

# Geochemical interpretation of groundwater flow in the southern Great Basin

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## ABSTRACT

The study of geochemical processes and integrated water flow can help identify groundwater sources and improve predictions of contaminant fate and transport in groundwater systems. Understanding groundwater flow paths in and around the Nevada Test Site (NTS) is important due to the possible migration of contaminated groundwater to the neighboring communities. A total of 118 groundwater samples from the NTS and surrounding area (e.g., Oasis Valley, Ash Meadows, Death Valley, the Spring Mountains, and Pahranaagat Valley) were collected and analyzed for trace elements and major solutes. Cluster analysis and principal component analysis (PCA), along with geographical information systems (GIS), were used to interpret the resulting hydrogeochemical data. Cluster analysis was used to group the groundwater samples into four major clusters. PCA was used to reduce the data into three components that describe differences in ionic strength, groundwater compositions, reflecting interaction with volcanic and/or carbonate rock aquifers, and redox characteristics. Twelve potential flow paths, characteristic of those reported in earlier studies, were identified.

**Keywords:** geochemistry, groundwater, cluster analysis, principal component analysis, flow path.

## INTRODUCTION

Beginning in 1951, the Nevada Test Site (NTS; Fig. 1) was used for above-ground nuclear testing (U.S. Department of Energy, 2000). In 1957, underground nuclear testing was initiated at the NTS due to increased concerns of atmospheric fallout; much of the testing took place at or below the groundwater table (Winograd and Thordarson, 1975). Since this time, many studies on groundwater flow, geology, and geochemistry related to the NTS and the surrounding region have been conducted to evaluate the potential for contaminant migration into the underlying groundwater systems within southern Nevada and eventually Death Valley in California (e.g., Winograd and Friedman, 1972; Winograd and Thordarson, 1975; White, 1979; Kremer et al., 1996; Thomas et al., 1996; Johannesson et al., 1997a, 1997b; Lacznik et al., 1996, 1999; Zhou et al., 2000; Stetzenbach et al., 1999, 2001; Sweetkind et al., 2001; Belcher et al., 2001, 2002; Farnham et al., 2000, 2003).

Although a significant number of studies within this region have taken place, a considerable amount of uncertainty is still associated with the groundwater modeling efforts. Such uncertainty is due to the lack of spatial coverage of data, as well as the great complexity of the geology within this region. Because

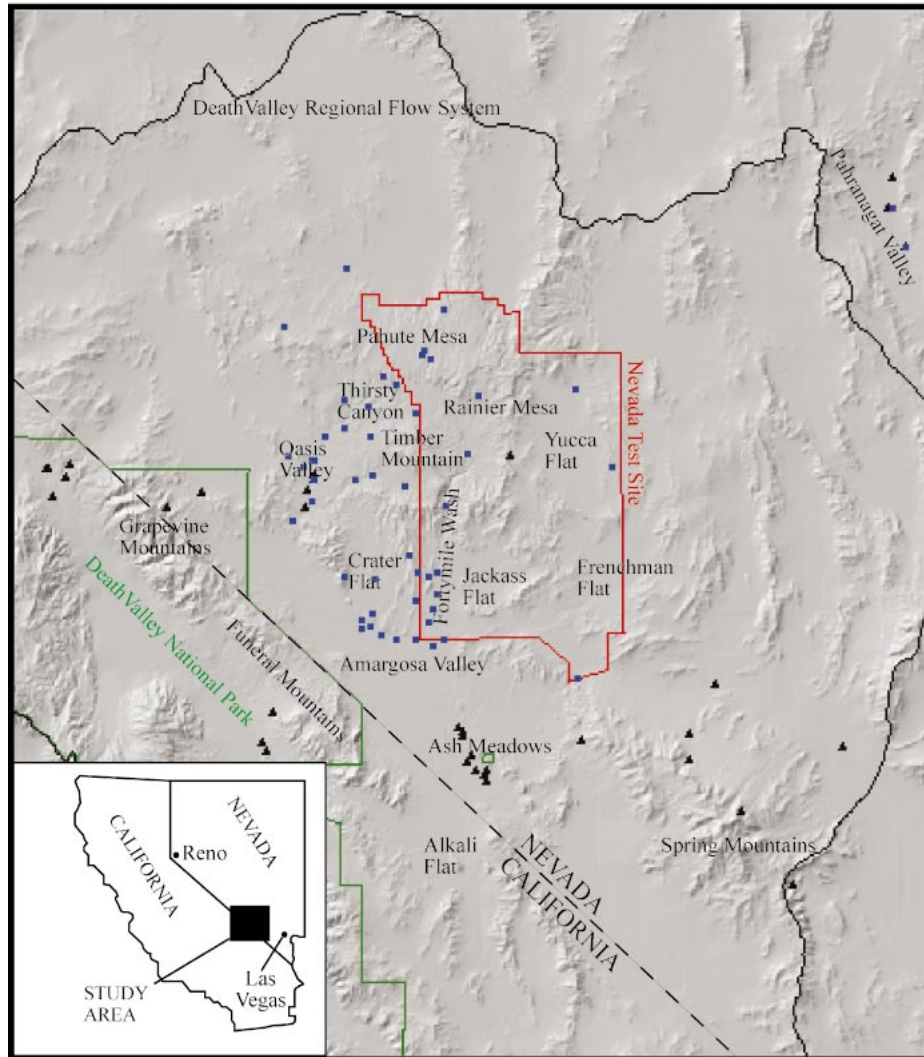
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current analytical techniques can be used to quantify trace elements as low as the parts per trillion (ppt) level in groundwater (Stetzenbach et al., 1994), recent geochemical studies, as well as recent sampling, of numerous springs and wells near the NTS have provided a significant amount of new information that can be used for further groundwater flow investigations within the Death Valley Regional Flow System (DVRFS). The boundaries of the DVRFS are presented in Figure 1.

Accumulated geological and geochemical data from groundwater wells and springs throughout Amargosa Valley, Oasis Valley, the NTS, Ash Meadows–Amargosa Desert, the Spring Mountains, and Death Valley were evaluated in this study (Figs. 1 and 2). Due to the large amount of geochemical data generated, application of multivariate statistical methods, including cluster analysis and principal component analysis (PCA), was used to group samples and detect patterns. The geology and geochemistry data were then evaluated with respect to groundwater flow in the hope of characterizing groundwater flow paths and mixing patterns. The results from this study improve our understanding of important natural geochemical processes, such as the partitioning of groundwater into different flow systems, rock-water interactions of trace elements along predetermined flow paths, and possible redox reactions.

## Regional Geology and Hydrology

The study area consists of three major groups of geologic formations: Paleozoic

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3,964,818 N

**Figure 1.** Map of the study area showing the Nevada Test Site (NTS), Death Valley National Park, Death Valley Regional Flow System (DVRFS) boundary, and the locations of springs (triangles) and wells (squares) sampled from March 1994 through October 2002.

rocks, Tertiary rocks, and Quaternary alluvial deposits (Winograd and Thordarson, 1975). The Paleozoic rocks are mostly carbonate, including dolomite, interbedded limestone, as well as thin layers of shale and quartzite (Laczniaik et al., 1996), which outcrop in various locations within the study region. The Tertiary rocks mainly consist of felsic volcanic rocks and are exposed widely within the area. Quaternary alluvial deposits are the weathering products of tuffaceous rocks derived from a Pleistocene unit consisting of gravels that represent earlier, dissected alluvial fans and a Holocene unit consisting of current

alluvial fans (Cornwall and Kleinhampl, 1961; White, 1979). The geology and hydrology of the DVRFS has been previously described by Winograd and Thordarson (1975), Laczniaik et al. (1996), Sweetkind et al. (2001), and Belcher et al. (2002), and the reader is therefore referred to these reports for more detail.

The lower Paleozoic rock aquifer and valley-fill aquifer are considered major aquifers in the region, although the fractured Tertiary rock aquifer also transmits significant amounts of groundwater (Winograd and Thordarson, 1975). The major hydrologic units were slightly revised from the earlier work of Win-

ograd and Thordarson (1975) by Laczniaik et al. (1996) to include (1) the basement confining unit, (2) carbonate rock aquifer, (3) Eleana confining unit, (4) the volcanic aquifers and confining unit, and (5) the valley-fill aquifer. The basement confining unit consists primarily of Precambrian (Middle to Late Proterozoic) metamorphic rock (Belcher et al., 2002) to Paleozoic (Early Cambrian) marine sediments (Winograd and Thordarson, 1975). The carbonate rock aquifer consists of Paleozoic carbonate rocks from the Middle to Late Cambrian up to the Lower to Middle Devonian. The upper carbonate aquifer, made up of the Tippah Limestone, is considered to be a localized aquifer located in the western area of Yucca Flat (Laczniaik et al., 1996). The lower carbonate aquifer, however, is of a regional extent and is very important in regard to groundwater flow (Belcher et al., 2002). The Eleana confining unit (including the Chainman Shale) consists of Upper Devonian Paleozoic siliceous siltstone, sandstone, and minor limestone conglomerate and is considered to be a clastic aquitard or confining unit (Winograd and Thordarson, 1975; Belcher et al., 2002). This unit separates the lower and upper carbonate aquifers. The volcanic aquifers and confining unit together make up the complex regional unit of welded and nonwelded tuffs, which overlie most of the Paleozoic rocks and consist of some Mesozoic through Tertiary volcanic rocks (Winograd and Thordarson, 1975; Laczniaik et al., 1996; Belcher et al., 2002). The valley-fill aquifer is a regional system and consists of Quaternary and Tertiary alluvium and playa deposits. Groundwater flow through both the valley-fill and volcanic aquifers appears to be controlled predominantly by faults and fractures (Blankennagel and Weir, 1973; Laczniaik et al., 1996).

The DVRFS boundary (Fig. 1), delineated by Bedinger et al. (1989), roughly corresponds to digital elevation model (DEM)-derived drainage networks. These drainage networks indicate that groundwater within Oasis Valley, Jackass Flats, Yucca Flat, and the Amargosa Desert drains south or southwest to Death Valley. The DVRFS can also be divided into three different groundwater subbasins, including Oasis Valley, Alkali Flat-Furnace Creek Ranch, and Ash Meadows (Waddell et al., 1984).

### Hydrogeochemical Setting

Groundwater throughout the region has been divided into different chemical signatures, or hydrochemical facies, based on major-ion chemistry. Groundwater in the lower

carbonate aquifer and valley-fill aquifer in the northeast and southeast part of the study area (i.e., Pahrangat Valley and the Spring Mountains in Fig. 1, respectively) is of the Ca-Mg-HCO<sub>3</sub> facies, whereas groundwater of a Na-K-HCO<sub>3</sub> facies is found in aquifers consisting of felsic volcanic rocks in the northwest and west (i.e., Frenchman Flat, Jackass Flat, Pahute Mesa, and Oasis Valley in Fig. 1) (Schoff and Moore, 1964; Winograd and Thordarson, 1975). According to Johannesson et al. (1997b), the groundwater within the Amargosa Desert is primarily Na-K-HCO<sub>3</sub>, similar to that of Pahute Mesa and Oasis Valley. Groundwater predominantly of a Ca-Mg-Na-HCO<sub>3</sub> facies occurs within the lower carbonate aquifer between Ash Meadows and eastern NTS and is thought to be a result of mixing of Ca-Mg-HCO<sub>3</sub> and Na-K-HCO<sub>3</sub> groundwater. Na-SO<sub>4</sub>-HCO<sub>3</sub> groundwater is restricted to the Furnace Creek Wash–Nevares Springs area, located in the west part of the study area (Winograd and Thordarson, 1975). Zhou et al. (2000) summarized major-ion chemistry results from extensive water sampling by the groundwater chemistry group of Harry Reid Center for Environmental Studies (HRC) at the University of Nevada, Las Vegas (UNLV).

**METHODS**

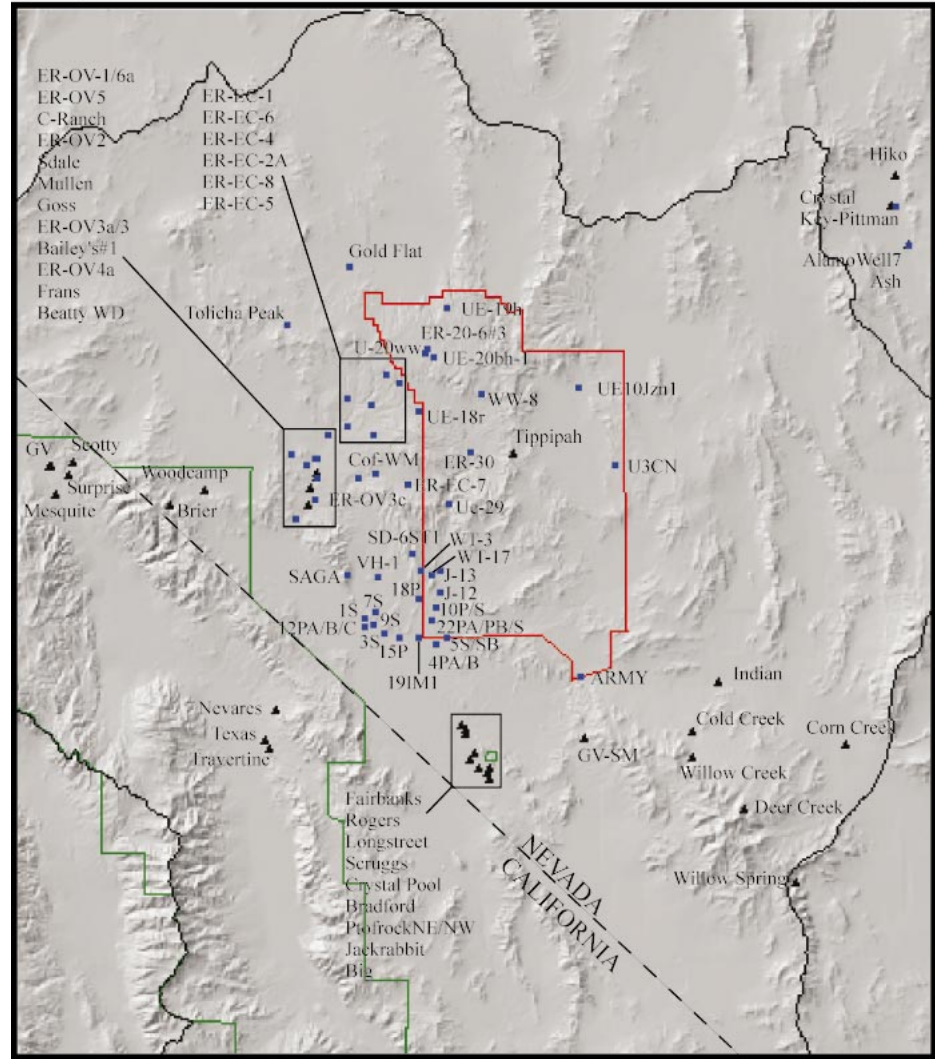
**Sampling and Analysis**

Groundwater samples were collected from 118 wells and springs within the DVRFS (Fig. 2), from March 1994 through October 2002, and analyzed for major ions (Cl, SO<sub>4</sub>, K, Na, Ca, and Mg) and trace elements (Li, Ti, V, Cr, Mn, Co, Ni, Ge, As, Se, Rb, Sr, Mo, Cs, Ba, W, Bi, and U) by the HRC groundwater chemistry group at UNLV (Koonce, 2004). The trace elements chosen for this study were based on the successful interpretation in similar statistical and geochemical studies conducted throughout the area (Stetzenbach et al., 1999, 2001; Hodge et al., 1996; Kreamer et al., 1996; Farnham et al., 2000, 2003).

The groundwater was pumped from its source using a peristaltic pump equipped with Teflon tubing that was precleaned via acid wash. The groundwater was then filtered through Gelman Sciences (0.45 μm) groundwater filter capsules into precleaned (acid washed with ultrapure HNO<sub>3</sub>) high-density linear polyethylene (HDPE, Nalgene) sample bottles. For the analysis of trace elements, samples were collected in 1 L sample bottles, which were then immediately acidified to pH <2 with ultrapure nitric acid (SeaStar, Inc). For the analysis of major cations and anions,

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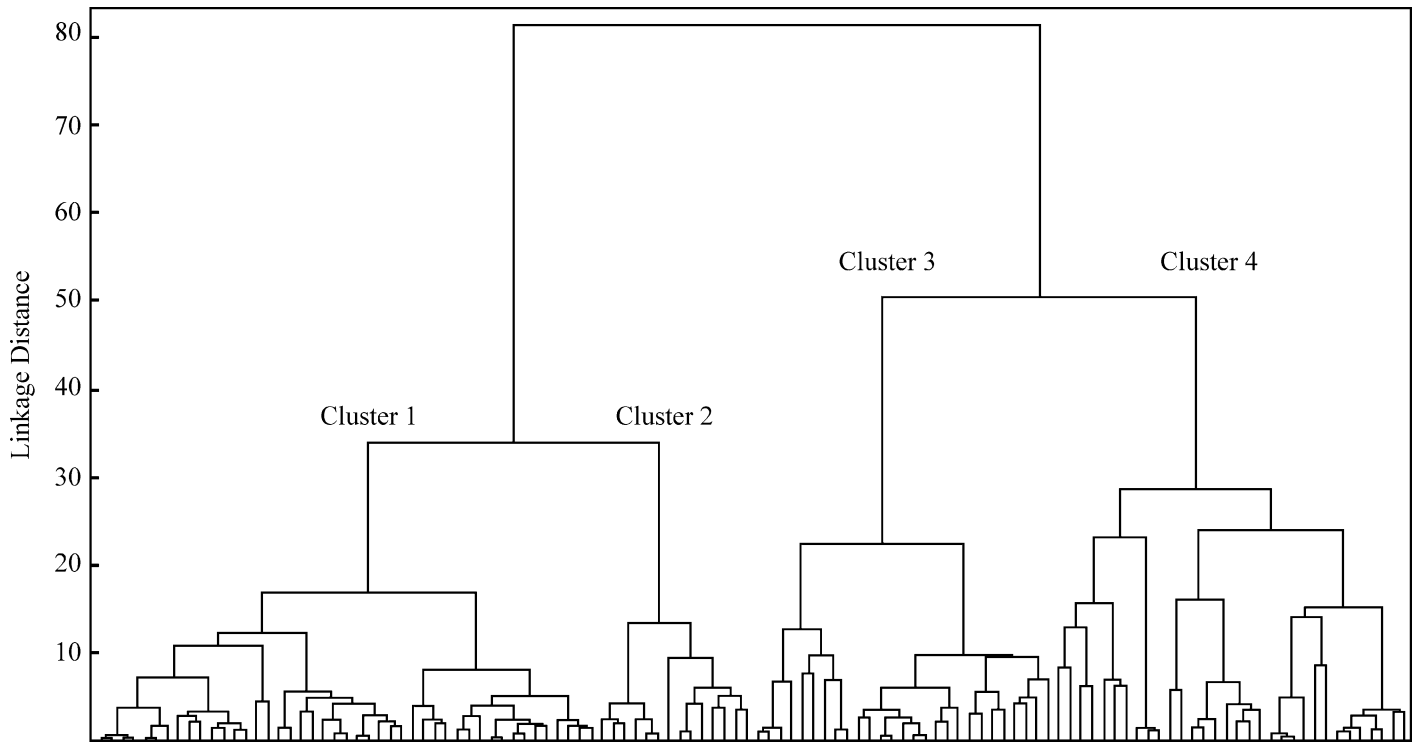
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**Figure 2. Map of the study area with springs (triangles) and wells (squares) marked.**

samples were collected in 125 mL sample bottles. Major cation samples were also immediately acidified to pH <2 with ultrapure nitric acid (SeaStar, Inc); however, major anion samples were not acidified. Prior to sample collection, sample bottles were triple rinsed with filtered groundwater from the spring or well of interest to remove any distilled/deionized water (or HNO<sub>3</sub>) remaining in the bottle. Samples were then placed in clean plastic bags, placed into clean plastic chests filled with ice, and then transported to the laboratory where they were stored at ~4°C and analyzed. Similar sample collection methods were used for springs and wells; however, in regards to well samples, wells were pumped

for a number of well volumes in order to ensure that a representative sample of groundwater was collected. The samples were collected after pH, temperature, and conductivity were stabilized. Special precautions were taken in sample collection and analysis in order to obtain trace-element results in units as low as parts per trillion (ppt; Stetzenbach et al., 1994).

Trace elements were analyzed via a Perkin-Elmer Elan 5000 inductively coupled plasma-mass spectrometer (ICP-MS), equipped with an ultrasonic nebulizer and an active film multiplier ion detector (ETP Scientific) (Stetzenbach et al., 1994). The analyses were performed following EPA Method 200.8 (Creed



**Figure 3. Dendrogram of Ward's hierarchical cluster analysis results. Individual clusters (clusters 1 through 4) are shown on subsequent figures (Figs. 4–7).**

et al., 1994). Major cations were analyzed using an atomic absorption spectrometer, and major anions were analyzed using an ion chromatograph. The analyses for cations were performed based on the *Standard Methods for the Examination of Water and Wastewater*, Method 3111 B (Eaton et al., 1995), and anions were performed following EPA Method 300.1 (Hautman et al., 1997).

### Statistical Techniques

Multivariate statistics can be used to evaluate large amounts of data in order to decipher patterns within the data set that otherwise might not be observed. The multivariate techniques used in this study were cluster analysis and PCA. Prior to any multivariate statistical analyses, the data were arranged in a ( $n \times p$ ) matrix, representing the number of samples ( $n$ ), including wells and springs, and the number of variables ( $p$ ), including major ions and trace elements. The elements of the data matrix ( $x_{i,j}$ ) consisted of the concentration of the  $j$ th hydrogeochemical constituent (major ion or trace element) measured in the  $i$ th groundwater sample. A standardized data matrix was then generated by mean subtraction followed by division by the column standard deviation. The hydrogeochemical constituents were pres-

ent in levels of differing orders of magnitude in the groundwater samples. By standardizing the data set, each analyzed component was assigned the same influence. For information regarding detailed descriptions of cluster analysis and PCA, substantial amounts of literature are available (Ward, 1963; Everitt, 1993; Everitt and Dunn, 2001; Johnson and Wichern, 2002; Davis, 2002).

### Cluster Analysis

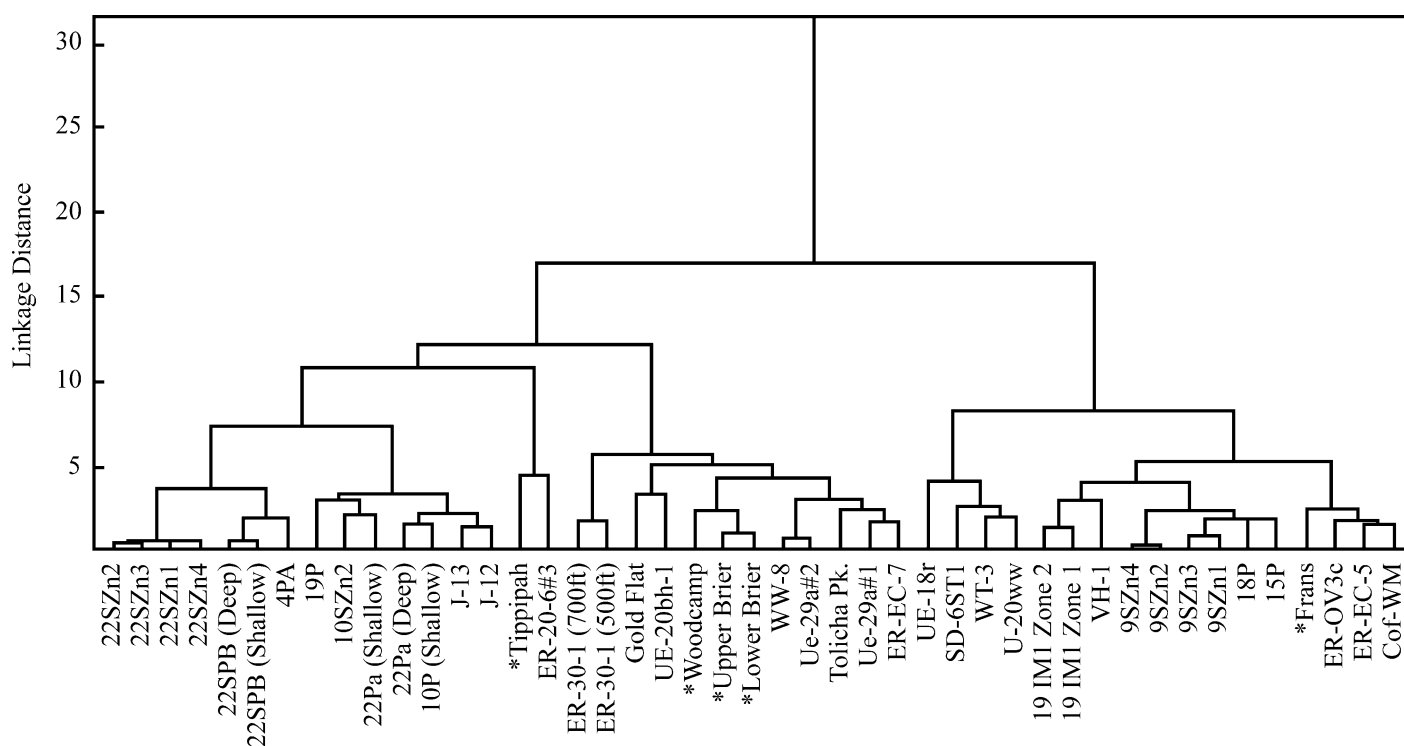
In this study, hierarchical cluster analysis was used to group similar wells and springs into separate clusters based on similar hydrogeochemical compositions. Although there are a number of hierarchical clustering techniques, all of which are regularly applied to the earth sciences, the most widely used measure of ordering is Ward's criterion, which uses an analysis of variance approach that minimizes the sum of squares within the clusters and maximizes the variance between separate clusters (Ward, 1963). The results are represented via a dendrogram, or tree plot, in Figure 3 and are separated into four different clusters represented by Figures 4 through 7. The sample locations are grouped on the horizontal axis, and the linkage distances, repre-

sented the relative differences between clusters, are shown on the vertical axis.

### Principal Component Analysis (PCA)

The objectives of PCA in this study were data reduction, data interpretation, and noise removal within the data set. PCA reduces the large data matrix into two smaller matrices called principal component (PC) loadings and PC scores, which are obtained through the process of eigen analysis. Because PCA is simply the generation of pairs of eigenvalues and eigenvectors, the data do not need to be normally distributed (Johnson and Wichern, 2002). Eigenvalues describe the amount of variation within the original data set explained by each principal component. Often the population variability for large data sets, such as those with large numbers of samples and variables, can be attributed to the first one, two, or three components (Johnson and Wichern, 2002).

PC loadings, the elements of the eigenvectors, indicate the relative contribution of each element to the PC score (Stetzenbach et al., 1999). A loading value of zero would indicate no relationship between the PC and the original variable. PC scores are linear combinations of the standardized data and the load-



**Figure 4. Dendrogram of cluster 1: groundwater with volcanic rock signature. Groundwater hydrogeochemistry consists of higher concentrations (highly loaded) of Na, Li, Mo, and Rb. Springs are noted with an asterisk.**

ings, and therefore combine information on all of the hydrogeochemical measurements for a given sample into a single number. The PC scores can then be plotted and interpolated on a two-dimensional graph using ArcView Geographical Information Systems (GIS) to display possible groupings of similar groundwater compositions (Figs. 8–10).

## RESULTS

### Cluster Analysis

The dendrogram resulting from hierarchical cluster analysis (Fig. 3) displays the presence of four clusters, which are presented further in Figures 4–7. The springs and wells are grouped according to the similarity of the hydrogeochemical compositions. Table 1 displays the means and standard deviations of the chemical constituents for each cluster. Groundwater is known to inherit the geochemical composition of the aquifer material through which it has flowed (Stetzenbach et al., 1999). Groundwater flowing through volcanic rock is typically dominant in K, Na,  $\text{SO}_4$ , and Cl, whereas groundwater flowing through carbonate rock is typically high in Ca and Mg (Schoff and Moore, 1964; Winograd and Thordarson, 1975; White, 1979; Thomas

et al., 1996). Based on the results of this study, groundwater that has flowed through the aquifers consisting of volcanic rocks (i.e., Oasis Valley and Nevada Test Site) exhibits high concentrations of Na, Li, Rb, and Mo, and groundwater that has flowed through a carbonate aquifer (i.e., Spring Mountains and Pahrnatag Valley) exhibits high concentrations of Ca, Mg, Sr, and Ba. The separation of the different groundwaters is exemplified in the results of the cluster analysis (Figs. 4–7). Cluster 2 consists of springs predominantly of carbonate-derived groundwater, such as the Pahrnatag Valley and Spring Mountain springs (Winograd and Friedman, 1972; Winograd and Thordarson, 1975; Johannesson, et al., 1997b; Stetzenbach et al., 2001), and clusters 1 and 3 consist of springs and wells predominantly of groundwater from an aquifer composed of volcanic rocks, such as groundwater from the many wells within the NTS and Oasis Valley (Winograd and Friedman, 1972; Winograd and Thordarson, 1975; Johannesson et al., 1997b; Stetzenbach et al., 2001; Farnham et al., 2000, 2003). Furthermore, mixtures of the two groundwaters might have similar characteristics of both carbonate and volcanic signatures, which may explain the differences between cluster 4 and clusters 1, 2, and 3. Most of the springs in

Ash Meadows, except Scruggs and Fairbanks, and springs discharging in Furnace Creek–Death Valley are grouped into cluster 4. Many studies suggest that the geochemical composition of the groundwater discharging from springs in the Furnace Creek area is dominated by carbonate-derived groundwater with a small percentage of groundwater from an aquifer composed of felsic volcanic rocks, possibly from the NTS (Winograd and Friedman, 1972; Winograd and Thordarson, 1975; Thomas et al., 1996; Johannesson, et al., 1997b; Stetzenbach et al., 2001). Cluster 4 may also be influenced by groundwater that has moved through valley-fill material consisting of Quaternary and Tertiary alluvial deposits. Groundwaters grouped into cluster 4 tend to be those of the mixed Ca-Mg-Na- $\text{HCO}_3$  facies.

### Principal Component Analysis (PCA)

Similar to cluster analysis, PCA was used to decipher patterns within the hydrogeochemical data set. PCA is a data reduction technique used to simplify data sets while capturing the underlying patterns within the data (Stetzenbach et al., 1999; Farnham et al., 2003). In the results presented here, PCA has reduced the data set from 24 variables to three

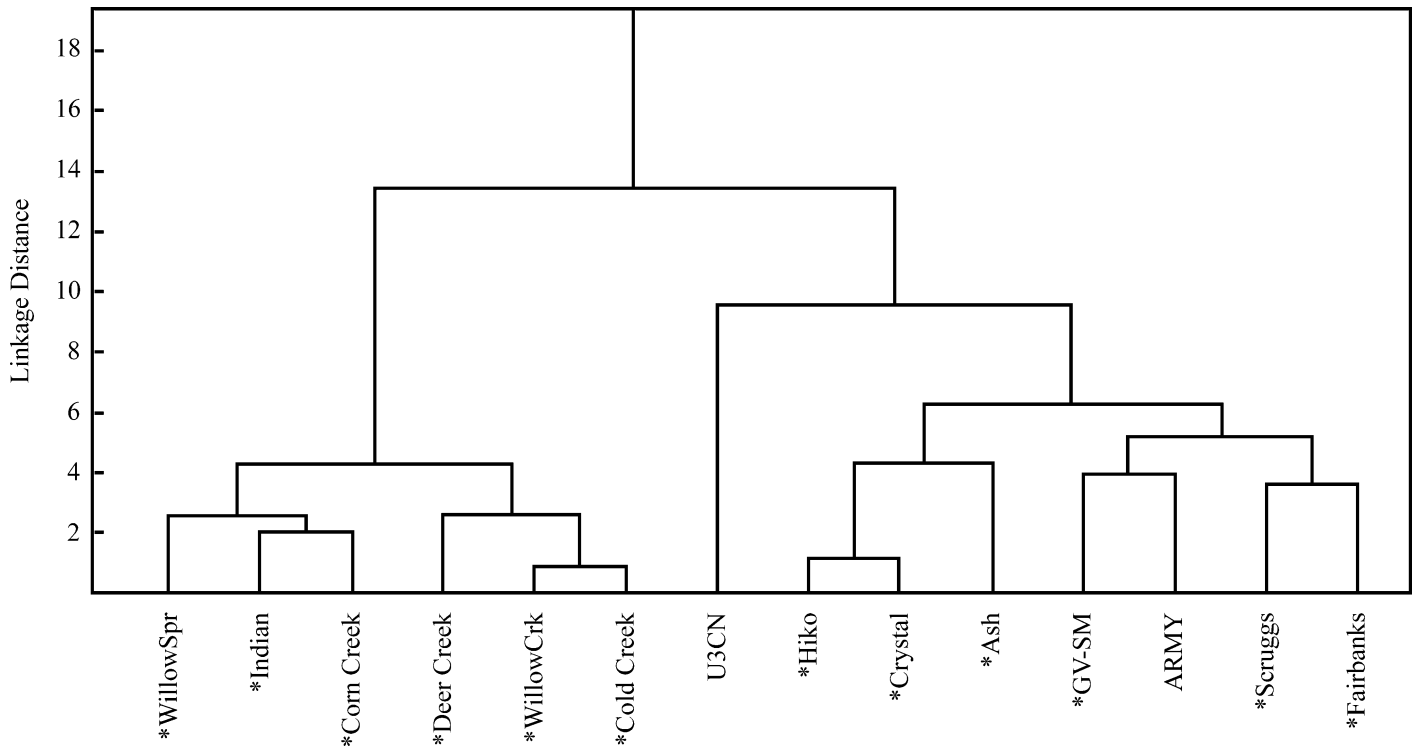


Figure 5. Dendrogram of cluster 2: groundwater with carbonate rock signature. Groundwater hydrogeochemistry consists of higher concentrations (highly loaded) of Ca, Mg, Sr, and Ba. Springs are noted with an asterisk.

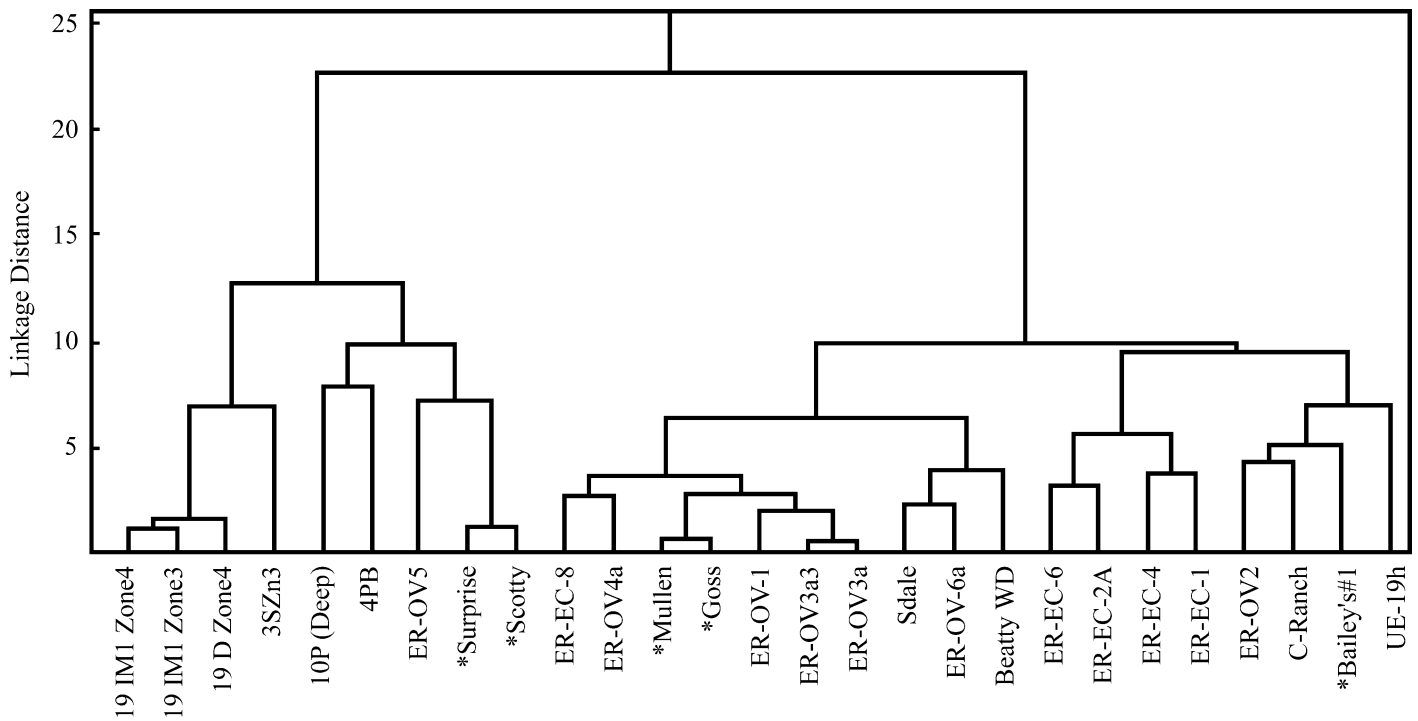
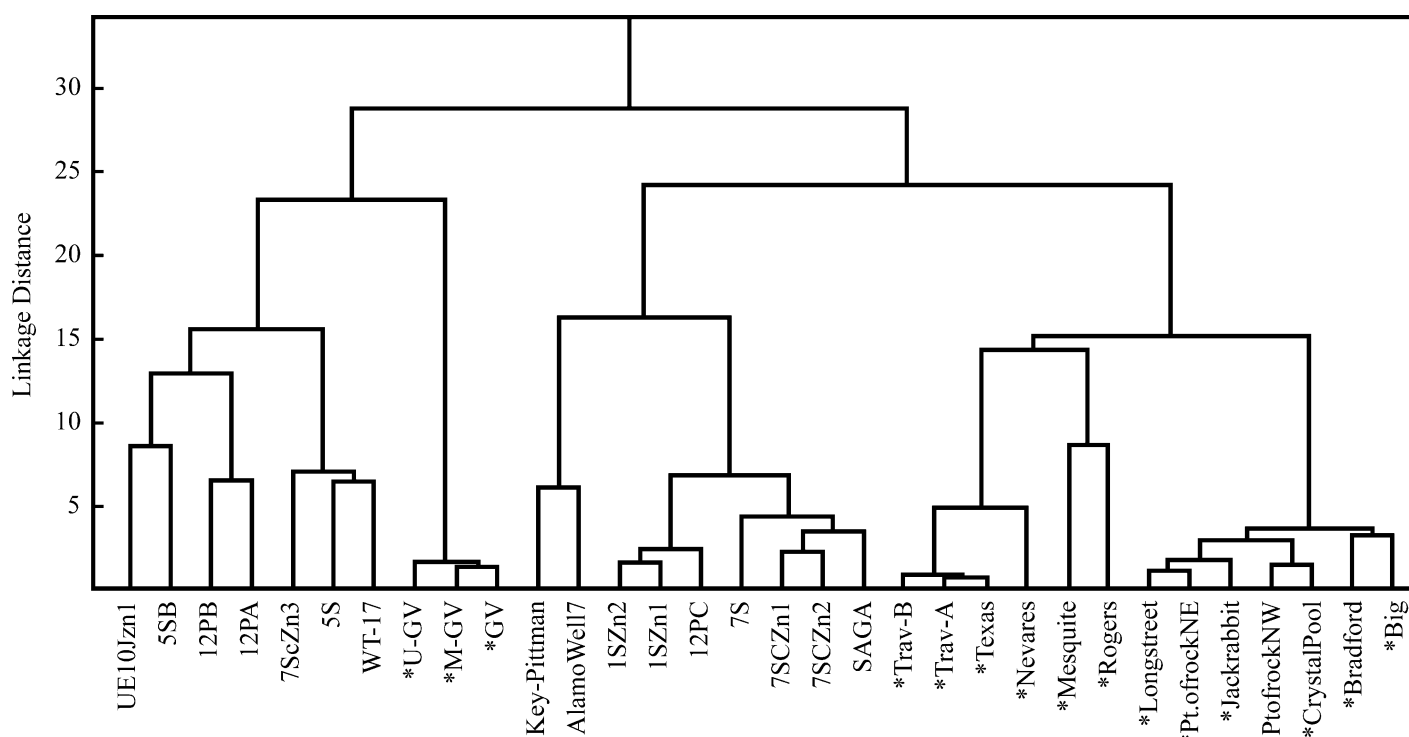


Figure 6. Dendrogram of cluster 3: groundwater with volcanic rock signature. Groundwater hydrogeochemistry consists of higher concentrations (highly loaded) of Na, Li, Mo, and Rb. Springs are noted with an asterisk.



**Figure 7. Dendrogram of cluster 4: groundwater with mixed signatures of volcanic, alluvium, and/or carbonate rocks. Groundwater hydrogeochemistry consists of higher concentrations (highly loaded) of Na, Li, Mo, and Rb, and Ca, Mg, Sr, and Ba. Springs are noted with an asterisk.**

**TABLE 1. MEANS AND STANDARD DEVIATIONS OF MAJOR SOLUTE AND TRACE-ELEMENT CONCENTRATIONS FOR THE FOUR GROUPS RESULTING FROM CLUSTER ANALYSIS**

Cluster	Major-ion concentration (meq/L)						Trace-element concentration (ppb)																		
	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Li	Ti	V	Cr	Mn	Co	Ni	Ge	As	Se	Rb	Sr	Mo	Cs	Ba	W	Bi	U	
<b>Cluster 1</b>																									
Mean	0.26	0.55	0.70	0.16	0.10	2.41	56.8	0.73	3.41	0.58	15.7	0.02	0.70	0.43	8.44	0.63	9.44	65.7	6.26	1.13	4.25	1.13	0.00	2.02	
Std. dev.	0.14	0.30	0.35	0.15	0.06	0.85	31.5	0.75	2.44	0.54	31.6	0.02	1.03	0.33	5.38	0.23	3.67	50.2	4.33	1.20	3.98	0.92	0.00	1.64	
<b>Cluster 2</b>																									
Mean	0.29	0.77	2.56	1.66	0.10	1.15	27.0	0.43	0.92	0.53	2.51	0.04	1.05	0.16	7.66	0.62	6.82	423	2.89	1.35	74.4	0.33	0.00	1.98	
Std. dev.	0.24	0.67	0.71	0.68	0.08	1.12	28.1	0.25	0.56	0.84	9.27	0.03	1.99	0.17	9.57	0.34	6.48	293	2.48	1.61	45.9	0.53	0.01	1.18	
<b>Cluster 3</b>																									
Mean	1.11	1.52	0.63	0.10	0.14	5.25	136	0.71	4.98	1.28	6.20	0.03	0.88	1.15	15.5	0.78	16.0	69.3	9.60	0.79	4.74	2.23	0.00	6.93	
Std. dev.	0.70	0.72	0.50	0.13	0.06	1.29	50.3	0.38	4.09	0.82	13.9	0.03	1.27	0.66	12.5	0.39	7.42	74.7	5.16	1.12	5.20	2.56	0.00	5.30	
<b>Cluster 4</b>																									
Mean	0.77	2.41	2.54	1.95	0.28	4.67	131	1.05	1.91	1.67	74.7	0.12	1.10	0.69	15.5	0.87	25.2	675	10.3	3.00	46.4	0.72	0.00	4.17	
Std. dev.	0.46	0.80	1.08	1.04	0.15	1.95	71.8	0.71	2.67	1.91	169	0.17	1.18	0.63	13.3	0.68	17.2	289	6.19	2.90	24.2	0.98	0.01	3.02	

principal components (PC loadings and PC scores), while still explaining ~51% of the total variance (Table 2). The first three PC scores for all sample locations were plotted and interpolated in GIS (Figs. 8–10). Although the total variance explained by the first three components is not as high as observed for other studies, such as Kreamer et al. (1996) (95% for PCs 1, 2, and 3), Stetzenbach et al. (1999) (99% for PCs 1 and 2 for major-ion data), Stetzenbach et al. (2001) (82% and 93% for PCs 1 and 2, for major-ion and trace-

element data, respectively), and Farnham et al. (2003) (71% for PCs 1, 2, and 3), these PCs provide insight into the characteristics of the groundwater within the DVRFS and help delineate possible groundwater flow paths.

As displayed on Figure 8, groundwater samples of wells and springs located in the Spring Mountains, western NTS (i.e., Timber Mountain, central Pahute Mesa, and Fortymile Wash), and Death Valley (Lower Brier, Upper Brier, and Woodcamp springs) generally exhibit high positive PC 1 scores, whereas Death

Valley (northwest portion and Furnace Creek Ranch area), Oasis Valley, and Ash Meadows samples exhibit high negative PC 1 scores. The magnitudes of the PC scores are due primarily to the elements with high negative PC 1 loadings (SO<sub>4</sub>, K, Na, Li, and Rb). Therefore, springs and wells with high negative PC 1 scores have higher concentrations of these constituents, whereas springs and wells with high positive PC 1 scores have lower concentrations of these constituents (Farnham et al., 2003). As indicated on Table 2, however, the

TABLE 2. LOADINGS, EIGENVALUES, AND CUMULATIVE VARIANCES FOR PC 1, 2, AND 3

Geochemical constituent	PC 1	PC 2	PC 3
Cl <sup>-</sup>	-0.66	-0.34	-0.02
SO <sub>4</sub> <sup>2-</sup>	-0.87	0.10	-0.08
Ca <sup>2+</sup>	-0.42	0.81	-0.07
Mg <sup>2+</sup>	-0.48	0.78	-0.20
K <sup>+</sup>	-0.77	0.06	0.14
Na <sup>+</sup>	-0.77	-0.54	0.00
Li	-0.74	-0.40	0.32
Ti	-0.24	0.11	0.01
V	0.06	-0.50	-0.50
Cr	-0.27	0.05	-0.51
Mn	-0.08	0.08	0.53
Co	-0.34	0.21	0.58
Ni	-0.20	0.08	0.49
Ge	-0.50	-0.58	0.19
As	-0.38	-0.27	-0.63
Se	-0.32	0.14	-0.16
Rb	-0.76	-0.11	0.30
Sr	-0.60	0.59	-0.28
Mo	-0.48	-0.41	-0.04
Cs	-0.51	0.11	-0.07
Ba	-0.38	0.70	-0.18
W	0.03	-0.48	-0.27
Bi	-0.38	-0.15	-0.24
U	-0.39	-0.17	-0.08
Eigenvalue	5.98	3.91	2.33
% Total	25%	16%	10%
Cumulative total	25%	41%	51%

loadings for most of the constituents load negatively. As a result, the magnitudes of the PC 1 scores are also influenced by the other constituents but to a lesser degree.

Figure 11 displays a negative correlation between ionic strength and PC 1 scores ( $r = -0.87$ ); as the magnitude of the PC 1 scores increases (from negative to positive), the ionic strength decreases. This may suggest that PC 1 scores display concentration gradients within the DVRFS. The higher the negative scores, the more concentrated the samples due to increased concentrations along their respective flow paths. Areas shown in Figure 8 with high PC 1 scores are considered to be areas of recharge (Winograd and Thordarson, 1975; Waddell et al., 1984; Laczniak et al., 1996). As groundwater moves from areas of recharge downgradient, it increases in concentrations of respective aquifer materials and becomes more concentrated.

According to a number of studies (Kreamer et al., 1996; Stetzenbach et al., 1999; Farnham et al., 2000, 2003), PC 2 scores typically separate groundwater characteristics of a volcanic rock aquifer from that of a carbonate rock aquifer. It appears that PCA on this data set provides similar findings. All samples within the Pahranaagat Valley, Spring Mountains, and Ash Meadows and samples of groundwater from the eastern NTS exhibit high positive PC 2 scores, whereas all wells and springs within the Oasis Valley, Timber Mountain, Thirsty Canyon, and central Pahute Mesa consist of

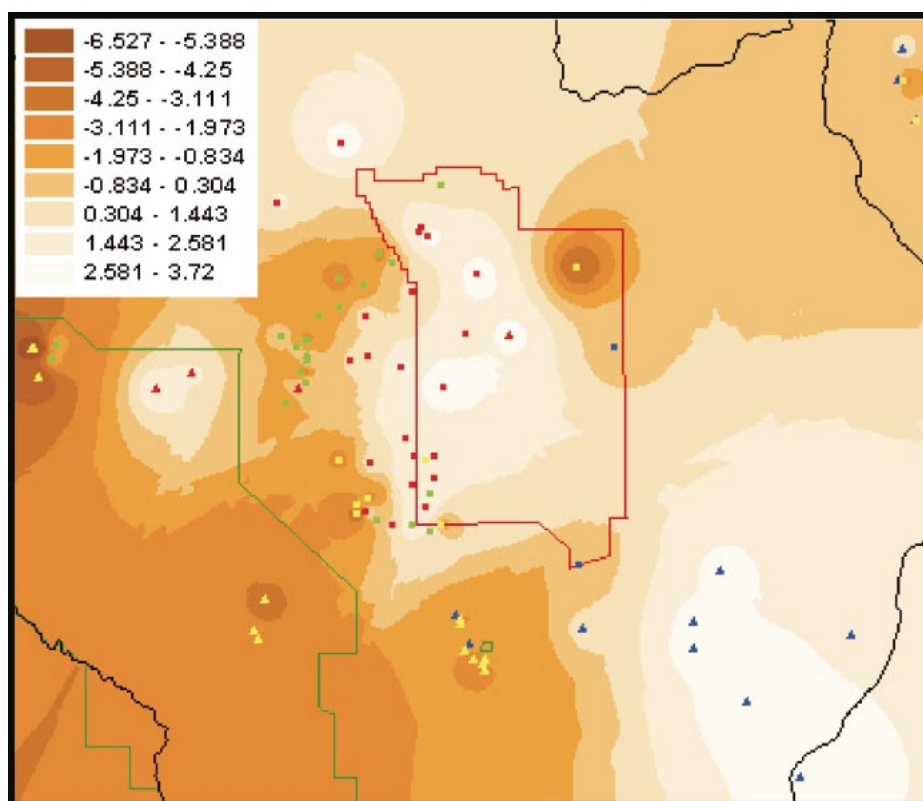


Figure 8. Geographic information system (GIS) map of interpolated PC 1 scores resulting from principal component analysis (PCA). Included in this figure are the springs (triangles) and wells (squares) color coded in relation to their clusters (cluster 1—red; cluster 2—blue; cluster 3—green; and cluster 4—yellow).

negative PC 2 scores. Springs and wells within Crater Flat, Death Valley, and Fortymile Wash, as well as the Nye County Early Warning Drilling Program [NCEWDP] wells, exhibit both positive and negative PC 2 scores depending on the particular aquifer sampled.

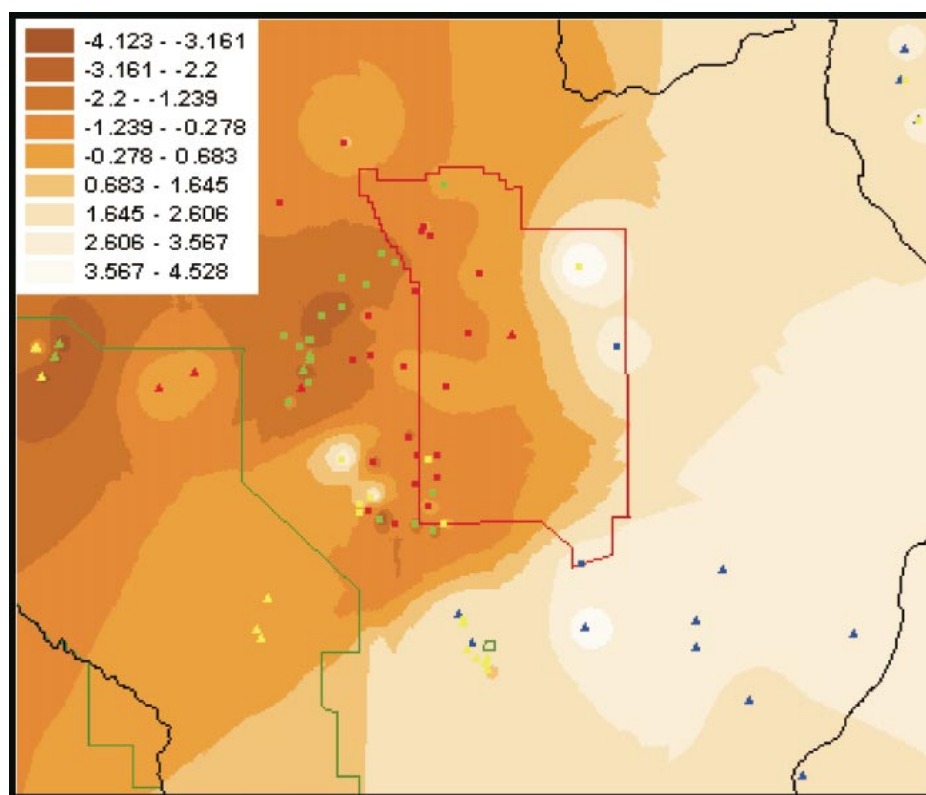
The magnitudes of the positive PC 2 scores are due primarily to the constituents with high positive PC 2 loadings (Ca, Mg, Sr, and Ba), whereas the magnitudes of the negative PC 2 scores are due primarily to the constituents with high negative PC 2 loadings (Na, Li, Ge, V, and W). It appears that samples with high positive PC 2 scores represent groundwater that has flowed through carbonate-derived rocks, such as limestone and dolomite, and likewise, samples with high negative PC 2 scores represent groundwater that has flowed through volcanic-derived rocks.

The chemical constituents with the high positive PC 2 loadings (Ca, Mg, Sr, and Ba) all fall within group IIA of the periodic table (alkaline earth metals). These constituents tend to have higher concentrations in groundwater dominated by carbonate rocks (Farnham et al., 2003). Barium appears to be somewhat

of an anomaly. It is typically found with higher concentrations in volcanic rock and shale compared to limestone (Drever, 1988). Two of the chemical constituents with high negative PC 2 loadings (Na and Li) fall within group IIA (alkali metals) and tend to be observed in greater concentrations in groundwater of volcanic rock aquifers. Intermediate PC 2 scores may represent mixing of groundwater from volcanic and carbonate aquifers or the geochemical signatures of alluvial aquifer systems. Figure 9 shows the interpolation of the PC 2 scores using GIS.

An array of positive and negative PC 3 scores is observed for the sample locations throughout the DVRFS (Fig. 10). In a recent study by Farnham et al. (2003), the third component provided details on the possibility of separating groundwater within the Nye County wells into reducing and oxidizing groundwater systems. Similar to the Farnham et al. (2003) study, the results from this study indicate that the PC 3 scores are loaded negatively with V, Cr, and As, and positively with Mn and Co (Table 2). According to Hem (1989), V, Cr, and As typically occur as sol-





**Figure 9. Geographic information system (GIS) map of interpolated PC 2 scores resulting from principal component analysis (PCA). Included in this figure are the springs (triangles) and wells (squares) color coded in relation to their clusters (cluster 1—red; cluster 2—blue; cluster 3—green; and cluster 4—yellow).**

uble oxyanions in oxidizing waters, and Mn and Co typically are more soluble in reducing waters.

## DISCUSSION

The groundwater within the DVRFS typically flows south or southwest. Based on the statistical analyses, separate flow paths within the groundwater system can be identified. Based on the cluster analysis alone, it appears that four major groundwater systems are present; however, by including the PCA results, a number of additional flow paths may be identified. In the following subsections, individual areas within the DVRFS are described separately. The information from all of these areas is combined to investigate the potential groundwater flow paths within the DVRFS.

### Pahranagat Valley and Spring Mountains

Samples collected from Pahranagat Valley and Spring Mountains were collected from two wells and ten springs. Groundwater from these samples reflects recharge into the re-

gional carbonate aquifer (Winograd and Thordarson, 1975; Thomas et al., 1996). The Spring Mountains, an exception to the typical arid climate of this area, receives up to 10–30 in of precipitation annually (Winograd and Thordarson, 1975). Most of the springs in the eastern part of the study area issue from the lower carbonate aquifer, controlled by localized faults or joints (Winograd and Thordarson, 1975). Many studies have suggested that groundwater flows through the limestones and dolomites of Lower Paleozoic strata from Pahranagat Valley down through the southeast corner of the NTS and discharges from springs within Ash Meadows. Winograd and Thordarson (1975) and Thomas et al. (1996) suggested that discharging water from Pahranagat Valley may represent an older carbonate source compared to the springs of Spring Mountains. In the PC 1 score plot (Fig. 8) and the graph of ionic strength versus PC 1 score relationship (Fig. 11), results from this study appear to support this idea of older source water, or at least source water from a longer distance, in the Pahranagat Valley. Groundwaters in Pahranagat Valley appear to be less dilute

compared to Spring Mountains, where groundwater has been more recently recharged (Winograd and Thordarson, 1975; Thomas et al., 1996).

Groundwater is thought to flow through the lower carbonate aquifer from Spring Mountains into Ash Meadows (Winograd and Friedman, 1972; Winograd and Thordarson, 1975; Thomas et al., 1996; Johannesson et al., 1997a, 1997b). The statistical outcome of this study shows that groundwaters from the Pahranagat Valley and Spring Mountains are similar in their hydrogeochemical composition. The dendrogram of cluster 2 (Fig. 5) groups all of the Spring Mountain springs together into one subgroup, except for GV-SM, and groups the three Pahranagat Valley springs into another subgroup.

Groundwater discharging from the GV-SM spring has a similar geochemical composition to ARMY well, Scruggs and Fairbanks Springs in Ash Meadows, and Hiko, Crystal, and Ash Springs in Pahranagat Valley compared to the other Spring Mountains springs, which were grouped together in cluster 2 (Fig. 5). The GV-SM also has higher concentrations of Na, Li, and  $\text{SO}_4$ , which tend to be in greater concentrations in volcanic rock aquifers compared to the other springs in Spring Mountains. According to Zhou et al. (2000), higher total dissolved solids were also observed in these waters. Zhou et al. (2000) suggested that this might be due to the alteration of soil zone minerals during groundwater flow. As the water passes through the NTS, such as U3CN and ARMY wells, it may inherit the geochemistry of the volcanic-derived groundwater. Similarities in the chemical compositions were also demonstrated by the PC 2 scores for these springs; the scores are in the higher positive range (2.0–4.2). There is a slight decrease in the PC 2 scores downgradient, thereby suggesting some influence from the volcanic rock aquifers of the NTS. The samples from Pahranagat Valley typically have high negative PC 3 scores and therefore might be oxidized waters. Although most of these samples are springs, the highest negative PC 3 scores are found in the results of the two wells, AlamoWell 7 and Key-Pittman, which also suggests that the groundwater in these wells is relatively oxidizing. The contouring of PC 3 scores in Pahranagat Valley suggests that groundwater movement toward the southwest is transitioning from a more oxidized state to a more reduced state, which is consistent with what is generally observed along flow paths (Fig. 10). The springs in the Spring Mountains have intermediate PC 3 scores; however, as groundwater moves west, an in-

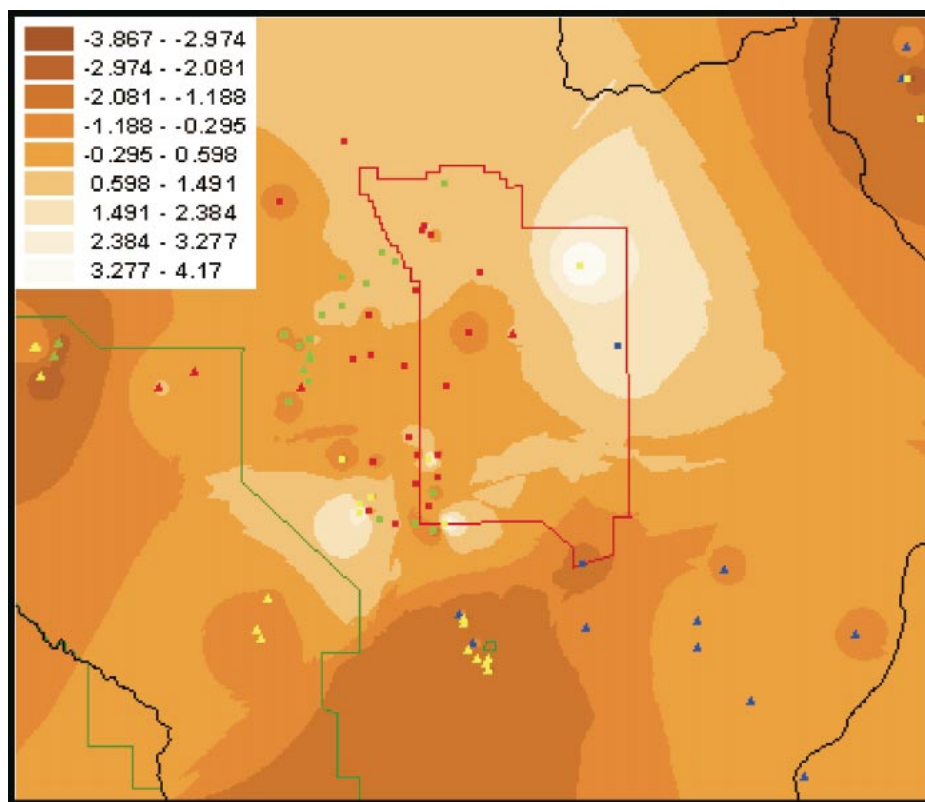


Figure 10. Geographic information system (GIS) map of interpolated PC 3 scores resulting from principal component analysis (PCA). Included in this figure are the springs (triangles) and wells (squares) color coded in relation to their clusters (cluster 1—red; cluster 2—blue; cluster 3—green; and cluster 4—yellow).

crease in the negative PC 3 scores occurs, contrary to what is generally observed along flow paths. As groundwater flows from the Spring Mountains toward Ash Meadows, it most likely comes into contact with groundwater from the northeast, which, according to the PC 3 scores, may be highly oxidized. Furthermore, the Spring Mountains is a source of recharge, and therefore an increase in groundwater oxidation may occur due to infiltration of meteoric water.

#### Eastern Nevada Test Site (NTS)

There were only four samples collected from the eastern NTS. These locations included three wells (ARMY, U3CN, and UE10Jzn1) and one spring (Tippipah). The three wells fall within the two clusters (cluster 2 and cluster 4) that appear to have characteristics of carbonate-derived aquifers (Figs. 5 and 7). Tippipah Spring is grouped within the first cluster, which consists of groundwaters with a signature derived from a volcanic rock aquifer (Fig. 4). The PC scores (1 through 3) for these groundwaters are also very different compared to the other sample locations. According to Zhou et al. (2000), the major-ion groundwater chemistry of the Tippipah Springs represents groundwaters discharging from the felsic volcanic rock aquifer. Tippipah Springs water, discharging from the base of the Shoshone Mountains, is believed to be perched groundwater from the felsic rock of these mountains (Zhou et al., 2000; Johannesson et al., 1997b). Results from other studies support this as well (Johannesson et al., 1997a; Stetzenbach et al., 2001). Both cluster analysis and PCA support these findings. It does appear that groundwater from Pahranaagat Valley moves down through the eastern side of the NTS. Based on the sample and statistical results of UE10Jzn1, groundwater in the overlying volcanic rock aquifers and aquitards of the NTS and Yucca Mountain region is influenced by carbonate-derived groundwater upwelling from the regional carbonate aquifer; this is similar to findings in Stetzenbach et al. (2001).

#### Ash Meadows

Ash Meadows is located just south of the NTS and west-northwestward of the Spring Mountains. The statistical results suggest that the hydrogeochemical composition is very similar to most carbonate-derived groundwater throughout the DVRES. All of the springs fall within either cluster 2 or cluster 4 (Figs. 5 and 7). The difference between the two

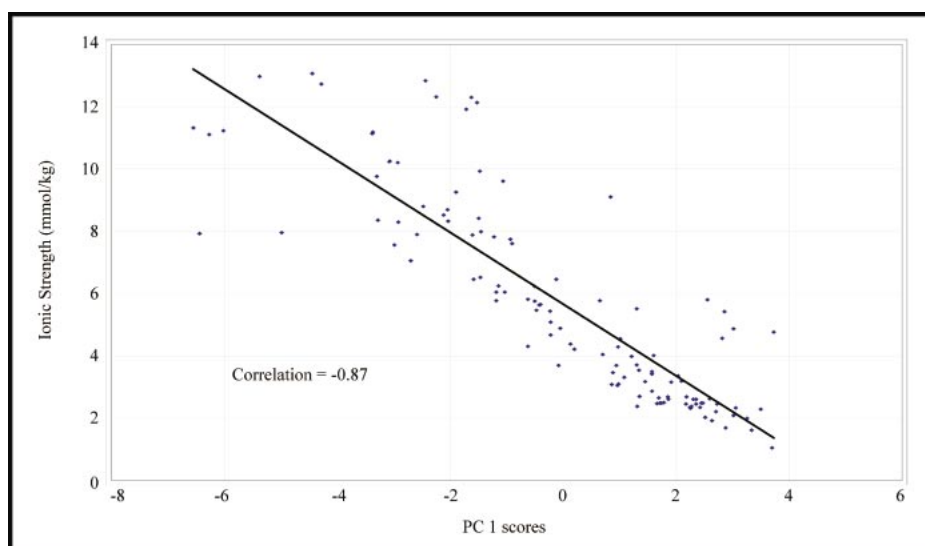


Figure 11. Relationship of PC 1 scores versus ionic strength for samples collected from the Death Valley Regional Flow System.

springs (Scruggs and Fairbanks) in cluster 2 compared to the springs in cluster 4 may be due to the differences in chromium (Cr). These two springs have low concentrations of Cr (0.11 and 0.27 ppb, respectively) compared to the springs in cluster 4 (ranging from 3.60 to 5.75 ppb). Due to the fact that most of the springs fall within cluster 4, it appears that these waters consist mostly of carbonate-derived water; however, there might be some influence of volcanic-derived water from the NTS. Ash Meadow springs grouped in cluster 4 have high concentrations of Na, similar to wells and springs located throughout the western border of the NTS, which suggests an influence from groundwater that has migrated from the volcanic material of the NTS and discharges from the springs in Ash Meadows. The PC 1 score plot also suggests that the groundwater has increased in the amount of dissolved constituents, suggesting groundwater flow from the east, and possibly, the north. The Ash Meadow springs that fall within cluster 4 are also very similar in hydrogeochemical composition to those springs of Death Valley that have been suggested to be carbonate as well as alluvial aquifer groundwaters (Kreamer et al., 1996).

Many studies have suggested that Spring Mountains and Pahrnagat Valley influence the spring water discharging from Ash Meadows, with some percentage of volcanic water from the NTS (Winograd and Thordarson, 1975; Thomas et al., 1996; Stetzenbach et al., 2001). Winograd and Thordarson (1975) suggested that 1% to 5% of the spring water composition of the Ash Meadows springs is from the NTS.

Ash Meadow springs with the lowest negative PC 1 scores (Fig. 8) include two springs from within cluster 2 (Scruggs and Fairbanks) and three springs from within cluster 4 (Longstreet, PtofrogNE, and PtofrogNW). The water from these springs is more dilute compared to the water from other Ash Meadow springs. Studies conducted by Hodge et al. (1996) and Stetzenbach et al. (1999) have suggested that groundwater increases in concentration (or ionic strength) as the water flows along the general alignment of the Ash Meadows spring line and is likely due to evaporation and/or evapotranspiration. Although downgradient of the spring line, the Point of Rocks springs (PtofrogNE and PtofrogNW), which discharge directly from the Bonanza King Formation, are not subject to extreme evaporation and, therefore, do not increase in the amount of total dissolved solids (Stetzenbach et al., 2001).

### Oasis Valley and Thirsty Canyon

The hydrogeochemistry of all Oasis Valley springs and wells, except Frans Spring and Tolicha Peak well, resembles groundwater compositions typical of a volcanic-derived aquifer system. Most of these springs and wells are grouped into cluster 3 (Fig. 6). Frans Spring and Tolicha Peak well are grouped into cluster 1 (Fig. 4), which is also typical of volcanic-derived groundwater. The higher negative PC 2 scores also suggest that these groundwaters are consistent with water-rock interactions involving the local, felsic volcanic rocks, compared to water-rock interactions involving the regional carbonate rocks. Also included in this cluster are all of the Thirsty Canyon wells. These also have higher negative PC 2 scores compared to those of a carbonate-derived groundwater system. The similarities of both the Oasis Valley and Thirsty Canyon sample locations are further defined within the subgroups of cluster 3. The linkage distances are relatively minute.

The Oasis Valley subbasin stretches from Pahute Mesa in the north to Beatty in the south (Waddell et al., 1984) and consists of fractured Tertiary volcanic rocks and alluvial deposits as the principal aquifer systems (Blankennagel and Weir, 1973; Winograd and Thordarson, 1975; White, 1979). The gradients in Figure 8 of the PC 1 scores follow the contours outlined by Blankennagel and Weir (1973) and findings by White (1979) and Farnham et al. (2000). These gradients suggest an increase in ionic strength (Fig. 11) due to the influence of evapotranspiration in a shallow alluvial aquifer, such as Oasis Valley (White, 1979). Although most samples from Oasis Valley fall into cluster 1 (Fig. 4) and samples from central Pahute Mesa fall into cluster 3 (Fig. 6), the PC score gradients of both PC 1 and PC 2 plots (Figs. 8 and 9), as well as similar findings by Farnham et al. (2000), suggest that groundwater from this alluvial aquifer system may originate from the felsic volcanic rock aquifer system of the central Pahute Mesa, located in the upper part of the Alkali Flat–Furnace Creek subbasin.

### Pahute Mesa, Timber Mountain, and Crater Flat

This area was sampled predominantly on the west side of the NTS; it is an area of extreme complexity due to its structural geology and the numerous underground nuclear tests conducted in the Pahute Mesa. There are 10 wells in this area of the study, including wells in central Pahute Mesa (UE-19h, ER-20-6#3,

6-20ww, and UE-20bh-1), Crater Flat (Cof-WM, ER-EC-7, SAGA, and ER-OV3c wells), and Timber Mountain (ER-EC-5 and UE-18r). All of these wells were grouped into cluster 1 (Fig. 4) except for UE-19h and SAGA, which belong to clusters 3 and 4, respectively (Figs. 6 and 7). The eight samples that fall within cluster 1, as well as UE-19h, have groundwater consistent with water-rock interactions involving the local, felsic volcanic tuffs; however, UE-19h was grouped into cluster 3 and therefore has a similar hydrogeochemical signature to that of groundwater in Oasis Valley.

The PCA results for samples collected from Oasis Valley and Thirsty Canyon have high negative PC 2 scores, and samples collected from Pahute Mesa, Timber Mountain, and one well from Crater Flat (Cof-WM) have intermediate PC 2 scores. Due to this separation, it appears that this is a separate flow system compared to that of Oasis Valley. In a study by Farnham et al. (2000), similar findings resulted from PCA and cluster analysis (Hierarchical and K-Means), separating the NTS samples from the Oasis Valley and Thirsty Canyon samples.

These wells, as well as the NCEWDP and Fortymile Wash samples belong in the Alkali Flat–Furnace Creek Ranch groundwater subbasin outlined by Waddell et al. (1984). Laczniak et al. (1996) combined the work of Winograd and Thordarson (1975), Waddell et al. (1984), and Harrill et al. (1988) into a table discussing the three subbasins. Within this subbasin, one of the major areas of recharge is that of Pahute Mesa (Blankennagel and Weir, 1973), which might explain the high PC 1 scores in Figure 8. As previously stated for the Oasis Valley samples, the PC 1 score contours also follow the potentiometric contours of groundwater within the area outlined by Blankennagel and Weir (1973).

SAGA well is grouped into cluster 4 (Fig. 7) and suggests groundwater with a carbonate signature, although, due to the grouping into this cluster, it is possible that groundwater from the carbonate aquifer has percolated upward through some volcanic material. Ca, Mg, and trace elements of carbonate groundwater systems dominate this well, but it also has the high Na concentrations typical of volcanic aquifers. Due to the close proximity of an outcrop of carbonate rock on the western side of Crater Flat (Laczniak et al., 1996), and groundwater from NCEWDP and Fortymile Wash samples suggested by Farnham et al. (2003) to have moved through carbonate materials, groundwater collected from samples within this area might be influenced from the lower carbonate aquifers or carbonate-derived

alluvial aquifers via groundwater percolating up through fractures.

### NCEWDP and Fortymile Wash

NCEWDP and Fortymile Wash wells fall within an array of three different clusters (clusters 1, 3, and 4); however, most are within cluster 1 (Fig. 4). Most of these are typically dominated by volcanic felsic rock groundwater (Farnham et al., 2003). However, based on the statistical analyses, samples 1SZn1 and Zn2, 12PA, 12PB, 12PC, 5S, 5SB, and 7S (all zones) are influenced by carbonate-derived groundwater from either the lower carbonate aquifer or an alluvial aquifer dominated by carbonate rocks. These wells consist of intermediate to high concentrations of major solutes and trace elements characteristic of groundwater that has moved through the carbonate rock (Ca, Mg, Sr, and Ba). Farnham et al. (2003) discussed many of these wells in detail.

It appears that groundwater does flow from areas of recharge, such as Rainier Mesa and possibly Timber Mountain and Fortymile Wash, southward through Fortymile Wash (Lacznik et al., 1996). All of the Fortymile Wash wells have high positive PC 1 scores, consisting of possibly younger waters, or groundwater with shorter flow paths, due to the low ionic strength (Figs. 8 and 11), and seem to be predominantly volcanic-derived groundwater, based on the negative PC 2 scores. WT-17 was grouped into cluster 4 and is the only Fortymile Wash well that is grouped in this cluster, although the PC 1 and 2 scores are similar to the other Fortymile Wash wells. It does have a high positive PC 3 score, suggesting a more reduced groundwater system (Fig. 10). A potential flow path might exist following these wells. Figure 8 displays PC 1 score gradients following the Fortymile Wash wells, which is similar to the DEM-derived drainage network. This area was difficult to assess, but it does appear that the groundwater on this western border of the NTS predominantly flows south-southwest through volcanic material with some influence of carbonate material.

### Death Valley

Death Valley springs Trav-A, Trav-B, Texas, Nevares, and Mesquite, as well as the Grapevine Springs, are grouped into cluster 4 (Fig. 7). These are separated among different subgroups, although they are all dominated by the lower carbonate-derived aquifer system in the Furnace Creek area (Trav-A, Trav-B, Tex-

as, Nevares) and the Grapevine Mountains (U-GV, M-GV, GV) (Hodge et al., 1996; Kreamer et al., 1996; Zhou et al., 2000). Figure 9 further supports the influence of carbonate materials within the groundwater system flowing from the east. The springs of Furnace Creek appear to consist of groundwater that has moved through volcanic materials moving down from the north from the volcanic aquifer system of the NTS. Figure 7 suggests that the springs on the western side of the Grapevine Mountains consist of carbonate groundwater, and according to Steinkampf and Werrell (2001), discharge from carbonate materials. Based on Figure 9, these springs also appear to be influenced by volcanic-derived groundwater from the eastern side of these mountains, which are composed of an outcrop of volcanic material (Lacznik et al., 1996; Steinkampf and Werrell, 2001), and they are also possibly influenced from groundwater coming from the northeast and east, possibly from Bullfrog Hills.

Lower and Upper Brier and Woodcamp Springs are located on the east side of the Grapevine Mountains, which are composed of Miocene ash-fall tuffs and rhyolitic lavas (Reynolds, 1976; Strand, 1967; Maldonado, 1990). Therefore, these springs would have a groundwater signature typical of a volcanic aquifer system. Scotty and Surprise Springs emerge from Upper Oligocene and Miocene volcanic rocks from the western slope of the Grapevine Mountains (Kreamer et al., 1996). These springs exhibit typical volcanic signatures based on PC 2 scores (Fig. 9) and appear to consist of high ionic strength, thereby having older water or at least water that has traveled through long distances of an aquifer system. Cluster analysis has grouped these into cluster 3 (Fig. 6); therefore, they have a similar chemical signature to those samples collected in Oasis Valley. Kreamer et al. (1996) stated that Mesquite arises from alluvial basin-fill and Nevares and Travertine emerge from the carbonate aquifer percolating up through Quaternary gravels. Nevares, Texas, Trav-A, and Trav-B have a similar hydrogeochemistry to that of Ash Meadow springs and therefore might come from this area, which is similar to other findings (Winograd and Friedman, 1972; Winograd and Thordarson, 1975; Johannesson et al., 1997b; Stetzenbach et al., 2001). Based on Figures 8 and 9, PC 1 and 2 score plots show possible influence from the NCEWDP wells, thereby adding more of a volcanic signature to these Death Valley springs, and hence clustering these springs and some of the NCEWDP wells (1S, 12PC, and 7S) in cluster 4 (Fig. 7).

### Potential Groundwater Flow Paths

Groundwater movement throughout the DVRFS is very complex, and it is possible that groundwater flow moves via interbasin and/or intrabasin paths, causing different geochemistry for the different aquifer systems. Figure 12 summarizes the possible flow paths hypothesized here. These flow paths are inferred based on the previous studies mentioned throughout this report as well as the hydrogeochemical signatures of these waters.

It appears that groundwater from the carbonate aquifer system flows from the Pahrnagat Valley in the northeast and the Spring Mountains in the southeast of the DVRFS down through fractured rocks and discharges up through the springs in Ash Meadows. There also might be an influence of volcanic-derived groundwater coming from the north in the NTS. From Ash Meadows, this predominantly carbonate-derived groundwater moves toward the west and discharges from the Furnace Creek springs of the southern part of Death Valley. Also contributing to the groundwater flow into Furnace Creek is another potential flow path north of the Amargosa Valley. This area consists of two potential flow paths, one from the Timber Mountains down through Crater Flat and the other coming from Rainier Mesa down through Fortymile Wash. Three other potential pathways of groundwater travel within the DVRFS include the Oasis Valley flow path, central Pahute Mesa down through Bare Mountains, and another contributing to both these two flow paths coming from the north; all of these are predominantly volcanic-derived groundwater. Eventually these may converge and contribute to the carbonate groundwater emerging from the northern part of Death Valley near the Grapevine Mountains. A small but possibly significant flow path also exists from the eastern side of the Grapevine Mountains to the west into Death Valley.

### CONCLUSIONS

More than 100 samples have been collected throughout the NTS and surrounding area by the HRC groundwater geochemistry group at UNLV. By using multivariate statistics with the current hydrogeochemical data, it is possible to understand the geochemical processes occurring within the groundwater system, identify rock-water interaction, identify groundwater sources, and determine potential groundwater flow paths of the southern Great Basin. Due to the radioactive hazardous waste produced by nuclear testing at NTS, an un-

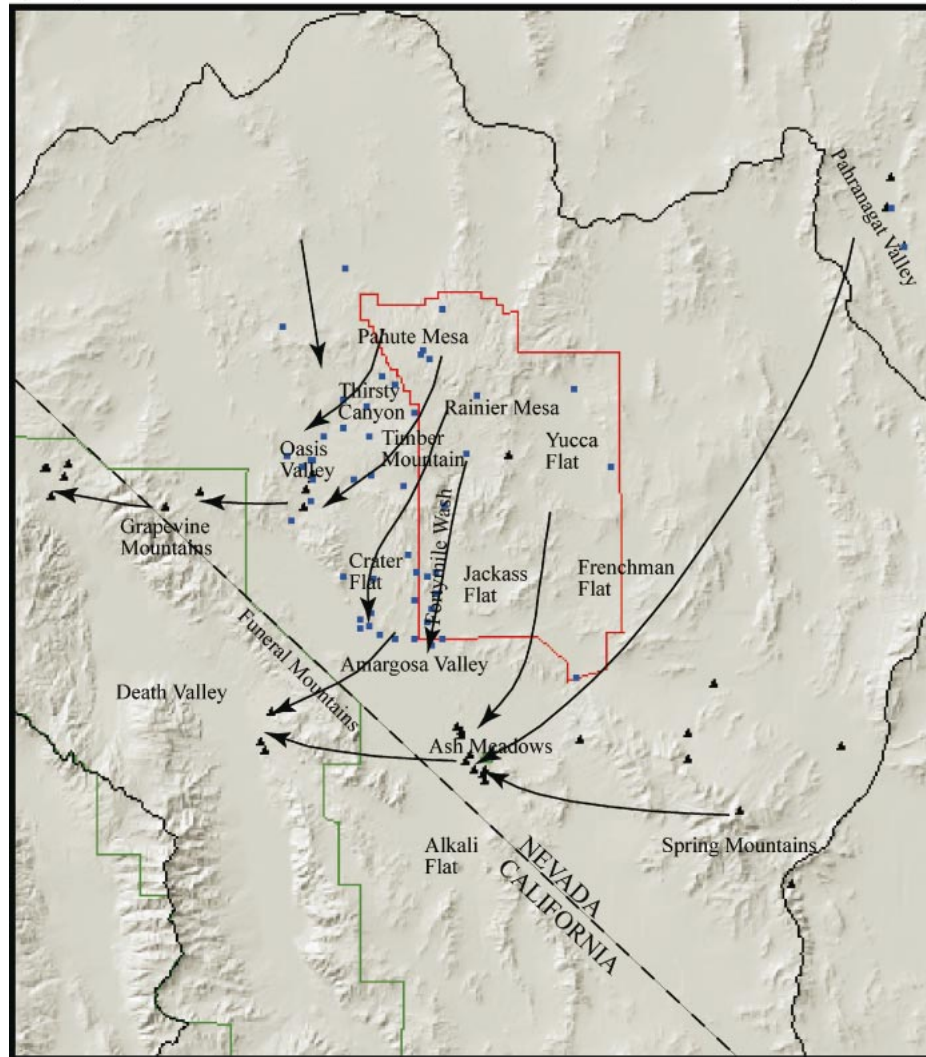
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Figure 12. Map of potential groundwater flow paths within the study area.

Understanding of the water flow paths and geochemical processes will be important to help improve the prediction of contaminant fate and transport in the groundwater systems.

In this study, cluster analysis and PCA have separated the hydrogeochemical composition of groundwater into individual components, such as dilute and concentrated, volcanic, carbonate and a combination of the two. Figure 12 graphically summarizes the potential flow paths throughout the DVRFS into 12 flow paths. It appears that both major ions and trace elements offer insight into groundwater characteristics; however, it must be noted that the results obtained in this paper are theoretical, and unless more wells and geologic and hydrogeologic profiling ensues, these results must be viewed with some caution. Future studies may also include other chemical constituents, such as the rare earth elements, in the analysis.

Understanding of the water flow paths and geochemical processes will be important to help improve the prediction of contaminant fate and transport in the groundwater systems.

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