GEOCHEMICAL AND PB, SR, AND O ISOTOPIC STUDY OF THE TIVA CANYON TUFF AND TOPOPAH SPRING TUFF, YUCCA MOUNTAIN, NYE COUNTY, NEVADA

by Leonid A. Neymark, Brian D. Marshall, Loretta M. Kwak, Kiyoto Futa, and Shannon A. Mahan

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CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
kilometer (km)	0.6214	mile
meter (m)	3.2808	foot
millimeter (mm)	0.03937	inch
nanograms (ng)	2.205×10^{-12}	pounds

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.

Geochemical and Pb, Sr, and O Isotopic Study of the Tiva Canyon Tuff and Topopah Spring Tuff, Yucca Mountain, Nye County, Nevada

By Leonid A. Neymark, Brian D. Marshall, Loretta M. Kwak, Kiyoto Futa, *and* Shannon A. Mahan

Abstract

Yucca Mountain, located in Nye County, Nevada, is currently being studied as a potential site for an underground repository for high-level radioactive waste. Because Yucca Mountain is located in a resource-rich geologic setting, one aspect of the site characterization studies is an evaluation of the resource potential at Yucca Mountain. Geochemical and isotopic signatures of past alteration of the welded tuffs that underlie Yucca Mountain provide a means of assessing the probability of hydrothermal ore deposits being present within Yucca Mountain.

In this preliminary report, geochemical and isotopic measurements of altered Tiva Canyon Tuff and Topopah Spring Tuff collected from fault zones exposed on the east flank of Yucca Mountain and from one drill core are compared to their unaltered equivalents sampled both in outcrop and drill core. The geochemistry and isotopic compositions of unaltered Tiva Canyon Tuff and Topopah Spring Tuff (high-silica rhyolite portions) are fairly uniform; these data provide a good baseline for comparisons with the altered samples. Geochemical analyses indicate that the brecciated tuffs are characterized by addition of calcium carbonate and opaline silica; this resulted in additions of calcium and strontium, increases in oxygen-18 content, and some redistribution of trace elements.

After leaching the samples to remove authigenic carbonate, no differences in strontium or lead isotope compositions between altered and unaltered sections were observed. These data show that although localized alteration of the tuffs has occurred and affected their geochemistry, there is no indication of additions of exotic components. The lack of evidence for exotic strontium and lead in the most severely altered tuff samples at Yucca Mountain strongly implies a similar lack of exotic base or precious metals.

INTRODUCTION

Yucca Mountain in Nye County, Nevada, is being studied as a potential site for the underground storage of high-level radioactive waste. It is also located in the resource-rich Basin and Range province. These resources include deposits of base, precious, and strategic metals; industrial minerals; hydrocarbons; and geothermal energy. The presence in Yucca Mountain of favorable host rocks for both metals and hydrocarbons requires a thorough assessment of its natural resource potential. Geochemical and isotopic investigations of fault zones and other zones of potential fluid flow are helpful for such an assessment, because exotic isotopic compositions (Pb, Sr, O) would be evidence of passage of hydrothermal fluids.

This study is based, in part, on the ability of natural isotopic ratios of both strontium and lead to be changed by small additions of these elements from foreign sources introduced during alteration. Significant variations in these ratios are observed in areas of known mineralization nearby at Bare Mountain (Peterman and others, 1994). The term "exotic" refers to isotopic signatures that are not typical of the unaltered volcanic rocks.

This preliminary report describes results of geochemical and isotopic (Pb, Sr, O) study of both altered and unaltered felsic tuffs of the Tiva Canyon Tuff and Topopah Spring Tuff. The scope of the work was:

1. To collect baseline data for unaltered tuffs (Antler Ridge reference section of outcrop samples for Tiva Canyon Tuff and UE-25a #1 drill core samples for Topopah Spring Tuff);

2. To analyze altered tuffs at three different localities (UE-25a #1, Trench 14, and Busted Butte).

3. To compare the results for altered felsic tuffs with the baseline data.

Sample Collection

Two suites of samples were selected to obtain baseline geochemical and isotopic data for unaltered felsic tuff in the Tiva Canyon Tuff and Topopah Spring Tuff, and three different localities were sampled to study its altered varieties. The sampling sites are located in proximity to the potential repository as shown in figure 1.

Drill hole UE-25a #1

Drill hole UE-25a #1 is located on the northeastern flank of Yucca Mountain (fig. 1). Among other stratigraphic units, it intersects high-silica rhyolite of the Topopah Spring Tuff in the depth interval from 155.6 to 403.6 m. In this drill hole, much of the basal vitrophyre and the lowermost part of the overlying high-silica rhyolite are variably altered along fractures to clays and zeolites (Levy and O'Neil, 1989). The eight samples analyzed were described by Peterman and others (1991). Samples 510.4 to 990.6 are from the densely welded, devitrified zone composed of unaltered high-silica rhyolite. Samples 1274.0, 1274.4, 1295.0, and 1324.3 are from the lower vitrophyre and represent various degrees of zeolitization.

Antler Ridge

A suite of 18 out of 35 outcrop samples (Singer and others, 1994) collected from a 91.5-m thick vertical transect of the Tiva Canyon Tuff along the southern flank of Antler Ridge (fig. 1) was selected for this study. Selected samples represent all lithologies (samples 9855 to 9880 are high-silica rhyolite, and from 9883 to 9889 are quartz latite) and textural zones (hackly, lower lithophysal, clinkstone, upper lithophysal, and upper cliff; Scott and Bonk, 1984) observed within the Tiva Canyon Tuff. This suite of unaltered tuff is used to obtain reliable baseline geochemical and isotopic data for this stratigraphic unit.

Busted Butte

Altered felsic tuffs at Busted Butte (fig. 1) are represented by brecciated Topopah Spring Tuff. Here sand ramps and bedrock are cut by the Paintbrush Canyon fault. Breccias contain variable amounts of tuffaceous clasts in a matrix of finely crushed tuff and authigenic mineral cements. Four samples of brecciated bedrock (HD-74-1, HD-74-2, HD-74-3, and HD-74-4) of about 20 g each, representing different proportions of clasts, matrix, and cement materials were drilled out of a breccia block (approximately 40 × 30 × 20 cm). Samples HD-74-2 and HD-74-3 contained maximum and minimum proportions of the tuffaceous clasts, respectively.

Trench 14

Bedrock breccias at Trench 14, which is located along the Bow Ridge Fault (fig. 1), are restricted to the Tiva Canyon Tuff. The section of Tiva Canyon Tuff exposed in Trench 14 is a densely welded, devitrified tuff. The breccias resemble those in Busted Butte, but contain more authigenic cement (Levy and Taeser, 1991). Three samples of the breccia (HD-41-1, HD-41-2, and HD-41-3) of about 20 g each were drilled out of a breccia block (approximately 30 × 20 × 15 cm) and analyzed during this work.

Study Methods

This paper reports new isotopic (Pb, Sr, O) and concentration (Pb, U, Th) data for Tiva Canyon Tuff from Antler Ridge (table 1), new U-Pb data for Topopah Spring Tuff from drill hole UE-25a #1 (table 2), and new U-Th-Pb, Sr and O isotopic, and energy dispersive X-ray fluorescence (XRF) concentration results for breccia samples from Busted Butte and Trench 14 (tables 3 and 4). Previously published Rb-Sr and XRF concentration data for drill hole UE-25a #1 (Peterman and others, 1991) and XRF data for the Antler Ridge section (Singer and others, 1994; Z.E. Peterman and K. Futa, U.S. Geological Survey, written commun., 1994) were also used.

Minor and trace elements were determined on representative splits of approximately 3 to 5 grams of 250-mesh rock powder by energy-dispersive X-ray fluorescence. Replicate analyses of the USGS GSP-1 geochemical reference standard (Govindaraju, 1989) indicate precisions of better than ±4 percent (1σ) for all elements analyzed except Y and La, which have a reproducibility of ±8 percent. The Rb/Sr ratio in the standard reproduces to better than ±3 percent.

Sr was separated from a split of 200-mesh rock powder by conventional ion-exchange chromatography after dissolution in a mixture of concentrated hydrofluoric (HF) and sulfuric (H_2SO_4) acids. Isotope analyses were performed automatically in static mode on a 7-collector Finnigan™ MAT-262 mass-spectrometer. Two samples of the USGS carbonate standard EN-1 (Futa, Peterman, and Hein, 1988) were analyzed in each turret of 13 samples and gave mean $^{87}Sr/^{86}Sr$ of 0.70911±0.00002 during the course of this study; Sr

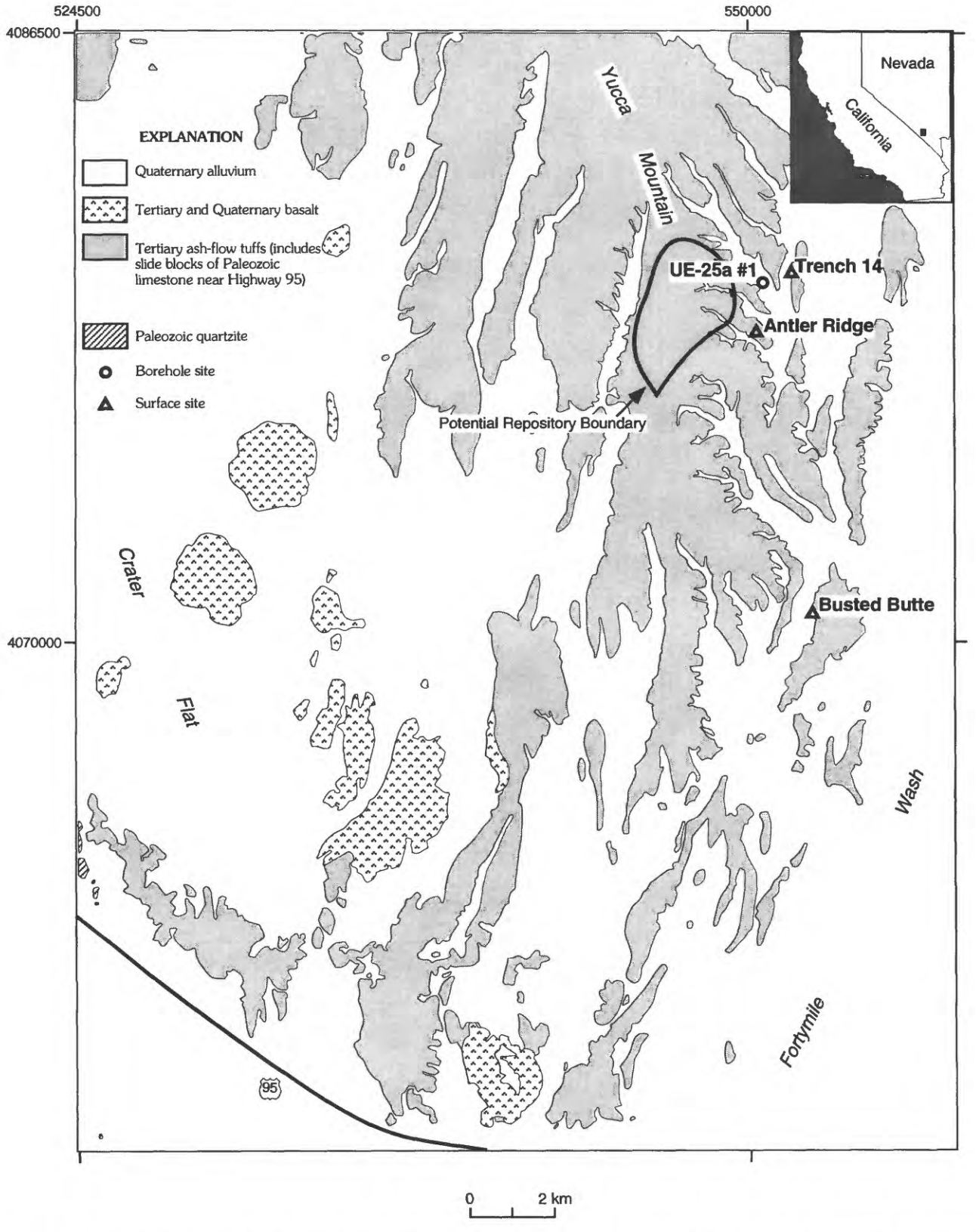

Figure 1. Generalized map of the Yucca Mountain region showing sampling localities. The site of the potential repository is outlined by a solid line. Geology based on Frizzell and Shulters (1990). Marginal ticks are Universal Transverse Mercator coordinates (in meters) in zone 11.

Table 1. U-Th-Pb, Rb-Sr, and oxygen isotope data for the Tiva Canyon Tuff, Antler Ridge section, Yucca Mountain, Nevada

[m, meters; ppm, parts per million]

Sample number	Elevation (m)	U (ppm)	Th (ppm)	Pb (ppm)	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$\delta^{18}O$	Th/U	$^{87}Sr/^{86}Sr$	$^{87}Rb/^{86}Sr$
9855	1286.3	4.86	25.0	31.3	18.157	15.557	38.985	9.3	5.14	0.71771	37.07
9857	1293.3	4.87	25.0	30.9	18.174	15.576	39.038	9.2	5.14	0.71715	31.53
9859	1297.8	4.88	24.8	30.0	18.200	15.613	39.163	9.4	5.09	0.71712	29.92
9860	1299.4	4.97	24.6	28.4	18.200	15.610	39.163	8.9	4.96	0.71605	23.92
9861	1302.4	4.76	25.1	31.6	18.186	15.598	39.120	9.2	5.28	0.71727	34.93
9863	1304.8	4.84	25.1	29.2	18.171	15.577	39.053	8.9	5.18	0.71672	29.57
9865	1309.4	4.71	25.0	29.3	18.184	15.592	39.100	9.0	5.31	0.71637	29.41
9867	1313.7	4.80	24.8	26.0	18.191	15.600	39.129	8.6	5.16	0.71658	29.72
9869	1318.0	4.80	25.6	27.6	18.196	15.606	39.136	8.7	5.33	0.71582	23.53
9871	1325.0	4.94	24.6	29.5	18.184	15.590	39.068	9.0	4.98	0.71518	18.72
9874	1330.8	4.80	25.1	17.0	18.207	15.617	39.170	9.1	5.23	0.71852	44.89
9876	1335.0	4.86	25.3	26.6	18.186	15.598	39.118	9.0	5.21	0.71619	26.35
9879	1340.2	4.95	24.6	23.3	18.179	15.586	39.083	9.5	4.98	0.71649	28.04
9880	1344.2	4.86	23.9	19.4	18.184	15.582	39.079	10.1	4.93	0.71503	18.30
9883	1349.3	4.58	24.2	25.5	18.189	15.604	39.138	9.2	5.27	0.71508	18.47
9885	1354.8	4.39	22.6	22.4	18.169	15.568	39.017	8.8	5.15	0.71353	8.79
9887	1360.3	4.19	37.6	13.2	18.209	15.586	39.088	8.8	8.97	0.71274	9.45
9889	1366.4	3.72	17.1	18.8	18.204	15.582	39.051	8.4	4.60	0.71088	2.67
Average		4.71	25.0	25.6	18.187	15.591	39.094	9.1	5.33	0.71580	24.74
Standard deviation		0.32	3.7	5.4	0.014	0.016	0.053	0.4	0.93	0.00187	10.61
Percent deviation		6.7%	14.7%	21.2%	0.08%	0.10%	0.13%	4.2%	17.4%	0.3%	42.9%

Table 2. U-Th-Pb data for selected samples of the Topopah Spring Tuff from the drill hole UE-25a #1

[Replicate analyses indicated by *; m, meters; ppm, parts per million]

Sample number	Depth (m)	U (ppm)	Th (ppm)	Pb (ppm)	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Th/U
510.4	155.6	4.51		26.5	18.125	15.588	39.177	
609.6	185.8	4.62		25.0	18.109	15.572	39.118	
669.5	204.1	4.47		27.5	18.127	15.573	39.190	
990.6	301.8	5.08		27.3	18.161	15.594	39.177	
Average		4.67		26.5	18.131	15.582	39.166	
Standard deviation		0.28		1.1	0.022	0.011	0.032	
Percent deviation		6.0%		4.3%	0.12%	0.07%	0.08%	
1274.0	388.3	3.73		36.8	18.110	15.574	39.119	
1274.0*		3.46	29.5					8.53
1274.4	388.4	3.09		21.0	18.095	15.557	39.076	
1274.4*		3.35	32.3					9.64
1295.0	394.7	3.76		31.6	18.153	15.622	39.284	
1295.0*		3.51	28.3					8.06
1324.3	403.6	2.65		14.0	18.123	15.577	39.162	
1324.3*		2.49	25.3					10.16
BCR-1		1.744		13.7	18.813	15.628	38.705	

Table 3. Geochemical data for unleached and acid-leached breccia samples from Trench 14 and Busted Butte

Sample number	74-1	74-1-r	74-2	74-2-r	74-3	74-3-r	74-4	74-4-r	41-1	41-1-r	41-2	41-2-r	41-3	41-3-r
Weight loss, %														
Acetic acid		13.1		1.6		14.6		12.7		5.3		14.5		13.1
HCl		14.3		1.8		16.3		10.5		13.9		16.8		13.1
K, %	2.32		3.46		2.03		2.53		2.81		3.02		2.75	
Ca, %	5.33		0.43		6.73		5.80		6.82		6.31		5.47	
Ti, ppm	440		768		342		457		518		609		897	
Rb, ppm	91	108	163	187	74	94	96	109	110	143	118	145	94	113
Sr, ppm	485	20.0	24.0	21.2	758	25.3	382	41.0	107	12.3	142	16.4	151	28.3
Y, ppm	14	14	24	24	5	10	15	14	20	18	22	23	20	17
Zr, ppm	90	93	140	163	82	93	91	91	124	147	139	163	212	239
Nb, ppm	10	13	21	21	5	10	11	13	14	21	17	22	15	15
Ba, ppm	53		89		77		61		60		71		164	
La, ppm	25		64		48		43		31		40		59	
Ce, ppm	39		93		48		67		55		50		90	

Table 4. U-Th-Pb, Rb-Sr, and oxygen isotope data for breccia samples from Trench 14 and Busted Butte

[Replicate analyses indicated by *]

Sample number	U, ppm	Th, ppm	Pb, ppm	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$\delta^{18}O$	Th/U	$^{87}Sr/^{86}Sr$	$^{87}Rb/^{86}Sr$
HD-41-1-r	8.94	16.0	11.0	18.166	15.559	38.996	16.9	1.79	0.71678	33.67
HD-41-2-r	7.74	17.5	11.9	18.205	15.604	39.149	16.3	2.26	0.71577	25.60
HD-41-2-r*				18.206	15.606	39.155				
HD-41-3-r	9.13	18.0	10.9	18.196	15.581	39.060	18.5	1.98	0.71290	11.56
HD-41-3-r*				18.224	15.617	39.174				
Average				18.199	15.593	39.107				
Standard deviation				0.021	0.023	0.076				
Percent deviation				0.11%	0.15%	0.19%				
HD-74-1-r	6.58	6.89	13.9	18.149	15.608	39.227	18.2	1.05	0.71479	15.63
HD-74-1-r*				18.149	15.609	39.229				
HD-74-2-r	3.99	9.80	20.3	18.149	15.615	39.260	12.1	2.46	0.71696	25.54
HD-74-3-r	6.10	9.85	12.8	18.128	15.576	39.113	20.4	1.61	0.71376	10.76
HD-74-4-r	7.36	12.2	15.5	18.129	15.577	39.115	17.4	1.65	0.71374	7.43
HD-74-4-r*				18.139	15.589	39.154				
Average				18.141	15.596	39.183				
Standard deviation				0.010	0.017	0.064				
Percent deviation				0.06%	0.11%	0.16%				
HD-74-1 (leach)	3.15	0.953	2.63	18.222	15.596	39.167		0.30		
HD-74-3 (leach)	5.04	3.27	5.12	18.300	15.611	39.182		0.65		
HD-41-2 (leach)	3.66	3.95	34.4	18.200	15.605	39.129		1.08		

ratios are normalized to an EN-1 value of 0.70920. Mass-fractionation correction was made by normalization to a $^{86}Sr/^{88}Sr$ value of 0.1194. Breccia samples from Trench 14 and Busted Butte were pre-treated in 1N hydrochloric acid (HCl) to eliminate the authigenic carbonate component, and the leached residues were analyzed for Sr.

U-Th-Pb isotopes were analyzed using 50–200 mg splits of the same rock powders. Samples from UE-25a #1 and Antler Ridge were decomposed in a mixture of HF and nitric (HNO3) acids in teflon™ bombs under pressure. Breccia samples from Trench 14 and Busted Butte were leached twice using 0.8 N acetic acid, and residues were digested in HF on a hot plate. Three out of seven leachates also were analyzed.

U-Pb systematics in UE-25a #1 borehole samples were determined at the Institute of Precambrian Geology and Geochronology (IPGG), St. Petersburg, Russia, using the conventional hydrobromic acid (HBr) technique (Manhes and others, 1978) for lead separation by ion-exchange chromatography (L.A. Neymark, U.S. Geological Survey, IPGG, unpublished data). Total chemistry blank at IPGG during the measurements was 0.8±0.2 nanograms (ng) Pb. Uranium and Pb concentrations were determined with a precision of ±1 percent by isotope dilution using a ^{235}U and ^{206}Pb mixed spike. The average for three separate runs of USGS BCR-1 standard (Doe and Rohrbough, 1977; Govindaraju, 1989) analyzed at IPGG during the course of this study is presented in table 2. Isotopic analyses were carried out on an 8-collector Finnigan™ MAT-261 mass-spectrometer in static mode. Numerous measurements of National Institute of Standards and Technology (NIST) SRM-982 Pb-isotope standard (Catanzaro and others, 1968; Todt and others, 1993) revealed a Pb mass-fractionation correction factor of 0.13±0.03% per mass unit. Pb-isotope ratio reproducibility of ±0.05% (2σ) per mass unit was considered acceptable.

The other U-Th-Pb analyses were done at the USGS (Denver) laboratory using the same chemical procedures as for silicate rocks. Concentrations were determined with a precision of ±1 percent by isotope dilution using ^{206}Pb, ^{235}U and ^{230}Th spikes. U and Th in altered samples from UE-25a #1 were measured with ^{236}U and ^{229}Th spikes. Pb, U and Th blanks were 0.5±0.2, 0.008±0.003, and 0.01±0.002 ng, respectively. Acid-leached carbonate fractions were analyzed using an ammonium hydroxide (NH_4OH) coprecipitation technique (Zartman and Kwak, 1993a), for which these blanks were 1, 0.04, and 0.08 ng, respectively.

Pb-isotope analyses were made automatically in static mode on a 7-collector Finnigan™ MAT 262 mass spectrometer. Measured lead isotopic ratios have been corrected for a mass-discrimination factor of 0.05 percent per mass unit obtained from analyzing the NIST SRM-982 lead standard. Data for the standard obtained in both laboratories also revealed strong correlations ($r > 0.95$) between errors of measured isotopic ratios caused by mass fractionation. The reported ratios are mass fractionation, blank corrected, and are accurate to within ±0.05% (2σ) per mass unit.

Oxygen isotope analyses of the Tiva Canyon Tuff from Antler Ridge were performed by Geochron Laboratories of Cambridge, Massachusetts. Oxygen isotope compositions of the other samples were measured at the Department of Geological Sciences, University of Saskatchewan, Canada. Oxygen was obtained by decomposition of about 10 mg of a sample powder using bromine pentafluoride (BrF_5). Calcite-containing altered samples were leached with 0.8 N acetic acid ($C_2H_4O_2$) prior to analysis. The isotopic composition of oxygen is reported as permil ‰ deviations ($\delta^{18}O$ values) from standard mean ocean water (SMOW). Estimated reproducibility of the oxygen isotope analyses is ±0.4 ‰ (2σ).

Acknowledgments

G. Ovchinnikova and B. Gorokhovskiy (IPGG, St. Petersburg, Russia) helped to obtain U-Pb data on samples from UE-25a #1. The U.S. Geological Survey is conducting geologic studies for the Department of Energy Site Characterization Project under Interagency Agreement No. DE-AI08-92NV10874.

GEOCHEMICAL AND ISOTOPIC CHARACTERISTICS OF THE TIVA CANYON AND TOPOPAH SPRING TUFFS

Antler Ridge

U-Th-Pb, Rb-Sr, and oxygen isotope data for unaltered samples of the Tiva Canyon Tuff are presented in table 1. This set of samples displays remarkably uniform geochemical and isotopic characteristics. Relative standard deviations for U, Th, and Pb concentrations and Th/U ratios are within a range from 6.7 percent to 21.2 percent (table 1). Lead isotopic compositions are also fairly uniform (fig. 2) and their standard deviation (table 1) does not exceed analytical precision. Variations in oxygen isotopic composition (fig. 3) are limited and not systematic. The average

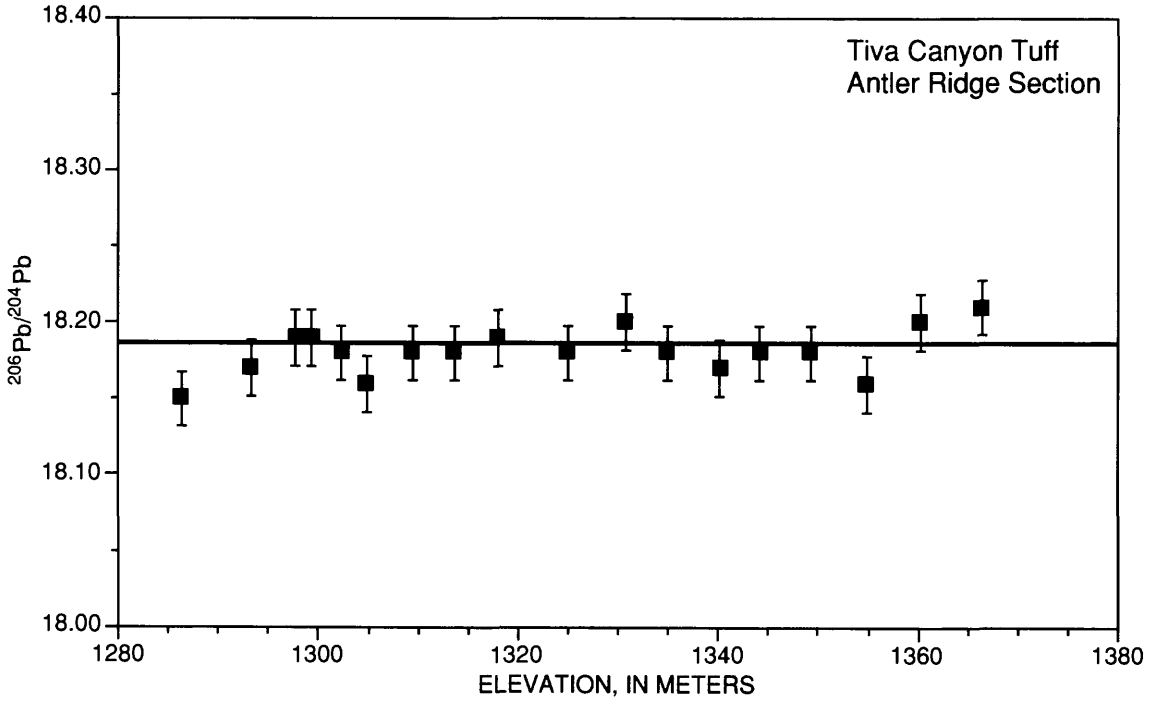

Figure 2. Variations of Pb isotopic composition in the Tiva Canyon Tuff, Antler Ridge section. Error bars (2σ) are shown; the horizontal line corresponds to the average value of $^{206}Pb/^{204}Pb = 18.187 \pm 0.014$.

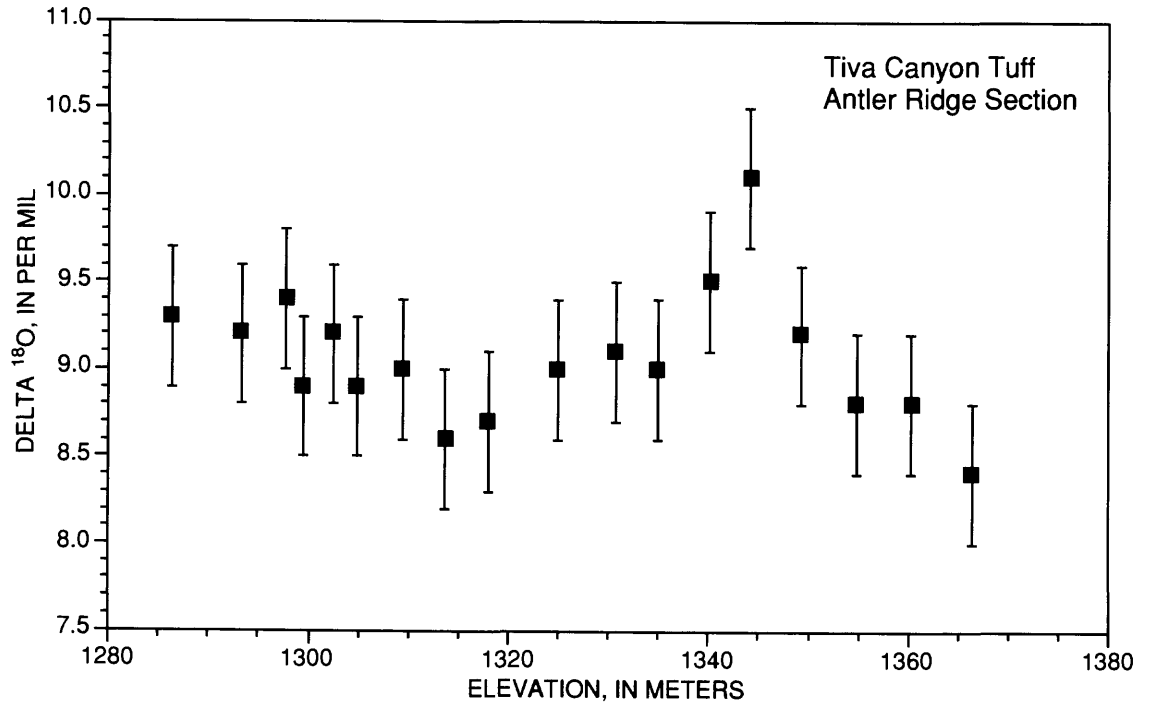

Figure 3. Variations in oxygen isotopic composition for the Tiva Canyon Tuff, Antler Ridge section.

value of $\delta^{18}O$ in 18 samples equals to 9.1±0.4 ‰ (1σ). The range of measured Sr isotopic compositions is age related, because measured $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios form an errorchron (not shown) corresponding to the age of 12±2 Ma, which agrees well with the Ar-Ar age of 12.7 Ma (Sawyer and others, 1994, p. 1305).

The variations in U, Th, and Pb concentrations, and Pb and oxygen isotope data for unaltered Tiva Canyon Tuff samples observed in this study range within narrow limits. Similar restricted variations have been reported for both a suite of selected major and trace elements and initial Sr isotopic ratios from the same set of Antler Ridge reference section samples (Singer and others, 1994), and for samples of the Tiva Canyon Tuff from drill hole UE-25 NRG #3 (Z.E. Peterman and K. Futa, U.S. Geological Survey, written commun., 1994). The uniformity of compositions for a large number of samples over a 90-meter-thick rhyolite tuff section provides a good basis for using the results as baseline data for comparison with altered tuff varieties.

Borehole UE-25a #1

The U-Th-Pb data for eight samples are presented in table 2. Previously reported geochemical and Sr isotopic results for these samples and others (Peterman and others, 1991) of unaltered high-silica rhyolite (HSR) (depth from 155.6 to 356.7 m) have shown very small variations in initial Sr isotopic compositions and in the concentrations of all the elements analyzed. Zeolitized HSR samples (depth 388.3 to 403.6 m) were variably depleted in K, Rb, and Y, and significantly enriched in Sr and Ca in comparison with unaltered HSR. U and Pb concentration data presented in figure 4 show uniform values throughout the unaltered HSR. Uranium in the altered zone is depleted relative to its concentration in the unaltered rocks by up to a factor of two. The same rocks show both gains and losses of Pb. Th/U ratios in the altered samples range from about 8.1 to 10.2 (table 2) and are significantly elevated relative to the average value of 5.3±0.9 (1σ) in unaltered Tiva Canyon Tuff samples (table 1). This indicates that during the process of zeolite formation, U follows K and Rb, but the behavior of Pb is more complicated. Lead gain observed in some samples could result in differences in Pb isotopic compositions between altered and unaltered samples analogous to those observed for Sr isotopes (Peterman and others, 1991). However, this is not the case, and no measurable Pb-isotope variations are observed (fig. 5). This means that lead was redistributed from sources with indistinguishable isotopic composition, most likely from local sources.

Trench 14 and Busted Butte

Geochemical and isotopic data for seven breccia samples are presented in tables 3 and 4, in which residues after acid leaching are denoted by sample name suffix "r". When normalized to average concentration data of the unaltered HSR from the Tiva Canyon Tuff (Peterman and Futa, written communication) and Topopah Spring Tuff (Peterman and others, 1991), unleached breccia samples (figs. 6 and 7) show significant enrichment (up to a factor of 20) in Ca, Sr, and Ba, and relative depletion in Ti, Rb, Y, and Nb.

The data may be explained by the presence of calcite ($CaCO_3$) which contains large concentrations of Sr and Ba and acts as a diluting component for other elements. Results of acid leaching presented in figures 8 and 9 partly support this suggestion, displaying significantly lower Sr concentrations in the residues after leaching. The HSR-normalized concentrations of Rb, Sr, Y, Nb, Th, and Pb from the leached residues are still below unity; but the U content is elevated, and the Th/U ratio (1.05 to 2.46) is much lower than the average value of 5.3±0.9 (1σ) obtained for samples of the unaltered Tiva Canyon Tuff (table 1). These data may either indicate gains or losses of the elements during breccia formation, or mixing with a component which is enriched in U but depleted in other elements. Opaline silica, which is a common constituent of the authigenic breccia cements (Levy and Naeser, 1991), is a good candidate for such a component. These samples fluoresce a bright yellow-green under short-wave ultraviolet light, which is typical for U-rich opals (Zielinski, 1982). According to Szabo and Kyser (1990), opals from fracture fillings in Yucca Mountain area drill holes USW G-2 and USW G-3/GU-3 are enriched in U (concentrations from 15 to 58 ppm) and have elevated values of $\delta^{18}O$ (up to +24.8). The oxygen isotope data on leached samples (table 4) give $\delta^{18}O$ values from +12.1 to +20.4 for the breccia samples and support the presence of opaline silica. The oxygen isotopic compositions of the Busted Butte breccia are linearly correlated with normalized concentrations of Ti, Nb, K, Y, and Pb (fig. 10). These negative correlations, if interpreted as two-component mixing lines, point to an end-member having elevated $\delta^{18}O$ (>+21) and variable depletion in these elements. This end-member is most likely opaline silica. It is more difficult to constrain the chemistry and oxygen isotopic composition of the other end-member. Obviously, it should be authigenic cement-free brecciated tuff. The breccia formation took place after solidification and cooling of the tuffs but before the fracture cementation with the authigenic carbonates and silica. If the brecciation was accompa-

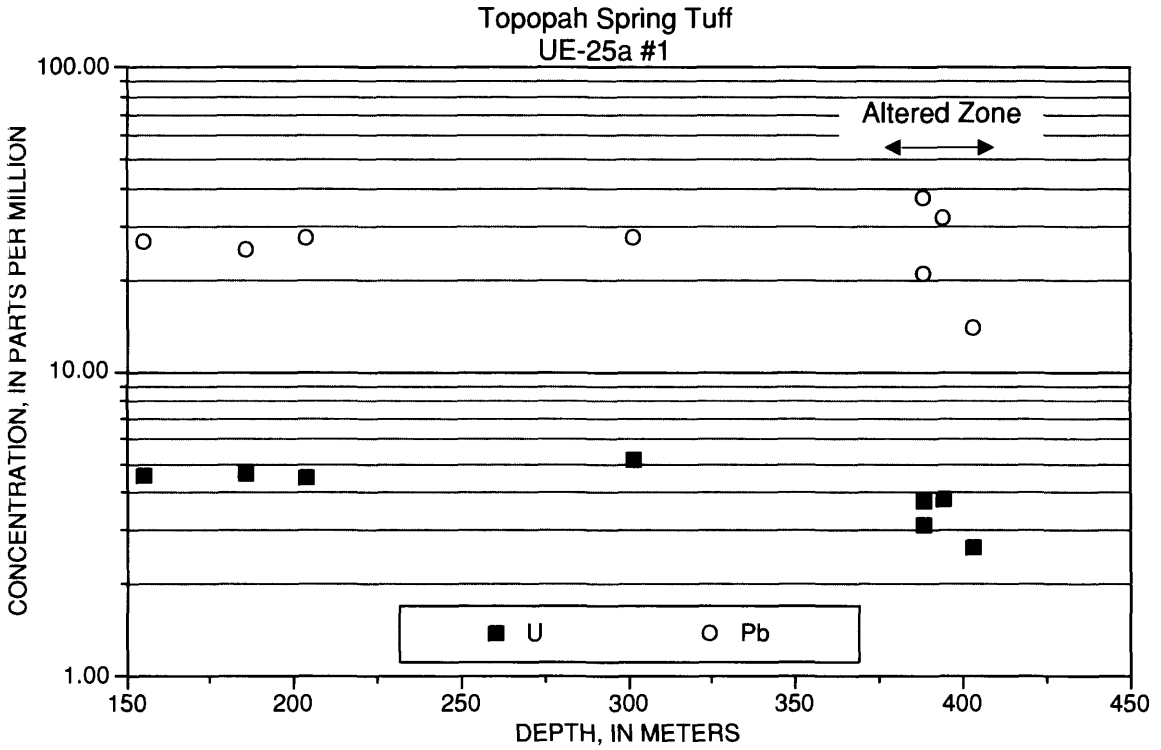

Figure 4. Uranium and lead concentrations in both unaltered and altered Topopah Spring Tuff from borehole UE-25a #1.

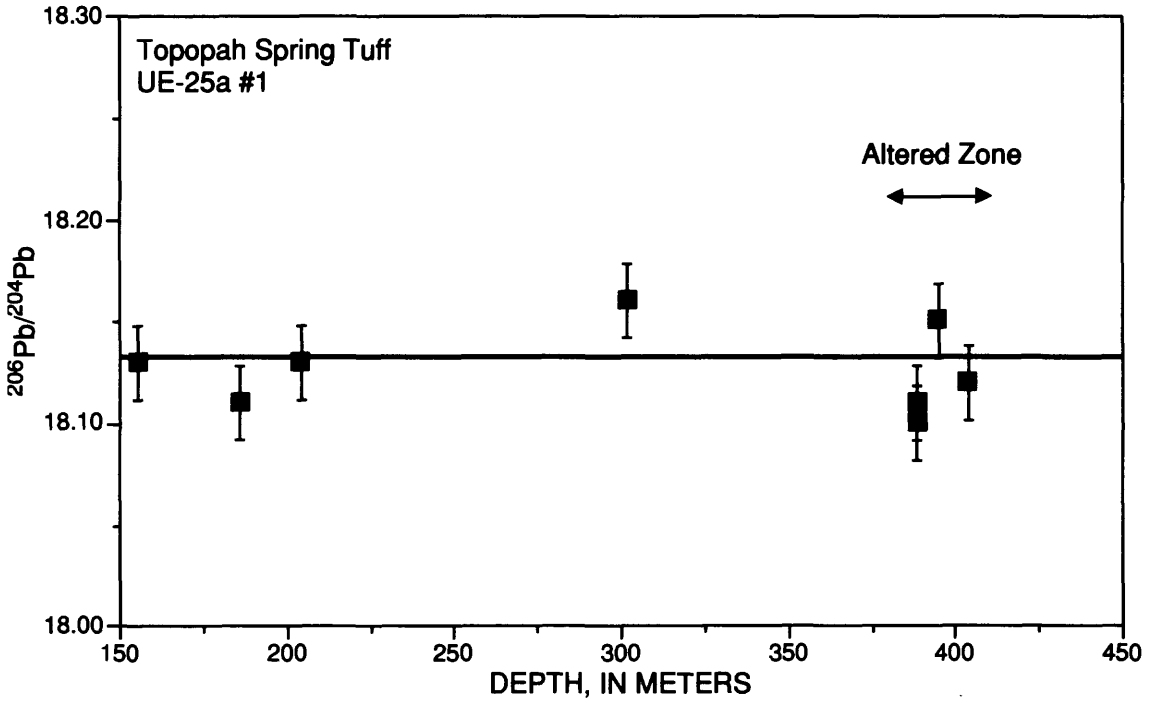

Figure 5. Uranium isotopic data with error bars (2σ) for both unaltered and altered Topopah Spring Tuff from borehole UE-25a #1. The horizontal line corresponds to the average value of $^{206}Pb/^{204}Pb$ = 18.131±0.022 for unaltered HSR samples.

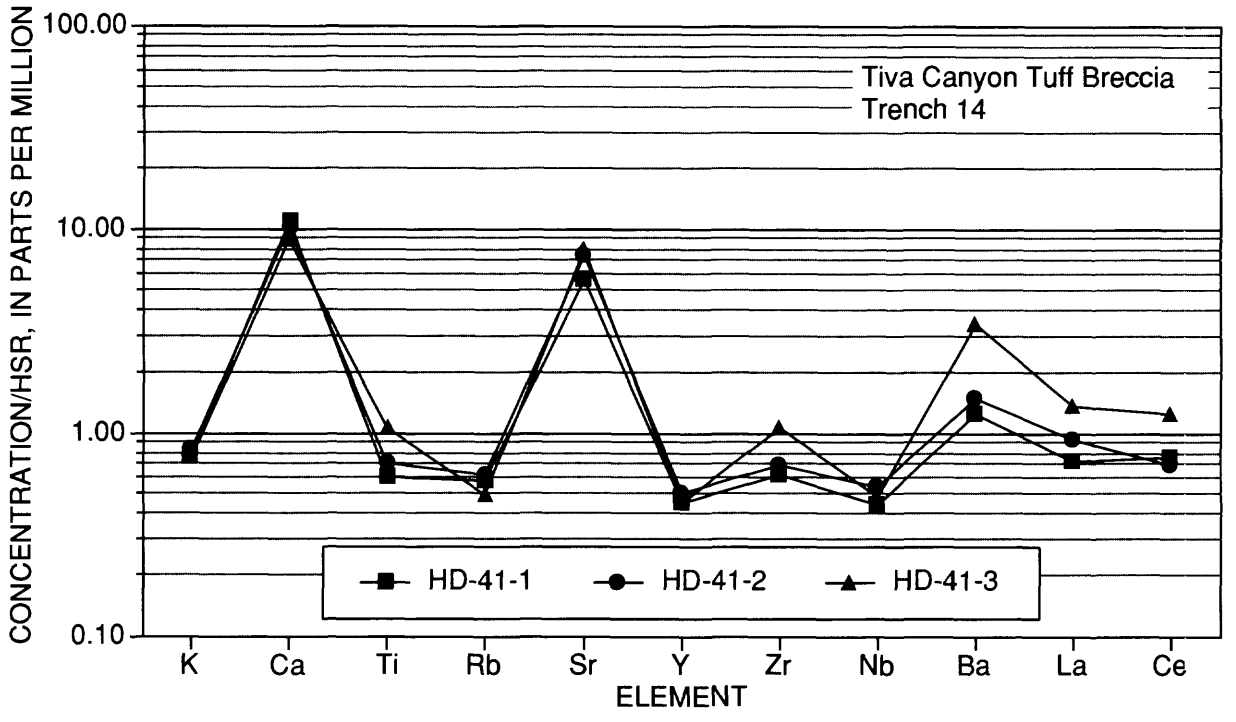

Figure 6. Concentrations of some elements in unleached breccia samples from Trench 14 and mean values of those in the Tiva Canyon Tuff high-silica rhyolite in the Antler Ridge section.

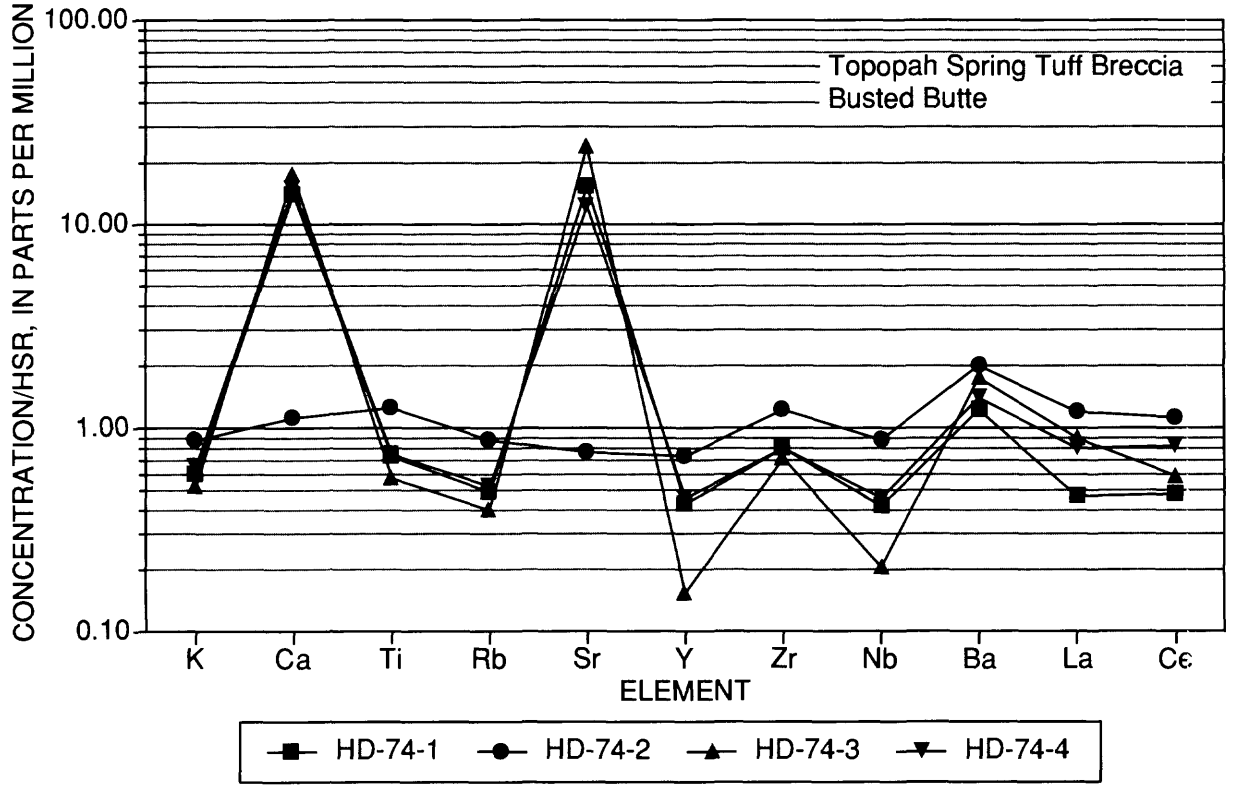

Figure 7. Concentrations of some elements in unleached breccia samples from Busted Butte and the mean values of those in the Topopah Spring Tuff high-silica rhyolite from borehole UE-25a #1.

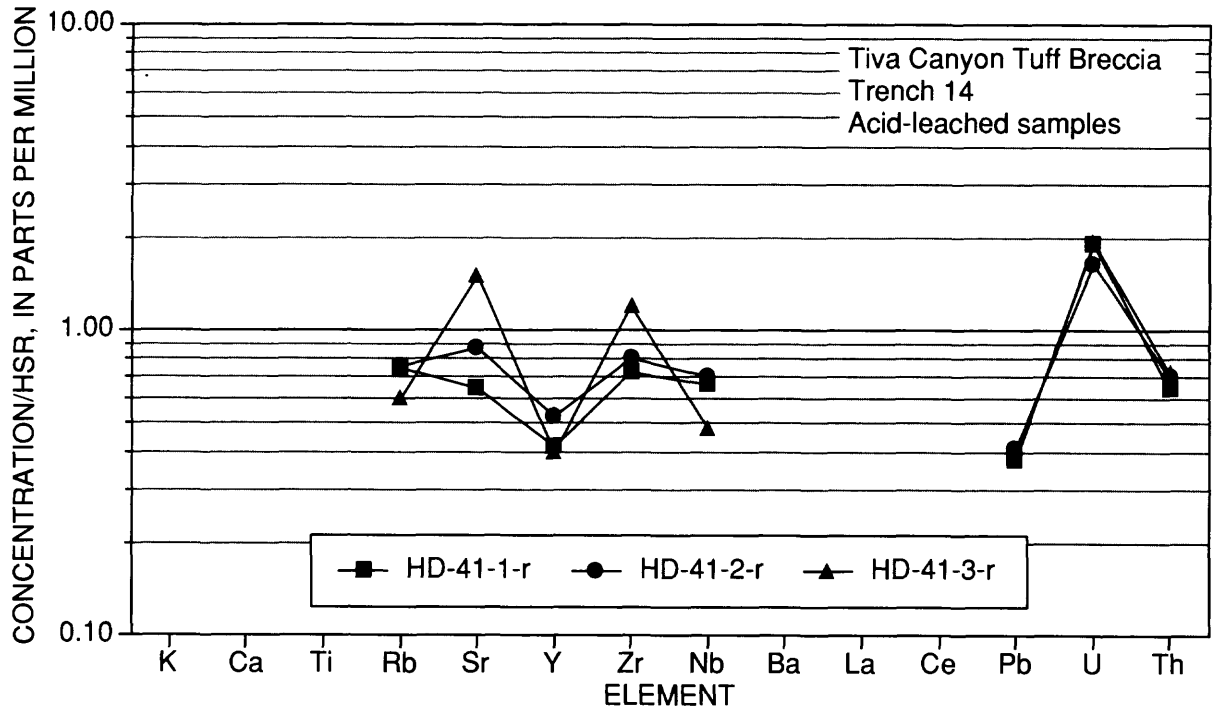

Figure 8. Concentrations of some elements in acid-leached breccia samples from Trench 14 and the mean values of those in the Tiva Canyon Tuff high-silica rhyolite in the Antler Ridge section.

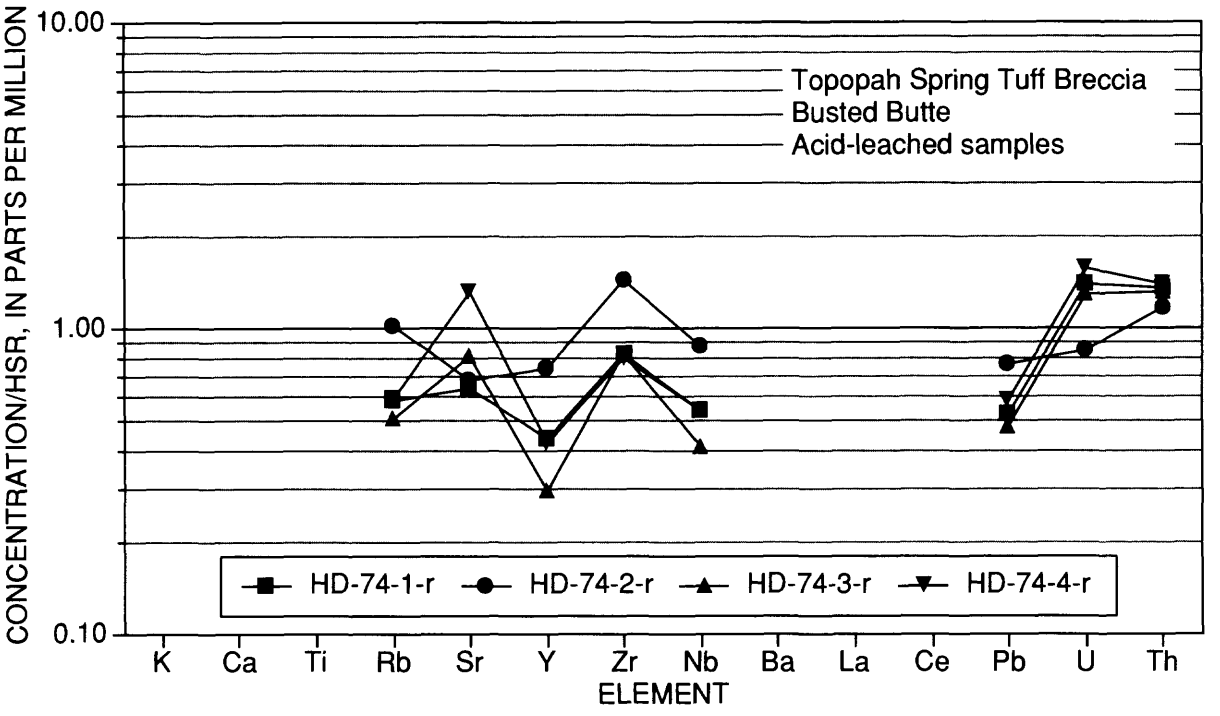

Figure 9. Concentrations of some elements in acid-leached breccia samples from Busted Butte and the mean values of those in the Topopah Spring Tuff high-silica rhyolite from borehole UE-25a #1.

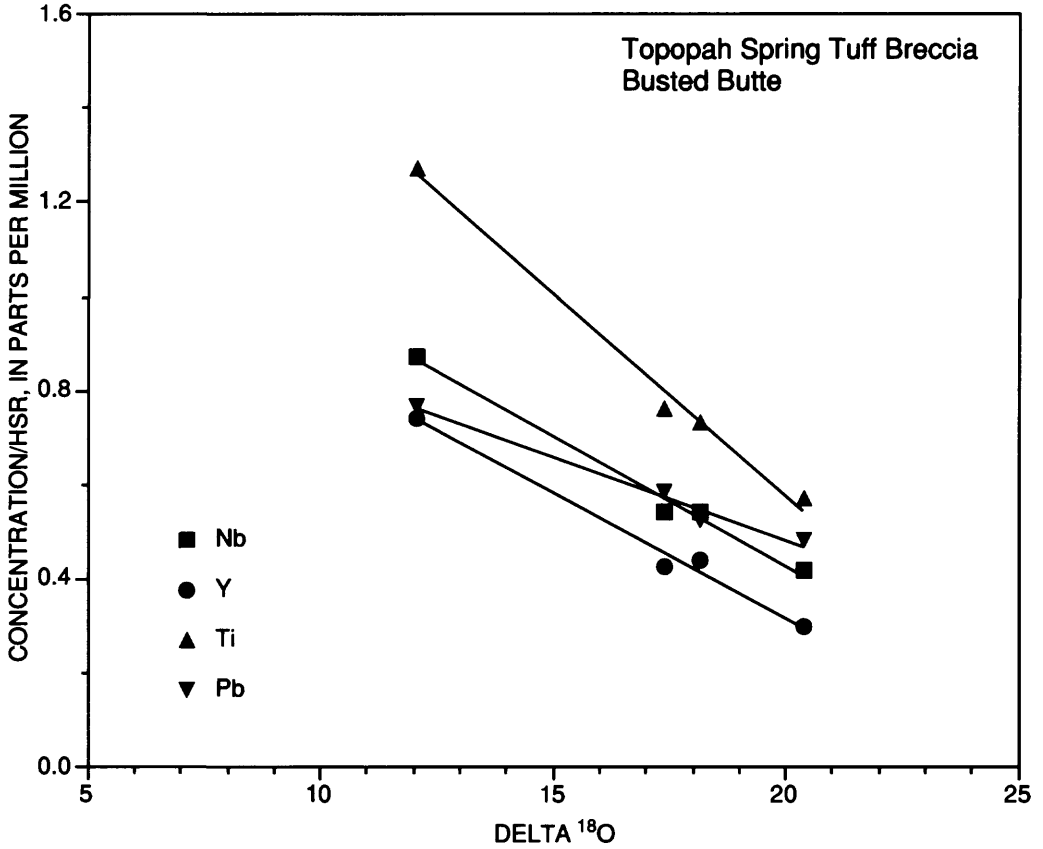

Figure 10. Correlations between oxygen isotopic compositions and concentrations of selected elements in breccia samples from Busted Butte.

nied by open-system behavior, then no plausible suggestions can be made about the breccia's oxygen isotopic composition. If it had the same oxygen isotopic composition as unaltered tuffs, the breccia would be slightly enriched in Ti and Nb. Proportions of the opaline silica end-member can be evaluated using simple two-component mixing equations (Faure, 1986). Assuming equal oxygen concentrations in both end-members and a value of $\delta^{18}O$ of +9 for one of them and of +25 for an authigenic opal component, the contribution of the latter is estimated to be in the range from 71 percent (sample HD-74-3) to 14 percent (sample HD-14-2). The numbers are fairly high if compared with proportions of carbonate authigenic components which were directly measured as sample weight loss after acid leaching (table 3) and did not exceed 17 percent even after strong acid (HCl) leaching. This observation may either reflect highly variable proportions of calcite and silica contents in authigenic components or inappropriate boundary conditions in the calculation. A significant decrease in the estimated opal proportion may be reached by assuming a much lower $\delta^{18}O$ value for rock component in the mixture.

In spite of the complexities in the geochemical and oxygen isotope data, Pb and Sr isotope results (table 4) do not display any exotic features. Sr isotopic compositions and $^{87}Rb/^{86}Sr$ ratios (fig. 11) are within the same range as those for the unaltered Tiva Canyon Tuff and Topopah Spring Tuff samples. Average Pb isotope ratios for the unaltered (table 1) and altered (table 4) samples are statistically indistinguishable and even 1σ error ellipses for the average values overlap on a Pb-Pb plot (fig. 12). In addition, Pb isotopic compositions of acid leachates (table 4) also are statistically identical to those in residues. The data provide no evidence for any involvement of external sources of Sr and Pb in the formation of the breccias as might be expected if hydrothermal fluids from deeper sources were responsible (Peterman and others, 1994). If such an involvement took place, it would measurably

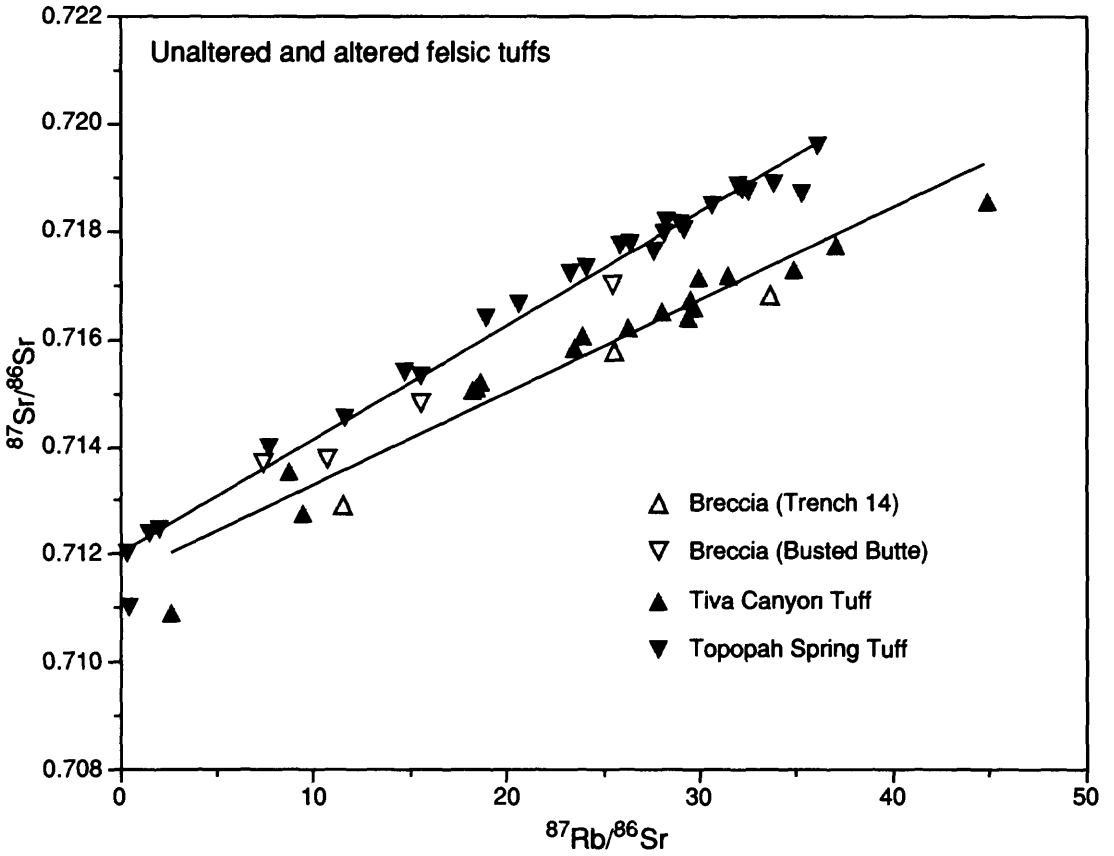

Figure 11. Comparison of rubidium and strontium data for the breccia samples from Trench 14 and Busted Butte with the data for unaltered Tiva Canyon Tuff from the Antler Ridge section and Topopah Spring Tuff from borehole UE-25a #1.

change Pb isotopic compositions, because underlying Paleozoic and Late Proterozoic sediments, for example, have significantly more radiogenic Pb-isotope compositions ($^{206}Pb/^{204}Pb$ from 19.2 to 29.1; Zartman and Kwak, 1993b) than those observed in the breccias from Trench 14 and Busted Butte. The data presented in figure 12 also show small, but measurable differences in Pb isotope compositions between both altered and unaltered varieties of Tiva Canyon Tuff and Topopah Spring Tuff. These differences may be used to distinguish these stratigraphic units when common geological criteria may fail, (for instance, in underground workings, where some of the features used in outcrops will be absent).

CONCLUSIONS

The following conclusions can be made based on the geochemical and isotopic analyses of the altered and unaltered samples of the Tiva Canyon Tuff and Topopah Spring Tuff.

1. U, Th, and Pb concentrations and Pb-isotope data, obtained for unaltered Tiva Canyon Tuff (Antler Ridge section) and Topopah Spring Tuff (borehole UE-25a #1) felsic tuffs, display uniformity of these characteristics which provides a good basis for using them as baseline data for further comparison with altered rock varieties.
2. Altered basal vitrophyre of Topopah Spring Tuff from borehole UE-25a #1 displays open system behavior of U, Th, and Pb that occurred during alteration of tuffs to zeolite and clay mineralogies. Up to 50 percent of U was lost during the process. Both gains and losses of lead were observed, but Pb isotope data point to redistribution of lead only from local sources.

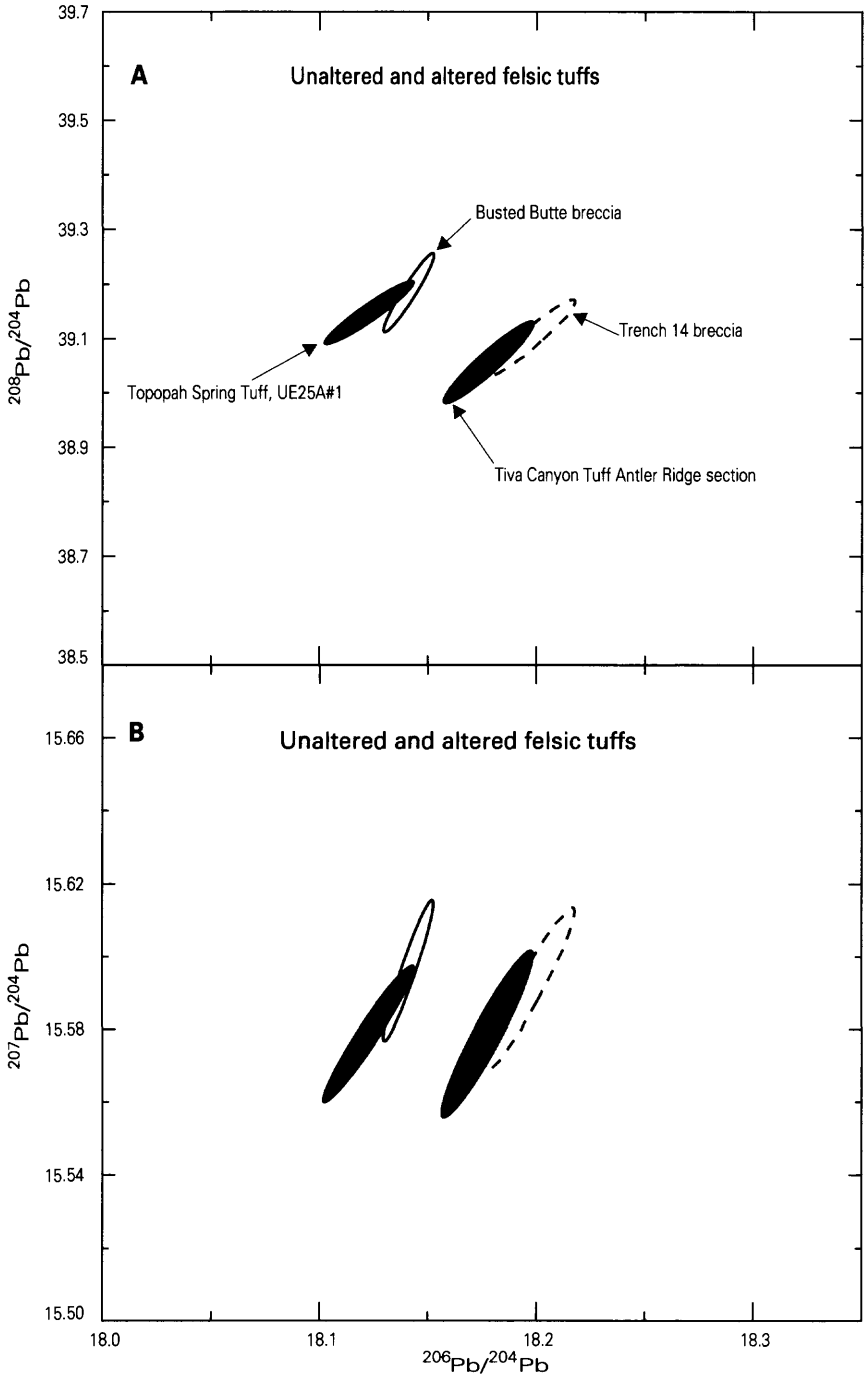

Figure 12. Average values for $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{206}Pb/^{204}Pb$ isotopic ratios for breccia samples from Trench 14 and Busted Butte and those for unaltered Tiva Canyon Tuff and Topopah Spring Tuff. The average values are shown as 1-sigma error ellipses.

3. Geochemical and oxygen isotope data for altered Topopah Spring Tuff and Tiva Canyon Tuff represented by breccia samples from Busted Butte and Trench 14 respectively, present evidence of significant proportions of both authigenic carbonate and opaline silica. They show elevated (relative to unaltered tuffs) concentrations of Ca, Sr, U, and Ba and their $\delta^{18}O$ values range from +12.1 to +20.4.

4. Pb and Sr isotope results for both leachates and residues from breccia samples are identical to those for unaltered tuffs and do not provide any evidence of involvement of external sources in their formation.

5. Isotopic data for altered tuffs studied along zones of potential fluid flow in three different localities in close proximity to the potential repository (borehole UE-25a #1, Trench 14 and Busted Butte) do not reveal any exotic isotopic compositions that would be evidence of passage of hydrothermal fluids which previously had been in interaction with any external source. A similar absence of exotic mineralization is inferred.

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