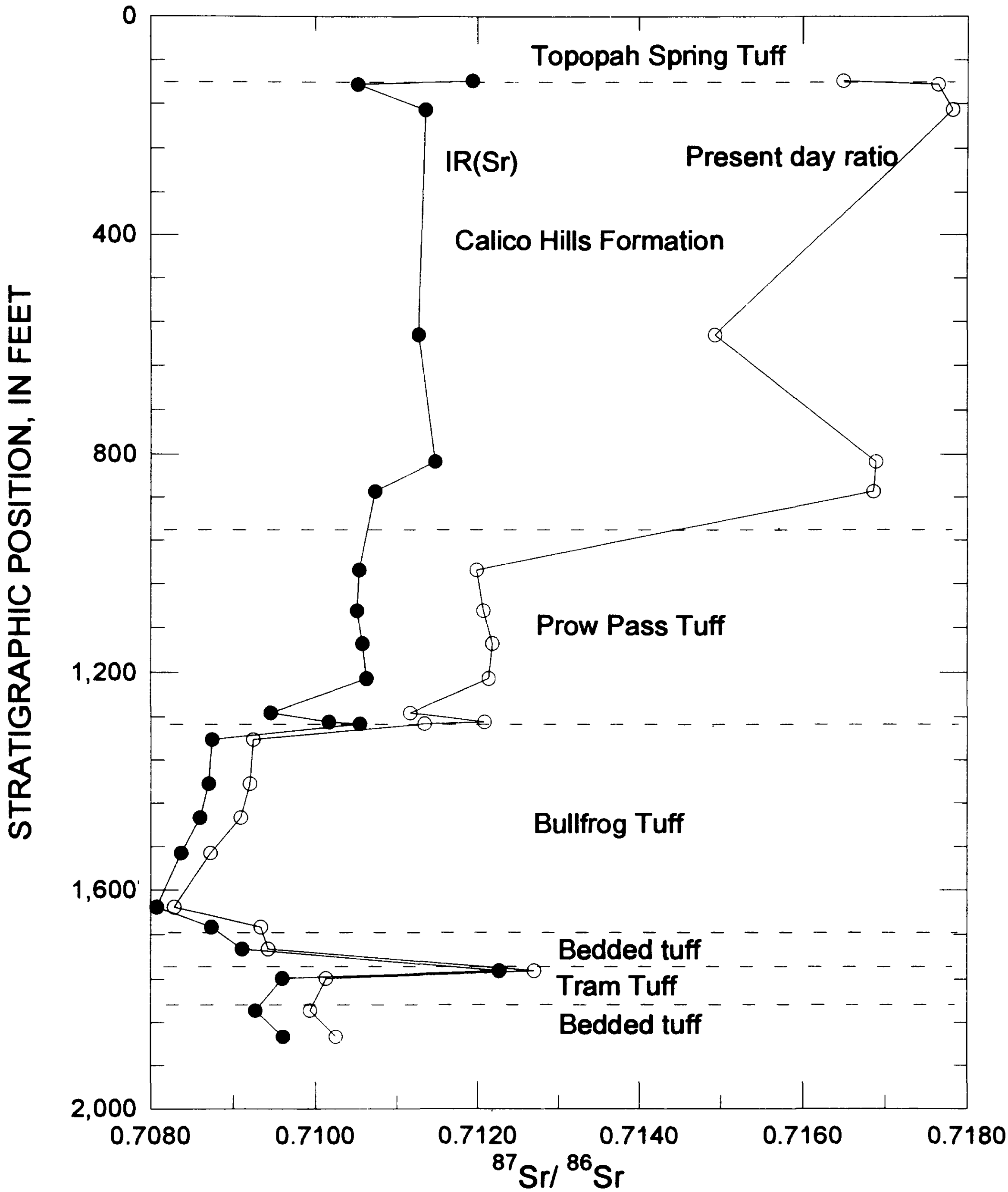

Figure 7. Present-day and initial $^{87}Sr/^{86}Sr$ values for samples from the Raven Canyon and Paintbrush Canyon reference sections.

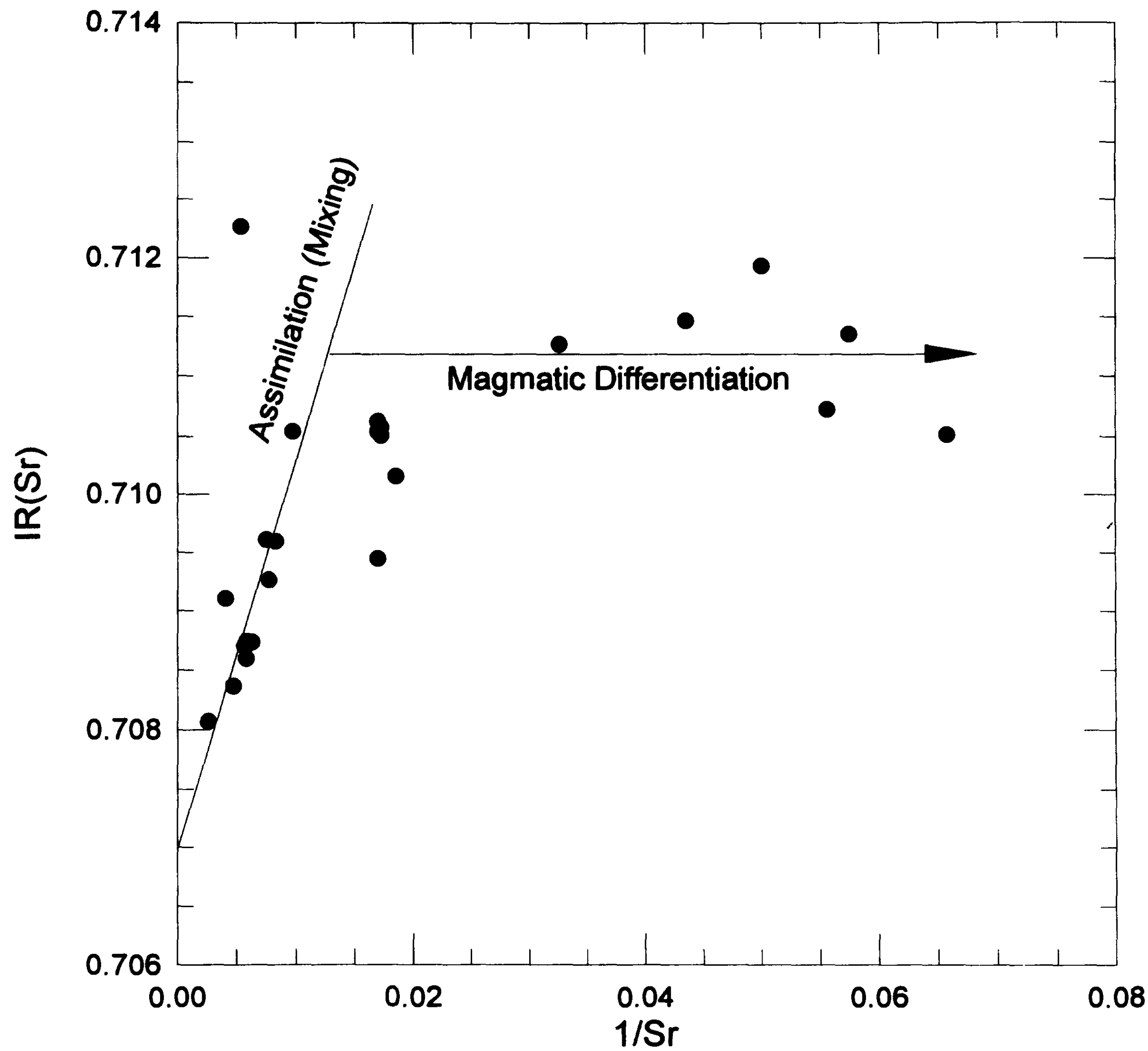

Figure 8. IR(Sr) values versus reciprocal strontium concentrations for samples from the Raven Canyon and Paintbrush Canyon reference sections.

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