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## Trace element geochemistry of groundwater flow systems in southern Nevada and eastern California

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**TRACE ELEMENT GEOCHEMISTRY OF GROUNDWATER FLOW  
SYSTEMS IN SOUTHERN NEVADA AND EASTERN CALIFORNIA**

by

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## ABSTRACT

### **Trace Element Geochemistry of Groundwater Flow Systems in Southern Nevada and Eastern California**

by

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Associate Professor of Geology  
University of Nevada, Las Vegas

The Nevada Test Site (NTS) was used for underground nuclear tests before the 1960's. Yucca Mountain in southern Nevada has been proposed as the site for the first high-level radioactive waste repository in the U.S. Because groundwater is a likely medium for transporting radio-nuclides to the accessible environment, determining the nature and path of groundwater movement through the aquifers at the NTS and Yucca Mountain is a critical task for assessing the risks and the future performance of the repository. In this study, systematic investigations of major ion and trace [mainly rare earth element (REE)] element geochemistry were conducted on different components of groundwater flow systems in southern Nevada, including groundwaters from representative springs and wells, aquifer rocks that comprise major aquifers, secondary minerals from fractures and veins in the aquifer rocks, and solutions from water/rock interactions. The geochemical data collected in this study help us characterize and

compare major ion and REE signatures in different sample media, study changes in trace elements and REEs resulting from water/rock interactions, and develop a geochemical framework to trace groundwater from sources and predict groundwater flow paths and fluid mixing at the Nevada Test Site and the Yucca Mountain region of southern Nevada. The study also enhances our geologic and hydrologic understanding of trace element and REE geochemistry in the groundwater flow systems.



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## CHAPTER 1

### INTRODUCTION

As a potential medium for transporting radio-nuclides to the accessible environments, groundwater has been intensively investigated at the Nevada Test Site (NTS) and the Yucca Mountain region in southern Nevada, where many underground nuclear tests were performed and a potential high-level radioactive waste repository has been proposed, respectively. Tracing groundwater sources and predicting groundwater flow paths are crucial tasks required for risk assessments in these sensitive areas. Geochemical data of groundwaters from the existing wells in this region are either limited or are not conservative natural tracers of geochemical processes (i.e., major elements). Drilling and developing more monitoring wells in this region is extremely costly. Therefore, sensitive and naturally-occurring tracers of geochemical processes in the groundwater flow systems are much needed.

Recent studies of rare earth elements (REEs), a special group of trace elements, in groundwater systems have shown promising results for tracing groundwater sources and predicting groundwater flow paths (e.g., Smedley, 1991; Fee et al., 1992; Gosselin et al., 1992; Stetzenbach et al., 1994, 1999, 2001; Kremer et al., 1996; Hodge et al., 1996, 1998; Johannesson et al., 1997, 1999, 2000; McCarthy et al., 1998). These studies indicate that groundwaters and some surface waters can inherit their REE and trace

element signatures from the rocks or aquifer materials with which they interact. Therefore, understanding the geochemistry of REEs and other trace elements in groundwaters is important not only for tracing groundwater flow, but also for investigating water/rock interactions.

However, previous studies of trace element and REE geochemistry in the southern Nevada aquifers mainly focused on groundwaters from springs and wells. Systematic studies of trace element and REE geochemistry of different components of groundwater flow systems in this region have not been conducted. Although many researchers have realized the impacts of aquifer rocks on the REE signatures of groundwaters, detailed comparative studies of REE and trace element signatures from both groundwaters and aquifer rocks and minerals with which the groundwaters interacted are fairly limited (Zhou et al., 1999; Johannesson et al., 2000). The mechanism and geochemistry of REEs and trace elements during the interactions between water and rock are still poorly understood. Thus, more and systematic studies of trace element and REE geochemistry in groundwaters, aquifer rocks, and secondary minerals are necessary. Experiments that simulate the interactions between groundwaters and aquifer materials, such as laboratory leaching tests, should be performed to determine trace element and REE signatures and changes during the water/rock contacts.

These issues are addressed in this dissertation by (1) characterizing major ion (Chapter 2) and REE behaviors (Chapters 3 and 4) in different components (groundwaters, aquifer rocks, and secondary minerals) of groundwater flow systems from a geologically and hydrogeologically representative area, southern Nevada; (2)

comparing REEs from groundwaters with those from representative rocks that comprise major aquifers in southern Nevada (Chapter 3); and (3) conducting leaching experiments in the laboratory to quantify changes in REEs resulting from water/rock interactions (Chapter 5).

### 1.1. Major Solute Chemistry in Groundwaters

The groundwater chemical data in southern Nevada were principally obtained from samples collected in the late 1950's and early 1960's. A few new wells were drilled and sampled in the late 1970's. Following the late 1980's, extensive water sampling has been reactivated and many samples have been collected from pre-existing and new wells and springs by several organizations. Since 1992, the groundwater geochemistry group at the Harry Reid Center (HRC) for Environmental Studies at the University of Nevada, Las Vegas (UNLV) has been involved in collecting water samples from more than 100 sites, including wells and springs in Amargosa Valley, Ash Meadows, Crater Flats, Death Valley, Nellis Air Force Range, Nevada Test Site, Oasis Valley, Pahranaagat Valley, and The Spring Mountains.

In Chapter 2 I have compiled the hydrochemical data of major ions for the above-mentioned sites, beginning in 1992, and summarized the general chemical characteristics of major solutes in the groundwater from the Nevada Test Site and adjacent areas of southern Nevada and eastern California. This study compliments the trace element investigations that are the focus of Chapters 3, 4, and 5.

### 1.2. REE Characterization in Groundwaters and Aquifer Rocks

In Chapter 3 I examine the hypothesis that REEs dissolved in the groundwaters are the result of the mobilization of REEs from aquifer rocks into the groundwater. I tested this hypothesis by characterizing and comparing REE signatures from both groundwaters and aquifer rocks. The comparative study of REEs in groundwaters and aquifer rocks in southern Nevada helps us determine the impact of tuffaceous and carbonate rocks on the geochemistry of groundwaters from the unsaturated zone and the saturated zone in this region, respectively. The data obtained in this study also allow us to evaluate the groundwater flow paths in southern Nevada and eastern California and the mixing of groundwaters originating on the NTS or at Yucca Mountain with those of the regional carbonate aquifer.

The REE data in representative rock samples of the aquifers in southern Nevada, or average REE concentrations of these representative aquifer rocks, provide a local REE-normalizing standard. The saturated zone and the unsaturated zone in southern Nevadan aquifers are mainly composed of carbonate (dolomite and limestone) and felsic volcanic (tuffaceous) rocks (i.e., Winograd and Thordarson, 1975; Stuckless and Dudley, 2002), so an appropriate REE standard based on these local rocks is better than the average chondrite- or shale-normalization.

### 1.3. REE Signatures in Secondary Minerals

Secondary minerals that occur in the fractures of both the unsaturated and saturated zones of aquifers precipitated from flowing groundwaters. The origin of

fracture-coating minerals, mainly secondary calcite and silica, at the NTS has been debated for the past several years. Two competing hypotheses have been proposed to explain the origin of these secondary minerals: (1) from infiltrating meteoric water (e.g., Szabo and Kyser, 1990; Peterman et al., 1992; Vaniman and Whelan, 1994; Whelan et al., 1994, 1998, 2002; Vaniman and Chipera, 1996; Marshall et al., 1998; Paces et al., 1998, 2001), or (2) from upwelling hydrothermal fluids (Hill et al., 1995; Dublyansky and Szymanski, 1996; Stuckless et al., 1998; Hill and Dublyansky, 1999; Dublyansky et al., 2001).

These secondary minerals record geochemical changes and history that occurred in the paleo-groundwater that flowed through the fractures (Wallin and Peterman, 1999; Lee et al., 2003). Thus, the origins of these secondary minerals at Yucca Mountain and southern Nevada are crucial for evaluating hydrogeologic changes and the fate of the proposed nuclear waste repository.

In Chapter 4 I report the REE concentrations of twenty-six secondary mineral (mostly calcite) samples that were collected from southern Nevada. The origins of these secondary minerals are addressed based on their REE signatures. These data also help us understand sources of the mineral-precipitating waters, water chemistry, water/rock interactions, crystallization mechanisms, and mineral growth phases. By combining these analyses with other geochemical studies, such as isotopic and fluid inclusion studies, it may eventually be possible to characterize the geochemical history and movement history of groundwater in southern Nevada.

#### 1.4. REE Signatures from Leaching Experiments

In Chapter 5 I present the REE results of three leaching tests. The leaching experiments performed in this study used different aquifer rock samples and solutions and gave them sufficient contacting time to interact. Both the rocks samples and the leachates were analyzed for their REE concentrations. The REE concentrations and patterns during water/rock interactions demonstrate that different rocks and different solution compositions can affect trace element and REE signatures of the leachates.

The leaching study provides some baseline information (i.e., solid/liquid partitioning coefficients) during water/rock interactions. The results of these leaching experiments help elucidate the mechanisms associated with trace element and REE changes that occur during water/rock interactions and build a basis for the interpretation of trace element and REE data of groundwaters through different aquifers in this region.

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## CHAPTER 2

### MAJOR ION GEOCHEMISTRY OF GROUNDWATERS FROM SOUTHERN NEVADA AND EASTERN CALIFORNIA

#### 2.1. Introduction

The dissolved ionic constituents of groundwater are, in part, a record of the minerals and rocks with which the water has reacted (either dissolving or precipitating) as it moves through aquifer materials. In general, the chemical composition of water in carbonate-rock aquifers is dominated by calcium, magnesium, and bicarbonate, whereas sodium, chloride, and sulfate can be dominant ions in the water that comes from volcanic aquifers or clay minerals (e.g., Thomas et al., 1996). The movement of water from a volcanic aquifer into the regional carbonate aquifer in southern Nevada can be deduced in large part by an increase in sodium concentration in the carbonate aquifer groundwater sampled down gradient from the recharge area (Schoff and Moore, 1964). Thus, the geochemical characteristics of the water can be used to facilitate tracing groundwater sources and flow paths. The geochemistry of groundwater from the Nevada Test Site (NTS) and adjacent areas in southern Nevada and eastern California has been instrumental to the development of the fundamental groundwater flow hypotheses for the region (Schoff and Moore, 1964; Blankennagel and Weir, 1973; Winograd and Thordarson, 1975; White, 1979; Chapman and Lyles, 1993; Thomas, 1988, 1996;

Thomas et al., 1996).

However, the chemical data used by many researchers for their studies were mainly from samples collected 40 to 50 years ago or from pre-existing and new wells and springs in the late of 1980's. In order to update the geochemical data and to compliment the trace element geochemical studies, researchers at HRC started to collect groundwater samples from springs and wells in southern Nevada and eastern California a decade ago. The samples were analyzed for their major and trace element concentrations. The major ion geochemical data of groundwaters presented in this chapter were extracted from the HRC groundwater geochemical database.

## 2.2. Major Solute Chemistry in Groundwaters

Figure 2.1 shows the groundwater sample areas in southern Nevada and eastern California. Zhou and others (2000) discussed in detail the major ion chemistry of these groundwaters. This chapter only briefly summarizes the major ion chemistry of these groundwaters and provides a general geochemical framework of groundwaters in the study area. The GW Charts, developed by the U.S. Geological Survey (USGS), have been employed to build Piper diagrams (Fig. 2.2) to graphically demonstrate the characterizations of these groundwaters.

Groundwaters in the Amargosa Valley have relatively lower total dissolved solids (TDS) except for those of the McCracken Range (Fig. 2.2). The relative proportions of  $\text{HCO}_3^- + \text{CO}_3^{2-}$  and  $\text{Ca}^{2+}$  increase from Lathrop Well to T&T Range Wells, which suggests that the influence on the water chemistry by carbonate aquifer materials increase

from north to south within the valley (Fig. 2.2). Groundwaters from Cind R-lite, Jackass Aero Park, and Lathrop Wells are very similar (Fig. 2.2) and resemble groundwaters characteristic of the tuffaceous rocks of Shoshone Mountain (Johannesson et al., 1997) west of Yucca and Frenchman Flats, as well as those of Rainier and Pahute Mesas.

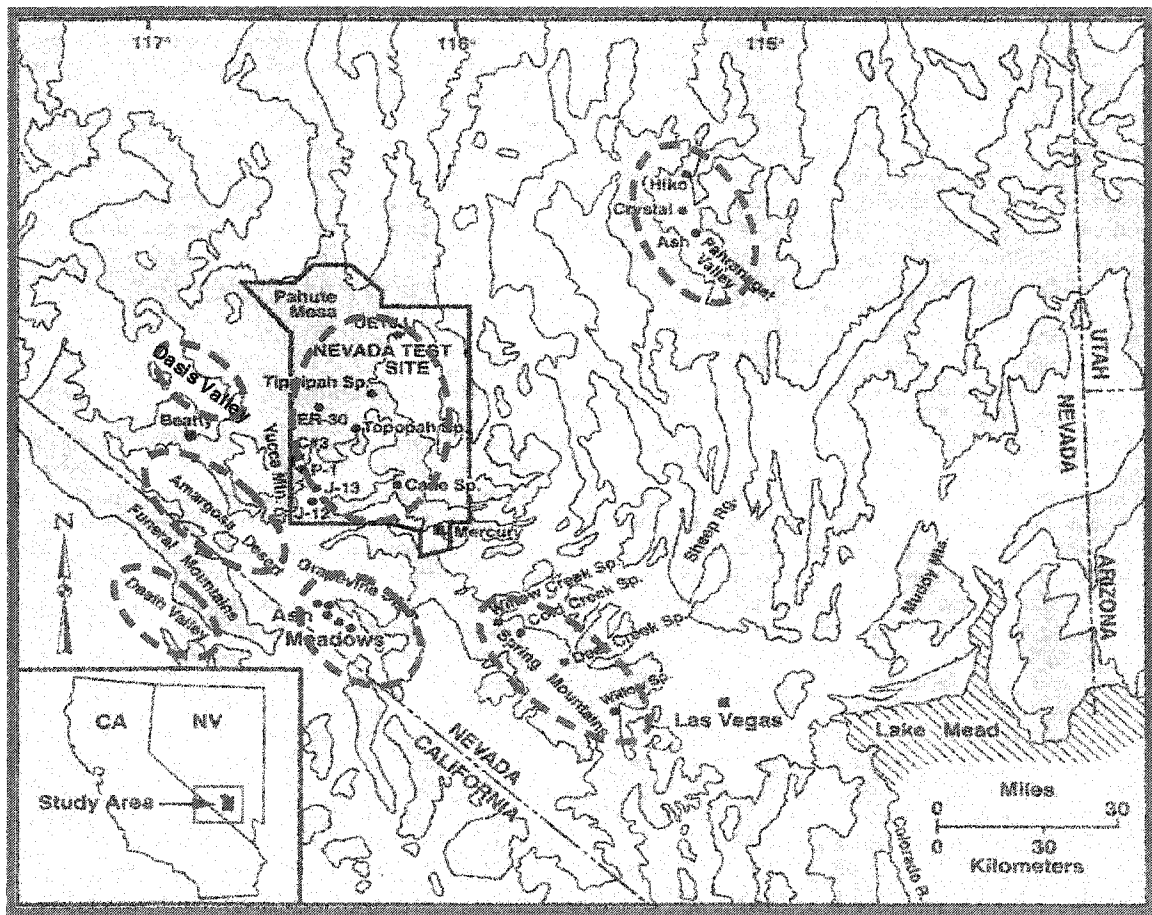


Fig. 2.1. Map of southern Nevada and eastern California showing groundwater sample areas discussed in this chapter (modified from Stetzenbach et al., 2001).

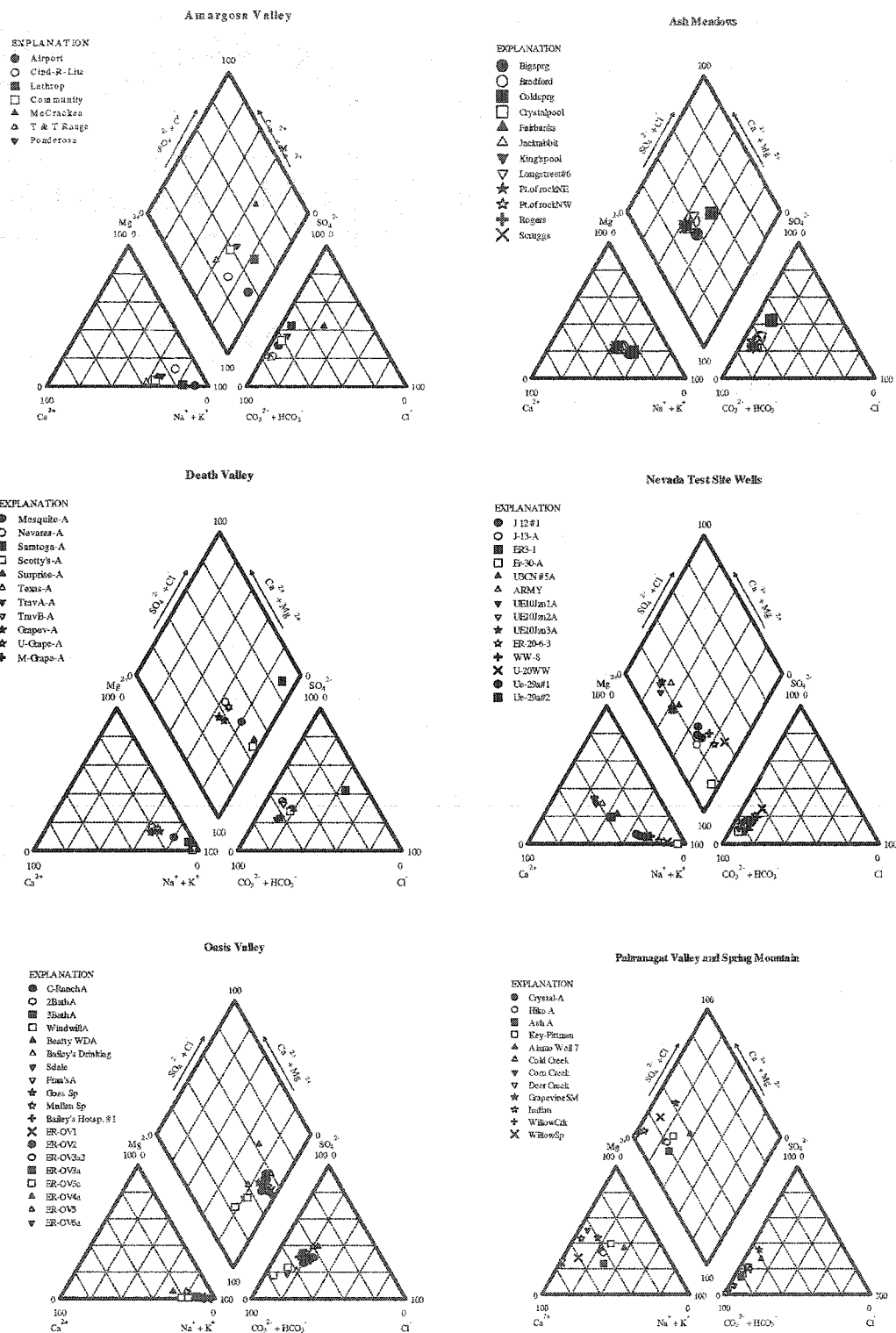


Fig. 2.2. Piper diagrams for groundwaters from springs and wells in southern Nevada and eastern California (data from HRC).

Ash Meadows groundwaters are more concentrated than the Amargosa Valley groundwaters. Except for the total dissolved solids, all waters have relatively similar major ion chemistry (Fig. 2.2). Previous studies have suggested that groundwaters at Ash Meadows represent groundwaters from The Spring Mountains and from the Pahranaagat Valley area (Winograd and Friedman, 1972; Winograd and Thordarson, 1975; Winograd and Pearson, 1976; Thomas, 1996). However, this model cannot explain the high concentrations of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{SO}_4^{2-}$  in the Ash Meadows spring waters. Obviously, another groundwater source with higher  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{SO}_4^{2-}$  concentrations is needed to produce the water chemistry of the Ash Meadows springs. Winograd and Thordarson (1975) pointed out that these groundwaters contain some contribution of "volcanic" groundwaters from the Nevada Test Site to Ash Meadows. The data of stable oxygen and hydrogen isotope analyses (Thomas, 1988, 1996), strontium isotopes (Peterman et al., 1992), trace element and multivariate statistical analyses (Johannesson et al., 1996), and rare earth element analyses (Johannesson et al., 1997) support this hypothesis.

Groundwaters from Death Valley springs are typically more concentrated than the Amargosa Valley groundwaters and similar to or slightly more concentrated than the Ash Meadows spring waters. Several sub-groups, however, can be identified on closer inspection of the Piper diagram (Fig. 2.2). Surprise and Scotty Springs essentially plot identically on the Piper diagram, forming one sub-group. Nevares, Texas, Travertine, and Grapevine Springs, also plot similarly, forming another sub-group. Mesquite and Saratoga Springs did not plot with any of the other spring waters. These observations based on major-ion chemistry, are consistent with the result obtained from the principal



component analyses of trace elements (Kreamer et al., 1996).

Topopah and Tippipah Springs at the NTS represent groundwaters that have interacted only with these volcanic rocks (i.e., no carbonate aquifer input), whereas groundwater collected from nearby Cane Spring may represent the mixing of groundwaters from both carbonate-rock and volcanic-rock aquifers. Groundwaters from the NTS wells fall into three distinct groups on Piper diagrams (Fig. 2.2). They basically represent groundwaters from the regional lower Paleozoic carbonate aquifer, the local felsic volcanic-rock aquifers, and the mixture of two, respectively.

Groundwaters in Oasis Valley and adjacent areas fall into a loose but distinct cluster within each field on Piper diagrams (Fig. 2.2). Most of these groundwaters are recharged by inflows from Pahute Mesa, Gold Flat, and other areas to the north and east (White, 1979), together with some flow through carbonate rock aquifers farther north and within central Nevada (Davisson et al., 1999).

Groundwaters from Pahrnagat Valley and the Spring Mountains are very similar and show a close cluster in each field of Piper diagrams (Fig. 2.2). Based on major ion chemistry, the groundwaters from both Pahrnagat Valley and the Spring Mountains are probably dominantly from carbonate-rock aquifers with little influence from volcanic aquifers and/or soil-zones.

### 2.3. Hydrochemical Facies

The concept of hydrochemical facies has been used to denote the diagnostic chemical character of water solutions in hydrologic systems (Back, 1966). The facies

reflect the effects of chemical processes occurring between the minerals within the lithologic framework and the groundwater. The flow patterns modify the facies and control their distribution.

Schoff and Moore (1964) and Winograd and Thordarson (1975) extensively studied the hydrochemistry of groundwaters in the Nevada Test Site and adjacent areas. Winograd and Thordarson (1975) recognized four hydrochemical facies based on major ion geochemistry (Table 2.1). The following discussion is based on their classification of hydrochemical facies.

The calcium-magnesium-bicarbonate facies is found in the Spring Mountains and in Pahranaagat Valley. Waters of this facies represent groundwaters that discharge either from the lower carbonate aquifer or from the valley-fill aquifer rich in carbonate-rock detritus (Winograd and Thordarson, 1975).

Table 2.1. Classification of hydrochemical facies at the Nevada Test Site and vicinity. (Winograd and Thordarson, 1975)

Hydrochemical facies	Ca+Mg	Na+K	HCO <sub>3</sub> +CO <sub>3</sub>	SO <sub>4</sub> +Cl
Calcium magnesium bicarbonate	75-100*	0-25	80-90	10-20
Sodium potassium bicarbonate	5-35	65-95	65-85	15-35
Calcium magnesium sodium bicarbonate	50-55	45-50	70	30
Sodium sulfate bicarbonate	30	70	60	40

- Note: Percentage range of milliequivalents per liter of major constituents.

The sodium-potassium-bicarbonate facies is represented by water from Oasis Valley, Pahute Mesa, Amargosa Valley, Tippipah Spring, Scotty's and Surprise Springs

in Death Valley, and groundwaters to the northwest and west of the Nevada Test Site. These groundwaters are mostly issued from or flow through felsic tuff, rhyolite, and valley-fill aquifers rich in volcanic detritus. The sodium-potassium-bicarbonate facies is also found in some thin carbonate strata within the upper clastic aquitard (Winograd and Thordarson, 1975).

The calcium-magnesium-sodium-bicarbonate facies, which was noted by Schoff and Moore (1964) as a mixing facies of both of the preceding types, is found in the east-central Amargosa Desert, Ash Meadows, and the Nevada Test Site. Schoff and Moore (1964) argued that this mixing type hydrochemical facies may have formed in one of three ways: (1) movement of water from tuffaceous rocks into carbonate rocks (or alluvium with carbonate-rock detritus), followed by dissolution of carbonate minerals; (2) movement of water from carbonate rocks into tuff (or tuffaceous alluvium), followed by acquisition of sodium either by solution or by ion exchange of calcium for sodium; or (3) mixing of calcium-magnesium-bicarbonate water with sodium-potassium-bicarbonate water.

The sodium-sulfate-bicarbonate facies was proposed by Winograd and Thordarson (1975). This hydrochemical facies appears to be restricted to the Nevares Springs area (i.e., Texas, Nevares, and Travertine Springs) of Death Valley, a few wells in the west-central Amargosa Desert, and Tolicha Peak to the north and west of the Nevada Test Site (Winograd and Thordarson, 1975).

It is worth noting that the boundaries between hydrochemical facies are transitional, which reflects gradually changes in the water chemistry during recharge and

movement of groundwaters. Some groundwaters may not fit into any of these hydrochemical facies due to complicated hydrologic and geochemical processes.

#### 2.4. Summary

Major ion chemistry of groundwater is mainly controlled by chemical and hydrologic processes between water and aquifer materials and by mineral compositions of aquifer materials through which groundwaters flow. Therefore, major-ion chemistry of groundwater can be used to reconstruct the hydrochemical framework of water and to trace groundwater flow patterns. The method used in this study graphically demonstrated the different patterns and distribution of major constituents of water chemistry. They also demonstrate the relationships among different springs and wells, which may eventually facilitate delineation of regional groundwater flow paths and sources. Four hydrochemical facies of groundwater have been distinguished in the study area through the examination of major cation and anion compositions. Groundwater that has moved only through the lower carbonate aquifer or through valley-fill rich in carbonate detritus is classified as calcium-magnesium-bicarbonate type (facies). Water that has moved only through volcanic rocks or through valley-fill deposits rich in volcanic detritus belongs to the sodium-potassium-bicarbonate hydrochemical facies. Groundwater that initially occurred within the lower carbonate aquifer, and that subsequently entered the volcanic-rock aquifers, is a mixture of these two hydrochemical types, designated as the calcium-magnesium-sodium-bicarbonate type. Further mixing with different quantities of source waters or mixing with the third hydrochemical facies identified, can form another type of

water, such as the sodium-sulfate-bicarbonate type.

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## CHAPTER 3

### COMPARATIVE STUDIES OF RARE EARTH ELEMENTS IN GROUNDWATER AND AQUIFER MATERIALS

#### 3.1. Abstract

In order to compare REEs in groundwater with those in aquifer materials, a total of 36 rock samples, each representing a different rock type (dolomite, limestone, and felsic volcanic rocks) of aquifers in southern Nevada and eastern California were analyzed for their REE concentrations in this study. Lower Paleozoic dolomites and dolomitic limestones exhibit relatively flat shale-normalized REE patterns with only slight LREE or HREE enrichments and weak Ce and Eu anomalies. Upper Paleozoic limestones exhibit strong shale-normalized HREE enrichments with strong Ce depletions; these patterns are essentially identical to those for modern seawater. Tertiary felsic volcanic rocks from the Nevada Test Site (NTS) show fairly strong shale-normalized LREE or HREE enrichments with substantial Eu depletion and no Ce anomalies. Groundwaters in southern Nevada and eastern California can be classified as “dolomite,” “limestone,” or “volcanic” groundwaters based on their REE signatures. Some of these groundwaters appear to be mixtures of two or more types of waters from different aquifers. REE signatures in both groundwaters and aquifer rocks strongly indicate that the REE patterns of groundwaters from the dolomite, limestone, and volcanic aquifers



resemble those in the respective rock types through which they flow. REE fractionations (HREE or LREE enrichments, and Ce and Eu anomalies) occurred during rock/water interactions. Groundwaters discharging from the Upper (younger) Paleozoic carbonate (limestone) aquifer have greater REE fractionations (stronger HREE enrichment and negative Ce anomalies) than those from the Lower (older) Paleozoic carbonate (dolomite) aquifer and from the volcanic aquifer. The origins of REE fractionations in these groundwaters are also discussed in this study.

### 3.2. Introduction

Because groundwater is a likely medium for transporting radio-nuclides to the accessible environment, tracing groundwater sources and predicting groundwater flow paths are crucial tasks required for risk assessments at the Nevada Test Site (NTS), where many underground nuclear tests were performed, and the Yucca Mountain region, where the first long-term geological repository for high-level radioactive waste will be located. Geochemical data of groundwaters from existing wells in this region are either limited or are not conservative natural tracers of geochemical processes (i.e., major elements). Drilling and developing more monitoring wells in this region is extremely costly. Therefore, sensitive and naturally-occurring tracers of geochemical processes in the groundwater flow systems are highly desirable.

Rare earth elements (REEs), a special group of trace elements, and some trace elements may play an important role in tracing groundwater flow. The unique and chemically coherent behavior of the REEs has spawned considerable interest in their

behavior in geologic systems. Because of their size and valence, REEs exhibit distinctive chemical properties, as compared to their nearest neighbors (barium and hafnium) on the periodic table. Also, the systematic decrease in ionic radius with increasing atomic number within the lanthanide suite imparts predictable chemical differences that can record subtle geochemical processes in natural systems. Consequently, REEs have been used extensively as sensitive tracers of geochemical processes in rock and seawater studies (e.g., Hanson, 1980; Elderfield and Greaves, 1982; DeBaar et al., 1983; Cullers and Graf, 1984). Recent studies of trace elements and REEs in groundwater systems and lakes have shown that groundwaters and some surface waters can inherit their REE and trace element signatures from the rocks or aquifer materials with which they interact. REEs can be used as natural tracers of groundwater flows and of groundwater and surface interactions (e.g., Smedley, 1991; Fee et al., 1992; Gosselin et al., 1992; Stetzenbach et al., 1994, 1999, 2001; Kreamer et al., 1996; Hodge et al., 1996, 1998; Johannesson et al., 1997, 1999, 2000; McCarthy et al., 1998; Ojiambo et al., 2003). Therefore, understanding the geochemistry of REEs and other trace elements in groundwaters is important not only for tracing groundwater sources and predicting groundwater flow paths, but also for investigating water/rock interactions and groundwater mixings. Moreover, due to the chemical similarities between REEs and trivalent transuranic ions (i.e.,  $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ ,  $\text{Cf}^{3+}$ ), REEs can be used as chemical analogs for studying the behavior of the radioactive actinides in natural waters (Choppin, 1983, 1986, 1989; Brookins, 1986; Krauskopf, 1986; Wood, 1990). This application of REEs is especially significant in the study of the fate and transport of the radioactive actinides in the groundwater systems in the vicinity of the

NTS and the Yucca Mountain region.

However, the use of REEs and other trace elements as geochemical tracers in terrestrial waters, particularly in groundwaters, is presently in the developmental stage due to the complexity of groundwater flow systems, ultra-low concentrations (normally at the parts-per-trillion level) of these trace elements in groundwaters, and limitations of analytical instruments. Comparative studies of REE and trace element signatures from groundwaters, and from aquifer rocks with which the groundwaters interacted, are fairly limited (Zhou et al., 1999; Johannesson et al., 2000). The geochemistry of REEs and trace elements during the interactions between water and rock is still poorly understood. Thus, more and systematic studies on trace element and REE geochemistry in groundwaters and aquifer rocks are much needed.

In addition, most researchers who have examined REE concentrations and patterns in groundwaters have used techniques that are more appropriate for igneous rock and seawater studies. Specifically, they commonly normalize the groundwater REE concentrations to the average shale REE values to obtain the relative fractionations of REEs in the natural waters. Such an approach is warranted if the aquifer material in the groundwater system is primarily composed of siliciclastic sedimentary rocks such as shale, but it is inappropriate for other groundwater systems that are composed of non-siliciclastic sedimentary rocks. In these cases, the REE normalization factors should resemble the rocks of which the aquifer material is composed. The saturated zone and the unsaturated zone in southern Nevadan aquifers are mainly composed of carbonate (dolomite and limestone) and felsic volcanic (tuffaceous) rocks (i.e., Winograd and

Thordarson, 1975; Stuckless and Dudley, 2002), so an appropriate REE standard based on these local rocks, or average REE concentrations of these local and representative aquifer rocks, is necessary.

This study analyzed REE concentrations from both groundwaters and aquifer rocks in southern Nevada and Death Valley, eastern California. The data presented in the study help us examine the hypothesis that REEs dissolved in the groundwaters are the result of mobilization of REEs from aquifer rocks into the groundwater. Systematic analyses of representative aquifer rocks in southern Nevada may provide a local REE-normalizing standard. By directly comparing the groundwater REE concentrations with the local rock REE concentrations, we are able to determine the impact of felsic volcanic (tuffaceous) and carbonate rocks on the REE geochemistry of groundwaters from both the unsaturated zone and the saturated zone. In addition, analyses of the REE concentrations in the felsic volcanic rocks of the NTS and the Yucca Mountain region will allow us to evaluate the contribution due to the mixing of groundwaters originating on the NTS or at Yucca Mountain with those of the regional carbonate aquifer.

### 3.3. Methods

#### 3.3.1. Rock Sampling and Analysis

Geological exposures of typical aquifer rocks (i.e., dolomite, limestone, and felsic volcanic rocks) were chosen for the collection of rock samples. These exposures are stratigraphically and lithologically correlative with the hydrostratigraphic units of the local volcanic aquifer and regional carbonate aquifer in southern Nevada (e.g., Winograd

and Thordarson, 1975). Therefore, the REE concentrations in these rocks can be applicable to our studies of REEs in groundwaters from these aquifers. Sampling localities include Frenchman Mountain near Las Vegas, Fossil Ridge in the Sheep Range, exposures near Mercury, and exposures within the NTS (Fig. 3.1). Geological sections at these localities are generally well exposed and allow for easy access and detailed sampling.

The REE data for a total of 36 rock samples were analyzed in this study. Sixteen of the 36 rock samples were collected from the Bonanza King Formation (dolomite, Cambrian) and Toroweap Formation (limestone, Permian) at Frenchman Mountain (samples BKD1, BKD2, BKD3, BKD4, BKD5, BKD6, BKD7, BKD8, BKD9, BKD10, BKD11, BKD 12, BKD13, BKD14, TW1, and TW2). Five rock samples (dolomite or dolomitic limestone) were collected from the Nopah Formation and Pogonip Group at Fossil Ridge (samples FR3, FR4, FR5, FR6, and FR7). Six rock samples (dolomite or dolomitic limestone) came from exposures near Mercury (samples HG1, HG2, HG3, HG4, HG5, and HG6). And three rock samples came from the Tippipah Formation (Permian limestone) at the NTS (samples NTS1, NTS2, and NTS3). Six Tertiary felsic volcanic rocks (samples BF Vitri, BF Ash Fall, BF Med., TM Nonw., TM Weld, and Paintbrush) were collected from the NTS (Johannesson et al., 1997).

The methods used to analyze the rock samples, using inductively coupled plasma mass spectrometry (ICP-MS), have been described elsewhere (Johannesson and Zhou, 1997; Zhou et al., 1999; Johannesson et al., 1997, 2000). In brief, all samples were cleaned and crushed into powder in the laboratory. Approximately 0.25 grams of each

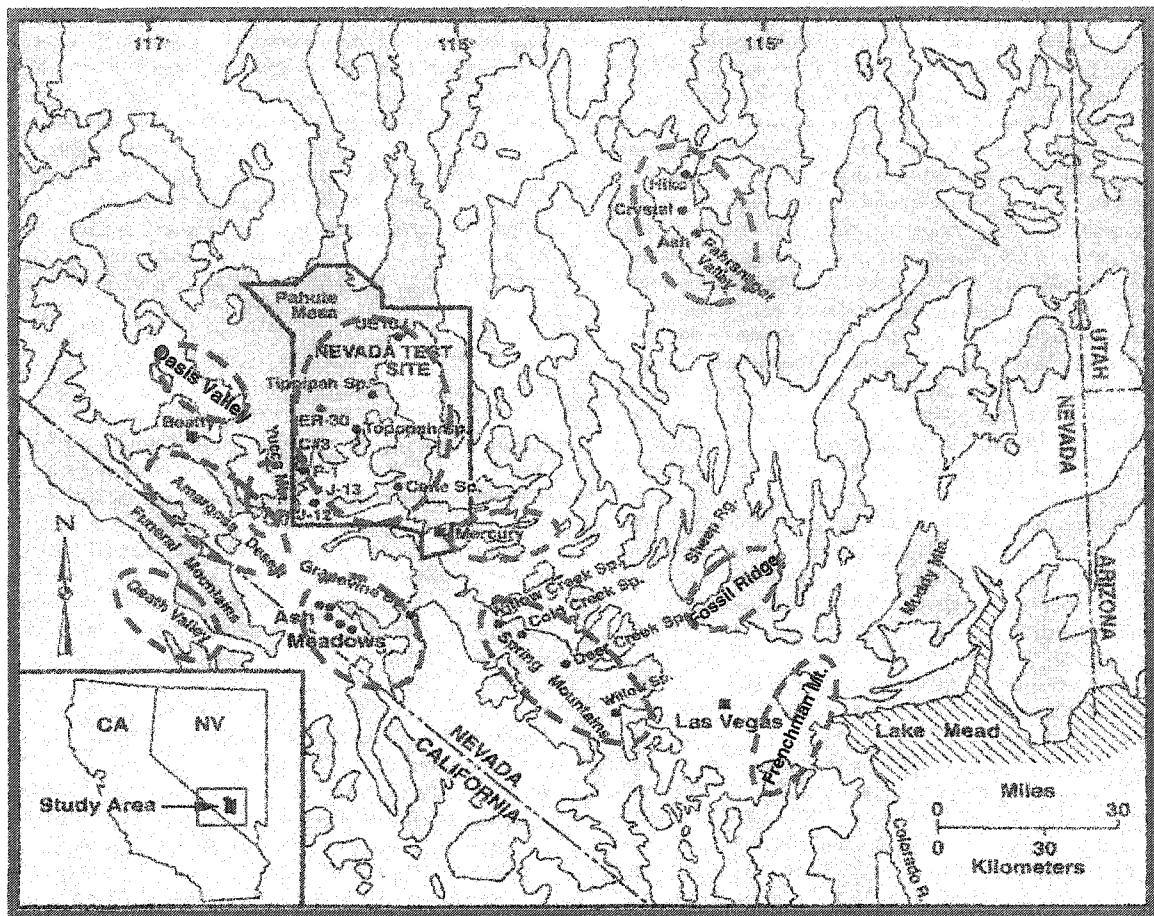


Fig. 3.1. Sample (both groundwater and rock) location map of southern Nevada and Death Valley, eastern California (modified from Stetzenbach et al., 2001).

rock (i.e., powder) sample were placed in precleaned Teflon®-lined microwave digestion bombs, followed by 5 mL of ultrapure HF (Seastar, Inc. double sub-boiling, distilled in Teflon®) and 5 mL of ultrapure HNO<sub>3</sub> (Seastar, Inc. double sub-boiling, distilled in quartz). The Teflon®-lined microwave digestion bombs were then sealed and placed in a microwave oven (CEM Corporation MDS-2100) and heated to 189°C and pressurized to  $8.62 \times 10^5$  Pa (125 p.s.i.) for 25 minutes. The samples were allowed to cool, and then 30 mL of a saturated boric acid solution was added to each sample. The samples were

subsequently heated again in the microwave for 5 minutes at 100°C and  $6.9 \times 10^4$  Pa -  $1.38 \times 10^5$  Pa (10 - 20 p.s.i.). If any residue still remained after this first digestion, these procedures were repeated. For the felsic volcanic rocks, the samples were fused by a lithium metaborate flux prior to dissolution in nitric acid solutions (Johannesson et al., 1997). Both the microwave digestion technique and the fusion method generate similar and reproducible results (Guo, 1996). The dissolved rock samples were then decanted into clean polyethylene bottles and diluted by a factor of 180 or more. Finally they were analyzed using ICP-MS. U.S. Geological Survey rock standards (RGM-1, SCo-1, W-2, G-2) were included as check standards during the analysis; our measurements never deviated more than 10% from the standards.

### 3.3.2. Groundwater Sampling and Analysis

Since the early 1990's, groundwater samples have been collected and analyzed from many springs and monitoring wells in southern Nevada and eastern California by the Groundwater Research Group at the Harry Reid Center (HRC) for Environmental Studies at the University of Nevada, Las Vegas (UNLV). Such springs and wells are located in Death Valley National Park, Ash Meadows National Wildlife Refuge, Pahrnagat Valley National Wildlife Refuge, the Spring Mountains, the Nevada Test Site, and Amargosa Valley (Fig. 1). The methods used to sample groundwater from the springs and wells have been well established by HRC (Stetzenbach et al., 1994, 1999, 2001; Kreamer et al., 1996; Hodge et al., 1996, 1998; Johannesson et al., 1997, 1999, 2000). In summary, springs were sampled by pumping groundwater from the springs using a

peristaltic pump with precleaned, acid-washed Teflon<sup>®</sup> tubing. The water samples were filtered through an in-line Gelman Sciences filter capsule (pore size 0.45  $\mu\text{m}$ ; polyether sulfone membrane) that was connected to Teflon<sup>®</sup> tubing and transferred directly to acid-washed, high-density linear polyethylene bottles. The samples were then immediately acidified to  $\text{pH} < 2$  with ultra-pure nitric acid, stored in acid-washed plastic bags, and transported to the laboratory for analysis. The same sampling procedures were used to collect water samples from wells, except that pumping was continued until the water pH stabilized (at least 24 hours); then the water samples were collected. This process insures that the samples are taken under a well-circulated condition and are representative of the local groundwater.

The REEs were determined using ICP-MS (Perkin Elmer Elan 5000) with ultrasonic nebulization after 50-fold preconcentration by cation-exchange (Stetzenbach et al., 1994; Johannesson and Lyons, 1994). The REE isotopes monitored with the ICP-MS (<sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>146</sup>Nd, <sup>149</sup>Sm, <sup>151</sup>Eu and <sup>153</sup>Eu (mean value), <sup>157</sup>Gd, <sup>159</sup>Tb, <sup>163</sup>Dy, <sup>165</sup>Ho, <sup>166</sup>Er, <sup>169</sup>Tm, <sup>172</sup>Yb, and <sup>175</sup>Lu) were free of elemental isobaric interferences. The ultrasonic nebulization (Catac Technologies Model U-5000) increased the sensitivity by roughly a factor of 30 over cross-flow nebulization and decreased the potential of interferences from oxide formation in the plasma stream (Stetzenbach et al., 1994; Hodge et al., 1996, 1998). Measured  $\text{REEO}^+/\text{REE}^+$  ratios were generally  $< 1\%$ ; for those which were  $> 1\%$ , appropriate corrections were made (Stetzenbach et al., 1994; Johannesson and Lyons, 1994; Johannesson et al., 1996). Interference from  $\text{BaO}^+/\text{Ba}^+$  on Eu was eliminated by extraction of Ba from separate aliquots of each water sample using diethyl-



hexyphosphoric acid (Hodge et al., 1998). The ICP-MS was also equipped with an active film, multiple ion detector (ETP Scientific) that further increased the sensitivity of the instrument by roughly 100 times along with the ultrasonic nebulizer. In order to calibrate the ICP-MS and verify the sample concentrations, a series of five REE standards of known concentrations (10 ng/kg, 50 ng/kg, 100 ng/kg, 500 ng/kg, and 1000 ng/kg) were included for each sample analysis.

Analytical precision for Ce, Pr, Gd, Tb, Dy, Ho, Er, and Yb was better than 5% relative standard deviation (RSD). For La, Nd, and Tm the precision was 7% (RSD) or better, for Eu the precision was 10% (RSD) or better, and for Sm and Lu the precision was 11% and 12% (RSD), respectively. Replicate analyses of water from Ash Meadows indicate that the measurement reproducibility was 10% (RSD) or better for the REEs except Sm and Er for which the reproducibility was 14% (RSD) or better and Ce, Tm, and Lu that were reproducible within 20% (RSD) (Stetzenbach et al., 1994).

### 3.4. Results and Discussion

#### 3.4.1. REEs in Aquifer Rocks

Concentrations (ppm) of the REEs in 36 rock samples analyzed using ICP-MS in this study, along with shale-normalized Yb/Nd ratios and Ce/Ce\* and Eu/Eu\* ratios, are presented in Table 3.1. REE abundances are commonly evaluated after normalizing the measured REE concentrations to the REE concentration in an average chondritic meteorite (in the case of igneous rocks or magmatic processes) or average shale (in the case of sedimentary rocks or weathering processes) or upper continental crustal (UCC)

values (Taylor and McLennan, 1985). This step smoothes out the atomic number dependent variations in the absolute abundances of the REE and facilitates the assessment of the processes under consideration. The shale- and UCC-normalized REE patterns are very similar, except the UCC REE values are ~20% lower than the shale (e.g., North American Shale Composite, NASC) values. Hence, normalization of REE data to UCC will generate relatively similar REE fractionation patterns but higher values (Johannesson et al., 2004) comparing with normalization of REE to the average shale (NASC), which was used in this study.

#### *3.4.1.1. REEs in Dolomite Rocks*

A total of 25 dolomite (or dolomitic limestone) rock samples, including BKD1 - BKD14, FR3 - FR7, and HG1 - HG6, were analyzed for their REEs. Concentrations of the REEs in these dolomite rocks are fairly low, ranging from 1 to 48 ppm for total REEs (TREEs) and 0.2 to 9 ppm for Nd (Table 3.1). The shale-normalized REE patterns (Figs. 3.2 - 3.4) for these dolomite samples are fairly similar except for slight difference in concentrations. They all are quite flat with only slight LREE or HREE enrichments [ $(Yb/Nd)_{SN}$  ratios from 0.61 to 2.11, SN = shale-normalized]. Most of these dolomite rocks don't exhibit negative Ce anomalies ( $Ce/Ce^* \cong 0$ ) and Eu anomalies ( $Eu/Eu^* \cong 0$ ). Several samples have very weak Ce and Eu anomalies, such as BKD11 with a negative Eu anomaly ( $Eu/Eu^* = -0.30$ ), FR6 with a positive Ce anomaly ( $Ce/Ce^* = 0.22$ ), and HG4 with a weak negative Ce anomaly ( $Ce/Ce^* = -0.08$ ) and a weak positive Eu anomaly ( $Eu/Eu^* = 0.10$ ) (Table 3.1). These dolomite samples also show some variations in their HREE concentrations (Figs. 3.2 - 3.4). However, the shale-normalized REE

Table 3.1. Rare earth element concentrations (ppm) of aquifer rocks from Southern Nevada for this study.  
SN = shale-normalized

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Yb/Nd) <sub>SN</sub>	Ce/Ce*	Eu/Eu*
BKD1	1.10	1.50	0.14	0.53	0.09	0.02	0.09	0.01	0.08	0.01	0.05	0.00	0.04	0.00	0.73	-0.05	-0.11
BKD2	0.61	1.24	0.14	0.53	0.09	0.02	0.11	0.01	0.10	0.02	0.06	0.01	0.05	0.00	0.98	0.02	-0.13
BKD3	3.22	7.00	0.81	3.07	0.62	0.15	0.60	0.11	0.66	0.15	0.47	0.07	0.47	0.07	1.66	0.03	0.01
BKD4	3.42	7.51	0.94	3.60	0.72	0.15	0.69	0.11	0.66	0.13	0.39	0.06	0.37	0.06	1.11	0.01	-0.04
BKD5	6.93	14.73	1.77	6.65	1.36	0.25	1.28	0.21	1.24	0.26	0.78	0.11	0.72	0.11	1.18	0.01	-0.10
BKD6	2.48	4.46	0.47	1.83	0.35	0.06	0.34	0.05	0.35	0.07	0.23	0.03	0.21	0.03	1.25	0.00	-0.10
BKD7	1.09	2.01	0.25	0.92	0.16	0.04	0.16	0.03	0.14	0.03	0.08	0.01	0.08	0.01	0.89	-0.02	0.07
BKD8	3.90	8.18	1.02	3.79	0.71	0.15	0.68	0.11	0.62	0.13	0.41	0.05	0.37	0.05	1.06	0.00	-0.03
BKD9	5.93	12.80	1.57	6.13	1.36	0.30	1.36	0.24	1.57	0.35	1.12	0.18	1.19	0.19	2.11	0.01	-0.02
BKD10	2.98	5.36	0.62	2.28	0.38	0.08	0.38	0.05	0.32	0.07	0.19	0.02	0.17	0.02	0.80	-0.02	-0.04
BKD11	5.03	9.78	1.07	4.33	0.80	0.09	0.74	0.07	0.70	0.14	0.47	0.02	0.50	0.04	1.26	0.01	-0.30
BKD12	5.07	11.26	1.47	5.56	1.24	0.30	1.29	0.23	1.50	0.33	1.03	0.16	1.06	0.17	2.05	0.00	0.01
BKD13	9.84	19.91	2.39	8.93	1.53	0.36	1.55	0.23	1.30	0.27	0.77	0.10	0.61	0.10	0.74	0.00	0.00
BKD14	3.22	6.72	0.90	3.31	0.65	0.16	0.64	0.10	0.57	0.13	0.37	0.05	0.36	0.05	1.16	-0.01	0.02
FR3	0.92	1.73	0.20	0.67	0.13	0.03	0.14	0.03	0.12	0.03	0.08	0.01	0.07	0.01	1.13	0.00	-0.08
FR4	0.63	1.49	0.15	0.54	0.12	0.02	0.11	0.02	0.11	0.03	0.07	0.01	0.06	0.01	1.24	0.07	-0.04
FR5	4.73	10.63	1.09	3.78	0.66	0.15	0.70	0.11	0.63	0.13	0.37	0.05	0.32	0.05	0.91	0.06	-0.04
FR6	6.35	16.08	0.80	3.00	0.45	0.11	0.46	0.07	0.37	0.08	0.22	0.03	0.17	0.03	0.61	0.22	-0.01
FR7	7.22	15.41	1.61	5.91	1.10	0.27	1.05	0.16	0.83	0.18	0.48	0.06	0.39	0.06	0.72	0.04	0.02

Table 3.1. (Continued)

HG1	0.50	0.90	0.12	0.39	0.08	0.03	0.13	0.02	0.06	0.02	0.04	0.01	0.04	0.01	0.97	-0.05	0.05
HG2	0.59	1.16	0.14	0.49	0.10	0.03	0.10	0.02	0.08	0.02	0.05	0.01	0.05	0.01	1.10	-0.01	0.08
HG3	0.48	1.00	0.12	0.40	0.08	0.02	0.07	0.02	0.06	0.02	0.04	0.01	0.03	0.01	0.90	0.02	0.01
HG4	0.32	0.53	0.07	0.24	0.04	0.01	0.05	0.01	0.04	0.01	0.03	0.01	0.02	0.01	1.06	-0.08	0.10
HG5	0.33	0.63	0.07	0.26	0.06	0.01	0.05	0.01	0.03	0.01	0.02	0.01	0.02	0.00	0.93	-0.01	0.03
HG6	0.37	0.63	0.08	0.29	0.05	0.01	0.06	0.01	0.05	0.01	0.03	0.01	0.03	0.01	1.04	-0.05	0.04
TW1	1.85	1.37	0.27	1.02	0.16	0.05	0.23	0.03	0.20	0.06	0.17	0.03	0.14	0.03	1.50	-0.34	-0.01
TW2	3.24	1.19	0.33	1.22	0.19	0.05	0.27	0.04	0.25	0.08	0.22	0.03	0.18	0.03	1.59	-0.59	-0.03
NTS1	3.87	4.29	0.75	2.87	0.56	0.22	0.70	0.10	0.57	0.14	0.40	0.06	0.34	0.05	1.27	-0.21	0.18
NTS2	2.13	2.39	0.44	1.68	0.32	0.11	0.46	0.07	0.38	0.10	0.26	0.04	0.23	0.04	1.46	-0.22	0.08
NTS3	2.53	2.19	0.46	1.85	0.37	0.09	0.50	0.08	0.48	0.12	0.38	0.05	0.32	0.06	1.87	-0.31	-0.08
BF Vitri*	79.69	149.70	16.36	53.14	8.40	1.08	7.09	0.95	5.20	1.05	3.10	0.43	3.12	0.48	0.64	0.01	-0.22
BF Ash Fall*	44.56	91.45	10.44	35.71	6.66	0.49	6.21	0.98	5.83	1.12	3.64	0.51	3.48	0.52	1.06	0.02	-0.48
BF Med.*	38.51	78.37	9.23	32.64	6.50	0.73	5.98	0.97	5.45	1.12	3.35	0.54	3.41	0.48	1.13	0.01	-0.30
TM Nonw.*	38.99	77.31	8.41	26.19	4.81	0.38	4.39	0.62	3.78	0.74	2.18	0.34	2.30	0.34	0.95	0.02	-0.45
TM Weld*	36.13	73.65	8.11	25.92	4.96	0.27	4.75	0.75	4.56	0.95	2.88	0.42	2.86	0.43	1.20	0.02	-0.63
Paintbrush*	31.86	71.70	8.15	26.65	7.02	0.35	6.87	1.15	6.79	1.39	3.99	0.57	3.82	0.56	1.55	0.04	-0.67

\* Data from Johannesson et al. (1997a).

 $\text{Ce/Ce}^* = \log \{2\text{Ce}_{\text{SN}}/[\text{La}_{\text{SN}} + \text{Pr}_{\text{SN}}]\}$ . $\text{Eu/Eu}^* = \log \{2\text{Eu}_{\text{SN}}/[\text{Sm}_{\text{SN}} + \text{Gd}_{\text{SN}}]\}$ .

patterns for these samples are generally flat. Currently, it is unclear whether the shale-normalized patterns of these dolomite (or dolomitic limestone) rocks reflect differences in the distribution of REEs in the early Paleozoic seas or redistribution of REEs in these rocks during late diagenetic processes, such as compaction, dolomitization, and thermal fluid alteration.

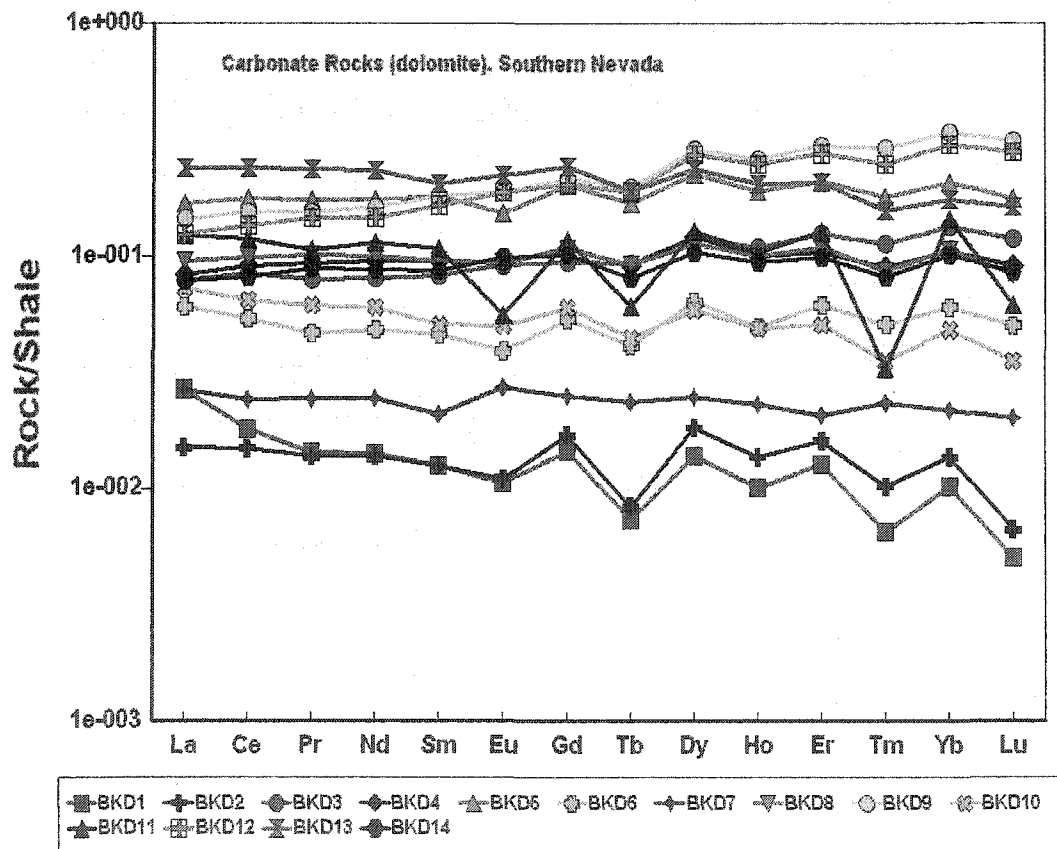


Fig. 3.2. Shale-normalized REE patterns for dolomite rocks from the Bonanza King Formation (Cambrian) at Frenchman Mountain near Las Vegas, Nevada.

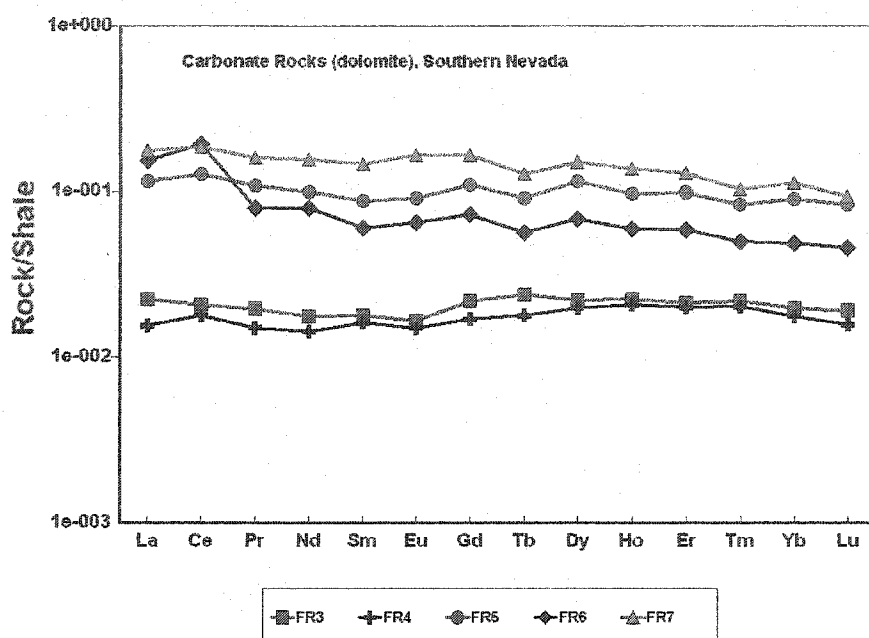


Fig. 3.3. Shale-normalized REE patterns for dolomite rocks (FR3 and FR4) from the Nopah Formation (Cambrian) and for Ordovician dolomitic limestone (FR5, FR6, and FR7) from Fossil Ridge in the Sheep Range, Nevada.

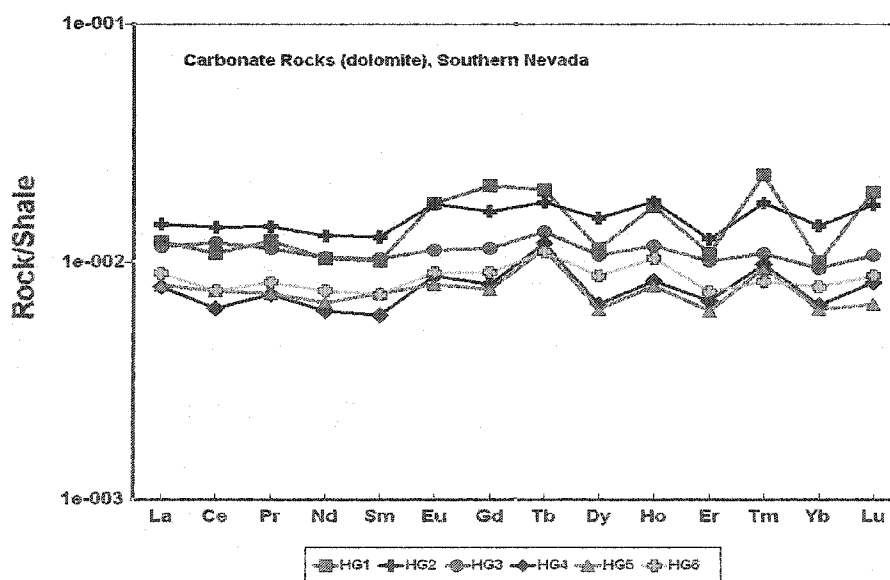


Fig. 3.4. Shale-normalized REE patterns for dolomite rocks from the Bonanza King Formation (Cambrian) near Mercury, Nevada.

#### 3.4.1.2. REEs in Limestones

Five limestone samples (TW1, TW2, NTS1, NTS2, and NTS3) were analyzed for their REEs. Collected from the Permian Toroweap Formation and the Tippipah Formation, these limestone samples are correlative in geological age. They have the lowest REE concentrations determined in this study, ranging from 1 to 3 ppm for Nd and less than 15 ppm for TREEs (Table 3.1). Both REE concentrations and shale-normalized REE patterns (Fig. 3.5) for these limestones are very similar. Unlike older carbonate (dolomite) rocks, the shale-normalized REE patterns for these younger carbonate (limestone) rocks show HREE enrichments [ $(Yb/Nd)_{SN}$  ratios from 1.5 to 1.9] with strong negative Ce anomalies ( $Ce/Ce^*$  ratios from -0.59 to -0.21, Table 3.1, Fig. 3.5) and no or weak Eu anomalies, such as NTS1 and NTS2 exhibiting weak positive Eu anomalies ( $Eu/Eu^* = 0.18$  and  $0.08$ , respectively, Table 3.1, Fig. 3.5). In addition, the shale-normalized REE patterns of these upper Paleozoic limestones are essentially identical to shale-normalized patterns for modern seawater (e.g., Elderfield and Greaves, 1982; Bertram and Elderfield, 1993). Bellanca and others (1997) showed that carbonate rocks could mimic seawater-like REE signatures by uptaking of dissolved REEs during calcite formation in seawater. Therefore, the REE data from Permian rocks in this study suggest that Permian seawater had relatively similar REE signatures to modern seawater. The late diagenetic processes might not dramatically modify REE signatures in these limestones. More REE data from the upper Paleozoic limestones are needed to verify this hypothesis.

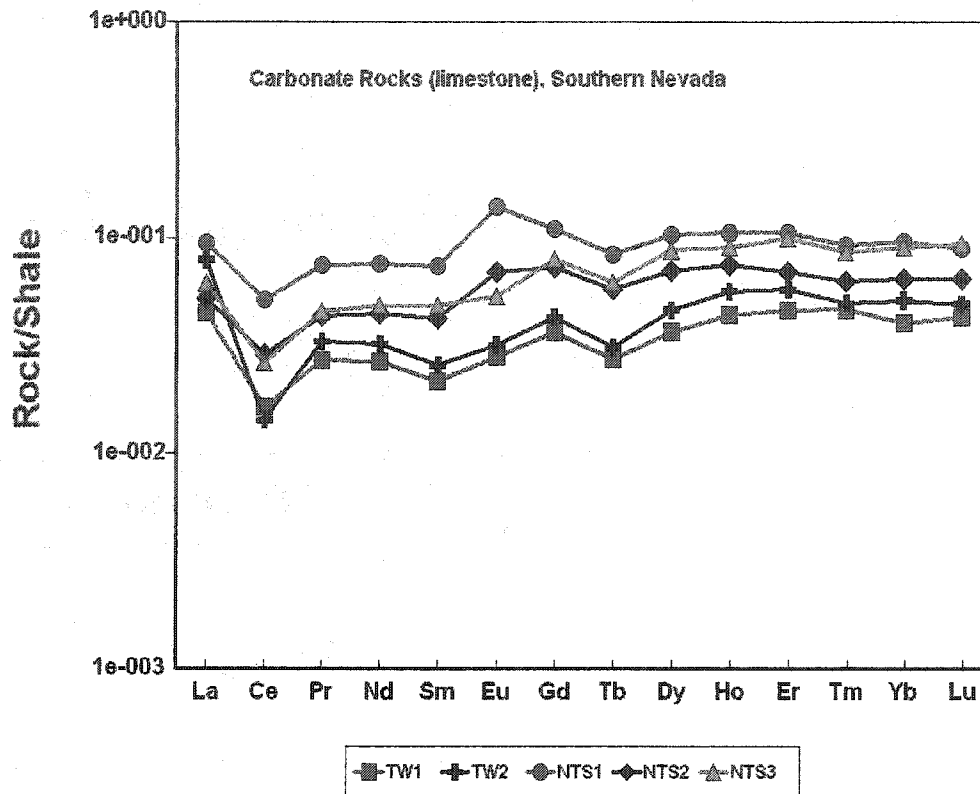


Fig. 3.5. Shale-normalized REE patterns for limestone rocks from the Toroweap Formation (Permian) (TW1 and TW2) at Frenchman Mountain near Las Vegas, and from the Tippipah Formation (Permian) (NTS1, NTS2, and NTS3) at the NTS, Nevada.

#### 3.4.1.3. REEs in Volcanic Rocks

The REE data for six volcanic rocks collected from the NTS, including BF Vitric, BF Ash Fall, BF Med., TM Nonw., and TM Weld, are also included in this study (Table 3.1). Concentrations of the REEs in these rocks range from 167 to 330 ppm for the total rare earth elements (TREEs) and 26 to 53 ppm for Nd. These values are predictably much higher than those in the carbonate rocks (Johannesson et al., 1997a). The shale-



normalized REE patterns (Fig. 3.6) for six volcanic rocks are almost identical. All six volcanic rock samples show fairly strong LREE or slight HREE enrichments [ $(Yb/Nd)_{SN}$  ratios from 0.64 to 1.55], with strong negative Eu anomalies ( $Eu/Eu^*$  ratios from  $-0.67$  to  $-0.22$ , Table 1) and no Ce anomalies in their shale-normalized REE patterns (Fig. 3.6).

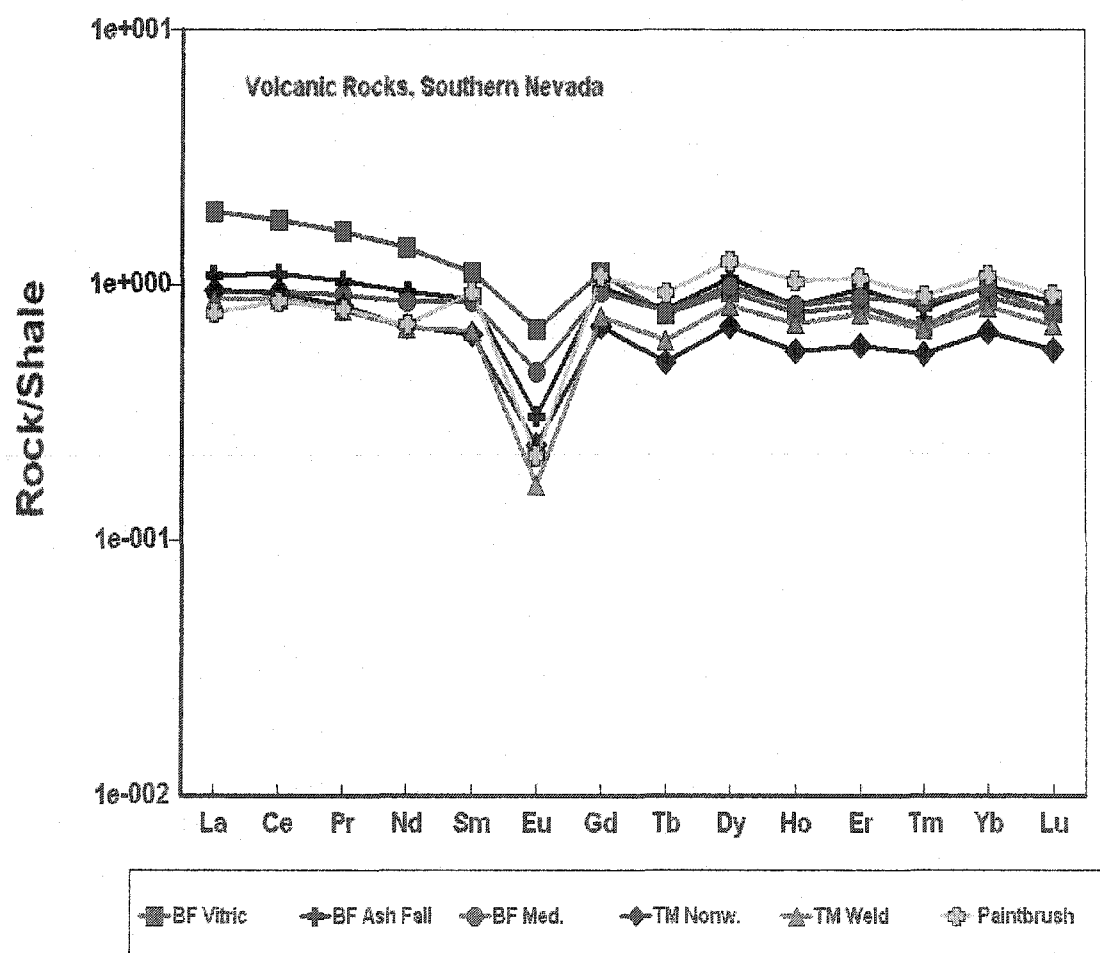


Fig. 3.6. Shale-normalized REE patterns for felsic volcanic rocks from the NTS, Nevada (Johannesson et al., 1997a).

#### 3.4.1.4. Average REEs in Local Rocks

The 36 rock samples in this study represent the three major aquifer-bearing rock types in southern Nevada. The REE data in these rock samples indicate that different types of rocks have their own distinctive REE signatures. However, the same type of rock exhibits a similar REE concentration and shale-normalized pattern. Therefore, it is statistically rational to compute average REE concentrations for each type of rock with more REE data available from local rocks to which groundwaters from this region can normalize.

Table 3.2 presents the average REE concentrations,  $(Yb/Nd)_{SN}$  ratios, and  $Ce/Ce^*$  and  $Eu/Eu^*$  ratios for three types of aquifer rocks (dolomite, limestone, and volcanic rocks) in southern Nevada. They were computed by averaging REE concentrations of 25 dolomite and dolomitic limestone samples, 5 limestone samples, and 6 felsic volcanic samples, respectively.

The shale-normalized REE patterns for the average dolomite, limestone, and volcanic rocks in southern Nevada are shown in Fig. 3.7. Three distinctive REE patterns can easily be recognized. Dolomite exhibits a flat shale-normalized pattern with a slight HREE enrichment [ $(Yb/Nd)_{SN} = 1.10$ ] and no obvious Ce and Eu anomalies. Limestone shows a seawater-like, shale-normalized REE pattern with a fairly strong HREE enrichment [ $(Yb/Nd)_{SN} = 1.54$ ], a strong negative Ce anomaly ( $Ce/Ce^* = -0.34$ ), and a weak Eu anomaly ( $Eu/Eu^* = 0.03$ ). In contrast to the two types of carbonate rock, volcanic rock is slightly enriched in LREE [ $(Pr/Yb)_{SN} = 1.11$ ] with a strong negative Eu anomaly ( $Eu/Eu^* = -0.42$ ) and no Ce anomaly. Concentrations of REEs in volcanic rocks

are one order of magnitude higher than those in carbonate rocks (Table 3.2).

Table 3.2. Average REE concentrations (ppm) in three types of local rocks, southern Nevada. SN = shale-normalized.

	Dolomite	Limestone	Volcanic
<b>La</b>	3.09	2.72	44.96
<b>Ce</b>	6.51	2.28	90.36
<b>Pr</b>	0.72	0.45	10.12
<b>Nd</b>	2.70	1.73	33.38
<b>Sm</b>	0.52	0.32	6.39
<b>Eu</b>	0.11	0.10	0.55
<b>Gd</b>	0.51	0.43	5.88
<b>Tb</b>	0.08	0.06	0.90
<b>Dy</b>	0.49	0.38	5.27
<b>Ho</b>	0.11	0.10	1.06
<b>Er</b>	0.31	0.28	3.19
<b>Tm</b>	0.04	0.04	0.47
<b>Yb</b>	0.30	0.24	3.17
<b>Lu</b>	0.04	0.04	0.47
<b>(Yb/Nd)<sub>SN</sub></b>	1.10	1.54	1.03
<b>Ce/Ce*</b>	0.01	-0.34	0.02
<b>Eu/Eu*</b>	-0.02	0.03	-0.42

$$\text{Ce/Ce}^* = \log \{2\text{Ce}_{\text{SN}}/[\text{La}_{\text{SN}} + \text{Pr}_{\text{SN}}]\}.$$

$$\text{Eu/Eu}^* = \log \{2\text{Eu}_{\text{SN}}/[\text{Sm}_{\text{SN}} + \text{Gd}_{\text{SN}}]\}.$$

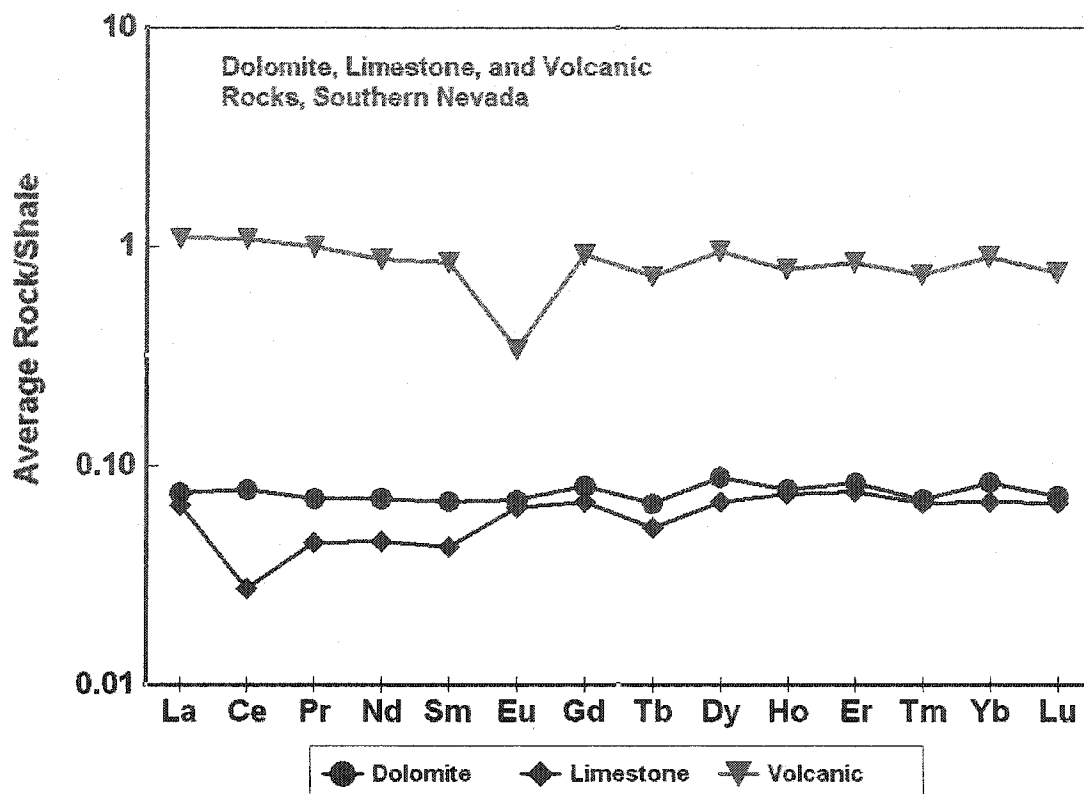


Fig. 3.7. Shale-Normalized REE patterns for average dolomite, limestone, and volcanic rocks in southern Nevada. Note: the average REE concentrations were computed based on the REE data from dolomite, limestone, and volcanic rock samples analyzed in this study.

### 3.4.2. REEs in Groundwaters

Concentrations (in pmol/kg) of the REEs in groundwaters from southern Nevada and eastern California, which are discussed in this study, are presented in Table 3.3.

Many springs and wells were sampled more than once, such as the springs and wells in Ash Meadows, Furnace Creek, Amargosa Valley, Spring Mountains, and Pahranaagat Valley. The geochemical data of these groundwaters were fairly consistent for multiple

Table 3.3. REE concentrations (pmol/kg) in groundwaters from southern Nevada and Death Valley, CA.  
SN = shale-normalized

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Yb/Nd) <sub>SN</sub>	Ce/Ce*	Eu/Eu*
Army*	8.39	17.48	2.19	9.08	1.87	0.28	1.77	0.32	1.45	0.39	1.19	0.18	0.83	0.17	1.18	0.00	-0.18
Ash Meadows*	27.17	48.17	6.62	26.67	5.40	1.05	5.63	0.82	4.65	1.05	3.07	0.48	3.00	0.53	1.46	-0.05	-0.10
Furnace Creek*	38.67	67.67	6.77	26.67	5.30	1.03	5.50	0.77	4.17	0.83	2.47	0.37	2.40	0.40	1.17	0.01	-0.09
Amargosa*	9.40		2.41	7.77	1.50	0.45	1.31	0.20	1.30	0.38	1.23	0.18	0.98	0.15	1.64	-0.04	0.13
Spring Mtns.*	21.37	4.60	3.61	16.29	4.64	1.28	6.02	0.96	5.69	1.44	4.33	0.57	3.58	0.58	2.86	-0.90	0.00
Pahranagat*	6.21	3.13	0.75	3.20	0.83	0.18	0.73	0.11	0.71	0.18	0.68	0.13	0.69	0.13	2.82	-0.47	0.00
Cane*	141.12	157.79	39.05	178.10	40.93		44.59	14.78	64.99	16.97	46.35	6.51	52.20	7.41	3.81	-0.28	-0.07
Tippipah*	2322.0	5053.0	468.6	1575.5	395.9	31.1	280.3	45.3	141.0	30.3	84.3	11.8	81.2	12.5	0.67	0.07	-0.40
Topopah*	1008.0	3213.0	234.3	863.1	181.2	17.9	184.7	32.1	190.0	36.4	138.5	18.4	124.7	20.5	1.88	0.21	-0.39
1S Zone1	30.88	32.77	2.84	11.27	2.19	0.06	3.96	0.77	6.52	2.09	8.19	1.51	10.73	2.13	12.37	-0.12	-1.13
9S Zone1	96.47	146.30	15.24	53.02	10.72	1.30	13.44	1.85	10.45	2.31	6.77	0.95	5.27	0.88	1.29	-0.04	-0.35
9S Zone2	44.31	61.23	5.88	21.10	4.07	0.53	5.24	0.81	5.24	1.30	4.07	0.60	3.96	0.65	2.44	-0.05	-0.32
9S Zone3	29.26	41.09	4.08	14.48	3.24	0.21	4.40	0.72	4.68	1.21	4.06	0.63	4.23	0.70	3.79	-0.05	-0.64
9S Zone4	29.08	43.41	7.06	25.24	5.13	0.16	6.56	1.05	6.72	1.59	5.04	0.82	5.04	0.80	2.59	-0.13	-0.96

$Ce/Ce^* = \log \{ 2Ce_{SN}/[La_{SN} + Pr_{SN}] \}.$

$Eu/Eu^* = \log \{ 2Eu_{SN}/[Sm_{SN} + Gd_{SN}] \}.$

\* Data from Johannesson et al., 2000.

sampling events at the same site. Therefore, the average REE concentrations were calculated and used for these springs (Table 3.3). The REE concentrations for these springs and wells were previously reported (Johannesson et al., 1997a, b; 2000). Wells 1S and 9S, with multiple zones (such as Zone1 through Zone2 at well 9S), are located on the southwest slope of the NTS and along the northeast side of Highway 95. As two of many newly-developed monitoring wells for the Nye County Early Warning Drilling Program (NCEWDP), 1S and 9S have been sampled periodically since 1999. The REE data for these two wells listed in Table 3.3 were from samples collected in May 1999.

Concentrations of the REEs in these groundwaters are substantially variable, ranging from  $< 20$  pmol/kg to  $>10,000$  pmol/kg for the TREE concentrations (Table 3.3). Two springs (Tippipah and Topopah Springs), located at the base of the Shoshone Mountain on the NTS, have the highest REE concentrations (1576 pmol/kg and 863 pmol/kg for Nd, respectively), followed by Cane Springs (178 pmol/kg for Nd) and well 9S Zone1 (53 pmol/kg for Nd). The springs in Pahrnagat Valley have the lowest REE concentrations (3.2 pmol/kg for Nd). Army Well and Amargosa Desert groundwaters have similar REE concentrations (9 pmol/kg and 8 pmol/kg for Nd, respectively). Groundwaters from Ash Meadows and Furnace Creek also show similarities in REE concentrations (both with 27 pmol/kg for Nd). In addition, groundwaters from Army Well, Amargosa Desert, Spring Mountains, and Pahrnagat Valley exhibit REE concentrations that are similar in magnitude to seawater values (Elderfield and Greaves, 1982; Elderfield, 1988; Bertram and Elderfield, 1993).

Based on different REE signatures, groundwaters in the springs and wells in

southern Nevada and eastern California were previously classified into “carbonate” groundwaters and “volcanic” groundwaters (Johannesson et al., 1997a, 2000), which represent groundwaters from the carbonate aquifer and the volcanic aquifer, respectively. The carbonate groundwaters have relatively low concentrations of REEs (up to two orders of magnitude lower than volcanic aquifer groundwaters) and show a flat or HREE-enriched pattern after shale-normalization. Also, the carbonate groundwaters, unlike the volcanic groundwaters, have more diverse shale-normalized REE patterns. In addition, some of these groundwaters appear to be mixtures of two or more types of waters from different aquifers (Winograd and Thordarson, 1975; Johannesson et al., 1997b, 2000; Stetzenbach et al., 2001).

However, more studies of REE signatures from different groundwaters in southern Nevada and eastern California, along with more REE data from local aquifer rocks, led us to believe that the “carbonate” groundwaters can be further divided into two groups: “dolomite” groundwaters and “limestone” groundwaters, which discharge from the Lower Paleozoic carbonate (mainly dolomite and dolomitic limestone) aquifer and the Upper Paleozoic carbonate (limestone) aquifer, respectively. Carbonate (both dolomite and limestone) rocks widely occur in southern Nevada and eastern California. They compose the major hydrolithological units in the regional groundwater aquifers in southern Nevada.

Three types of groundwaters are recognized in this study based on the REE signatures and the shale-normalized patterns in these groundwaters: dolomite, limestone, and (felsic) volcanic groundwaters. These three types of groundwaters represent the end-

members of groundwaters from three different types of aquifers. Mixings of any two or three types of groundwaters are common hydrogeological processes in southern Nevada and eastern California, especially in the areas where abundant faults occur and elevated hydraulic heads form (Fridrich et al., 1994; Stuckless et al., 1991; Geldon, 1993; Stetzenbach et al., 2001).

“Dolomite” groundwaters, such as those from Ash Meadows, Furnace Creek (Death Valley), Army Well, and Amargosa Desert (Fig. 3.1), have no (or slightly negative) Ce anomalies and possibly minor negative or positive Eu anomalies (Fig. 3.8).

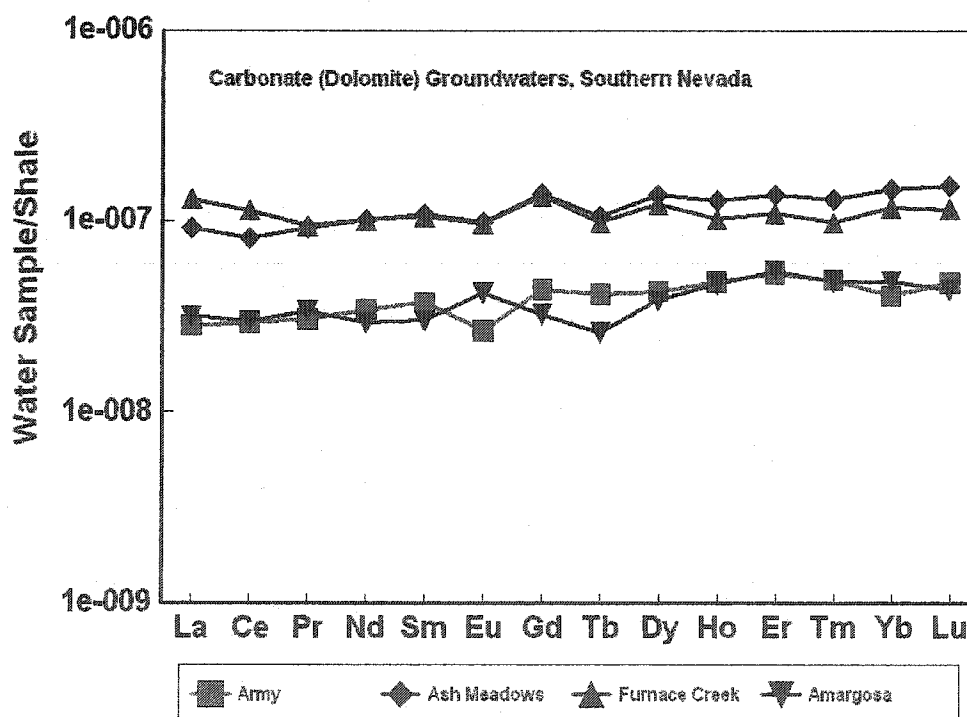


Fig. 3.8. Shale-normalized REE patterns for groundwaters from springs and wells in Army, Ash Meadows, Furnace Creek, and Amargosa Desert, southern Nevada and eastern California.



The shale-normalized REE patterns of these groundwaters are fairly flat, although slight enrichments of HREEs are observed. The patterns are similar to those from dolomite rocks (Figs. 3.2 - 3.4). Concentrations of the REEs in groundwaters from ash Meadows and Army Well are similar to those from Furnace Creek and Amargosa Desert, respectively.

“Limestone” groundwaters, including groundwaters from the Spring Mountains, Pahranaagat Valley, and Cane Spring on the NTS (Fig. 3.1), have strong negative Ce anomalies, substantial shale-normalized HREE enrichments, and minor Eu negative anomalies (Fig. 3.9) that closely resemble those in limestone rocks (Fig. 3.5) and those of

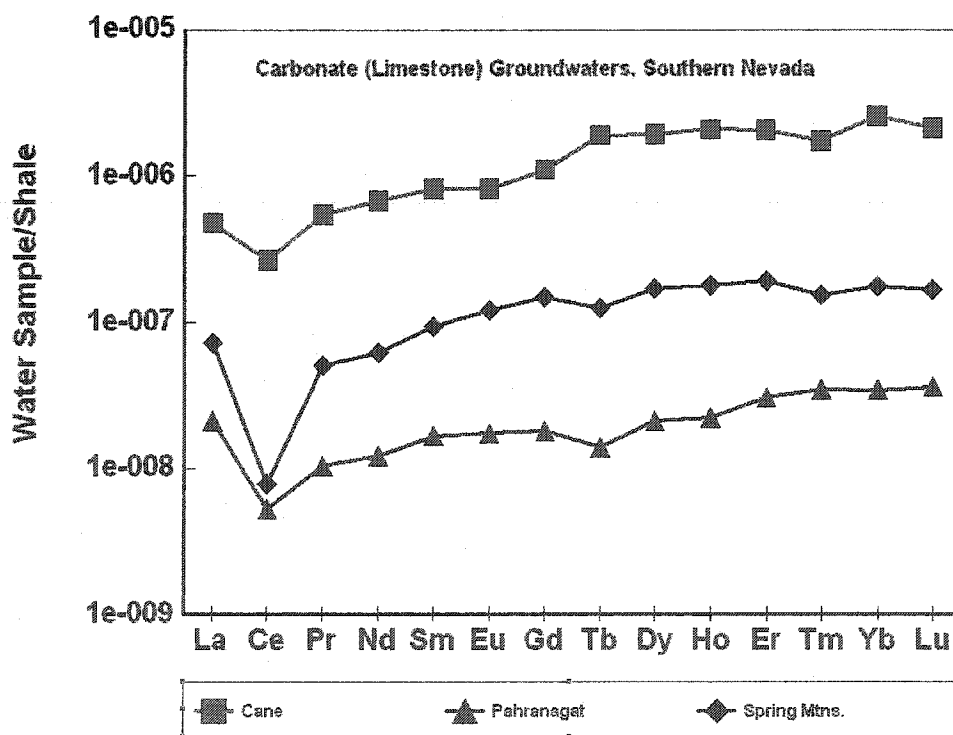


Fig. 3.9. Shale-normalized REE patterns for groundwaters from Cane Spring at the NTS and springs in Pahranaagat Valley and the Spring Mountains, southern Nevada.

seawater (Fleet, 1984). Other studies of carbonate groundwaters from southern Nevada and eastern California (Death Valley) also demonstrated remarkable similarities between groundwater trace element concentrations and those of modern seawater (e.g., Hodge et al., 1996, 1998). REE concentrations in groundwaters from Pahrnagat Valley and the Spring Mountains are much lower than those from Cane Spring.

“Volcanic” groundwaters, including groundwaters from Tippipah and Topopah springs on the Nevada Test Site and the NCEWDP wells (1S Zone 1 and 9S Zone1 - 4), exhibit distinctive LREE or HREE enrichments and substantial negative Eu anomalies for their shale-normalized patterns (Fig. 3.10); however, they do not exhibit Ce anomalies.

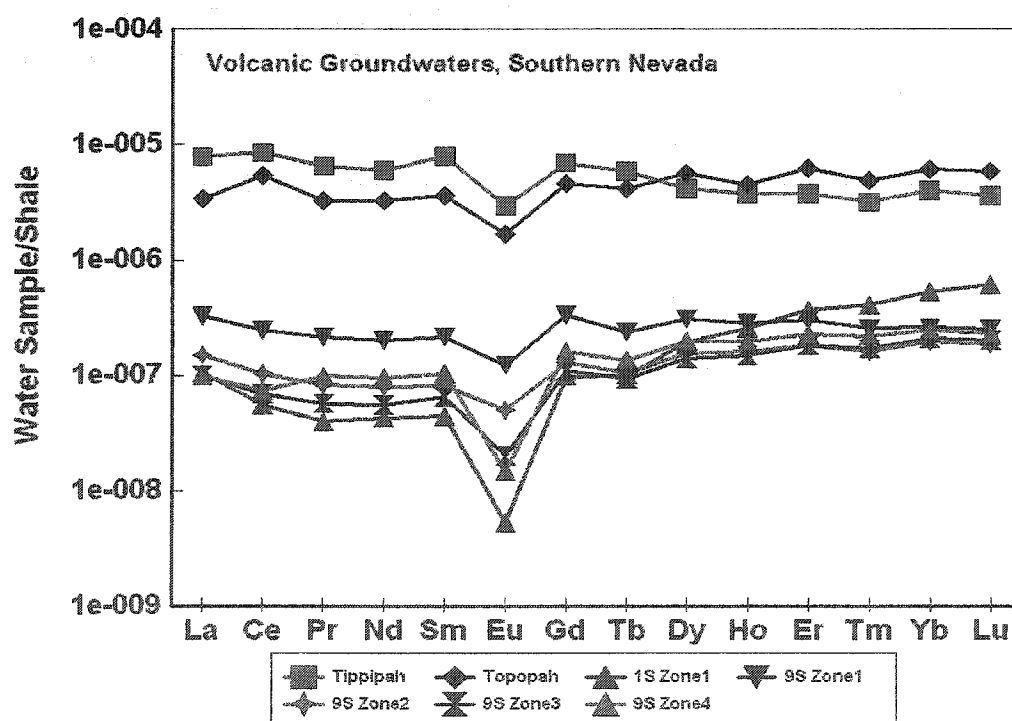


Fig. 3.10. Shale-normalized REE patterns for groundwaters from Tippipah and Topopah Spring at the NTS and from the Nye County Early Warning Drilling Program (NCEWDP) wells (1S and 9S), southern Nevada.

Compared to the shale-normalized REE patterns in volcanic rocks (Fig. 3.6), some volcanic groundwaters (e.g. 1S Zone 1) exhibit stronger HREE enrichments (Fig. 3.10).

#### 3.4.3. REE Normalization Using Local Rock Data

The average REE data from different rock types (Table 3.2) can be used as local rock standards to which REE concentrations in groundwaters from southern Nevada and eastern California can be normalized. Previous investigators commonly normalized the measured REE concentrations to the average shale (e.g., NASC) REE values to study relative fractionations of REEs in natural waters. This approach is warranted if the aquifer material in the groundwater system is primarily composed of siliciclastic sedimentary rock such as shale, but it is inappropriate for other groundwater systems that are composed of non-siliciclastic sedimentary rocks. Therefore, some researchers recently have used upper continental crustal REE values to normalize REE concentrations in natural waters (Ojiambo et al., 2003; Johannesson et al., 2004). However, REE data from local rocks of which the aquifer material is composed will be more appropriate to fit this purpose. The saturated zone and the unsaturated zone in southern Nevada aquifers are mainly composed of carbonate (dolomite and limestone) and felsic volcanic (tuffaceous) rocks (i.e., Winograd and Thordarson, 1975; Stuckless and Dudley, 2002), so local rock-based REE standards, or average REE concentrations of these local and representative aquifer rocks, are more appropriate.

REE signatures in groundwaters should resemble the rocks of which the aquifer material is composed. Normalizing REE concentrations in a specific type of groundwater

to those in a corresponding type of rock (e.g., dolomite groundwater normalized to dolomite rock) should produce a flat and smooth pattern if groundwaters proportionally inherit REE signatures from rocks. Otherwise, the variations in the patterns indicate REEs in groundwaters were fractionated (LREE or HREE enrichments) relative to those in rocks during water/rock interaction. On the other hand, groundwater-mixing processes add more complexity to the fractionations of REEs.

REE concentrations of three types of groundwaters were normalized to the average REE concentrations (Table 3.2) in dolomite, limestone, and volcanic rocks, respectively (Figs. 3.11 - 3.13) to verify the similarities of REE in both groundwaters and rocks. When “dolomite” groundwaters from Ash Meadows, Furnace Creek (Death Valley), Army Well, and Amargosa Desert are normalized to the average dolomite (Lower Paleozoic) rock, relatively flat patterns with no or very weak Ce and Eu anomalies are observed (Fig. 3.11), especially in groundwaters from Army Well and Furnace Creek [ $(Yb/Nd)_{SN}$  ratios  $\cong 1$ ]. Groundwaters from Ash Meadows and Amargosa Desert exhibit weak HREE enrichments [ $(Yb/Nd)_{SN}$  ratios = 1.23 and 1.38, respectively]. However, when “limestone” groundwaters from the Spring Mountains, Pahranaagat Valley, and Cane Spring are normalized to the average limestone (Upper Paleozoic) rock, these groundwaters all show strong HREE enrichments [ $(Yb/Nd)_{SN}$  ratios = 1.90, 1.87, and 2.53, respectively] with no or weak Eu anomalies (Fig. 3.12). There is no Ce anomaly in groundwater from Cane Spring, a weak Ce anomaly in groundwater from Pahranaagat Valley, and a strong Ce anomaly in groundwater from the Spring Mountains,

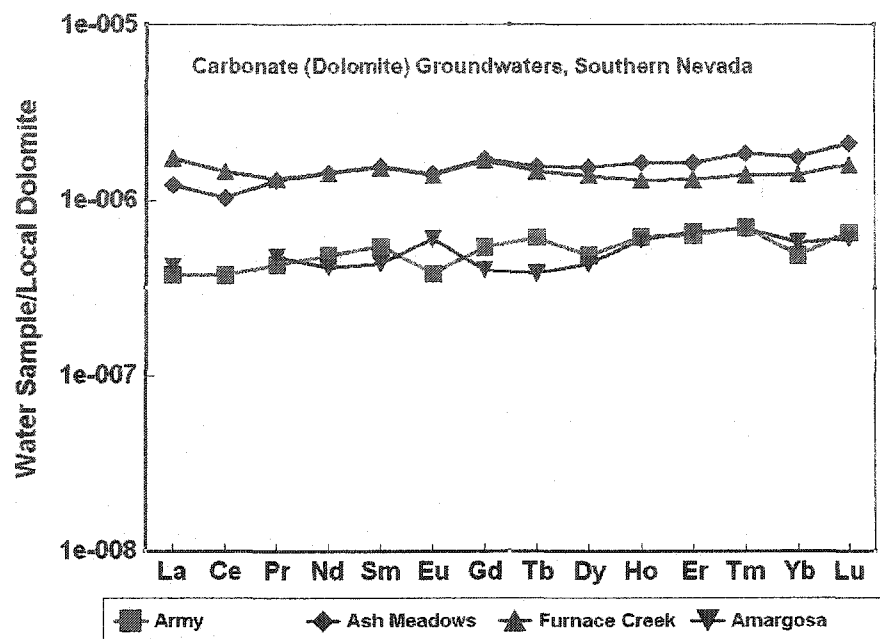


Fig. 3.11. Local dolomite-normalized REE patterns for dolomite groundwaters in southern Nevada and eastern California (their shale-normalized REE patterns are shown in Fig. 3.8).

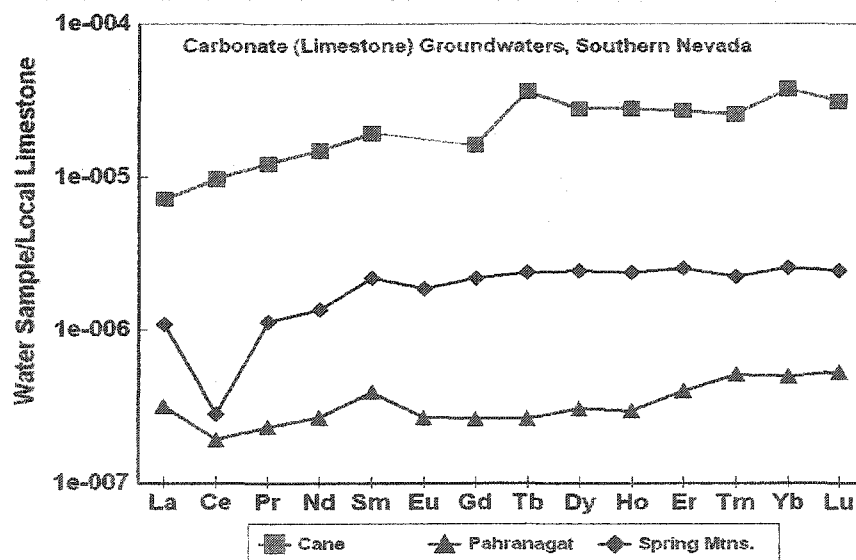


Fig. 3.12. Local limestone-normalized REE patterns for limestone groundwaters in southern Nevada (their shale-normalized REE patterns are shown in Fig. 3.9).

respectively (Fig. 3.12). Finally, when “volcanic” groundwaters from the NTS (Tippipah and Topopah springs) and the NCEWDP wells (1S Zone 1 and 9S Zone1 - 4) are normalized to the average volcanic rock, all groundwaters except those at Tippipah Spring show HREE enrichment patterns (Fig. 3.13). Interestingly, groundwaters from Tippipah and Topopah springs, 9S Zone1, and 9S Zone2 exhibit relatively smooth normalization patterns without noticeable negative Eu anomalies. The flat rock-normalization patterns indicate that these groundwaters are the end-member (perched) in the volcanic aquifer without mixing of other types of groundwaters. However, groundwaters from 1S Zone1, 9S Zone 3, and 9S Zone 4 still have strong negative Eu anomalies in their rock-normalized REE patterns (Fig. 3.13).

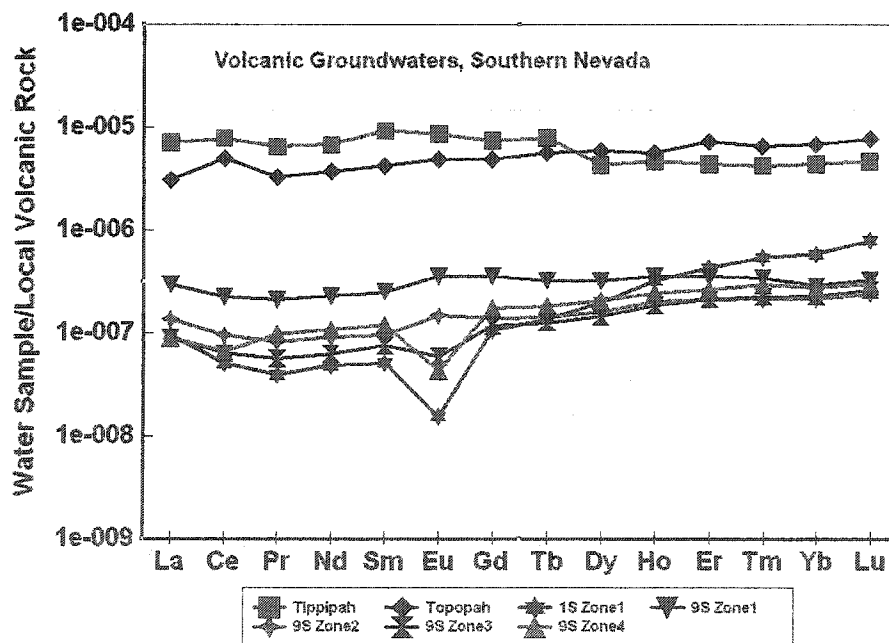


Fig. 3.13. Local felsic volcanic rock-normalized REE patterns for volcanic groundwaters in southern Nevada (their shale-normalized REE patterns are shown in Fig. 3.10).

#### 3.4.4. REE Fractionation Patterns

All groundwaters in this study show more or less HREE or LREE enrichments in their shale-normalized (Figs. 3.8 - 3.10) or local rock-normalized REE patterns (Figs. 3.11 - 3.13). However, groundwaters from the Lower (older) Paleozoic carbonate (dolomite) aquifer generally have less REE fractionation (HREE enrichment) than groundwaters from the Upper (younger) Paleozoic carbonate (limestone) aquifer. The shale-normalized Yb/Nd ratios (a measure of fractionation) in “dolomite” groundwaters are lower than those in “limestone” groundwaters (Table 3.3). Groundwaters from the volcanic aquifer have either HREE or LREE enrichments. Some volcanic groundwaters in the NCEWDP wells (1S Zone1 and 9S Zone2 - 4) are strongly enriched in HREE.

One explanation for the differences in the REE fractionations in groundwaters from southern Nevada and eastern California is aquifer rock through which these groundwaters flow. The REE data of representative aquifer rocks presented here strongly suggest that groundwaters inherit REE signatures from aquifer materials. When normalizing to the shale REE values, groundwaters and aquifer rocks through which groundwaters flow will demonstrate similar fractionation patterns.

Another explanation for the greater HREE enrichments “limestone” groundwaters compared to the younger Paleozoic carbonate aquifer rocks is the solution complexation reaction involving the REEs (Johannesson et al, 1996; 2000). The dissolved forms of REEs are dominated by carbonate complexes. Stability constants of the formation of REE carbonate complexes increase with increasing atomic number across the REE suite (e.g., Cantrell and Bryne, 1987; Millero, 1992; Lee and Bryne, 1993). Carbonate complexes of

the HREEs are more stable in solution than those of the LREEs. As a result, HREEs are enriched relative to LREEs in carbonate groundwaters.

The third explanation for enrichment of HREEs over LREEs in groundwaters compared to the younger Paleozoic carbonate rocks is related to preferential removal of LREEs to aquifer surface, which is governed by the REE solid-liquid partitioning coefficients ( $K_d$ ) (Benedict et al., 1997). The  $K_d$ 's for the carbonate rock materials are always greater than for the felsic volcanic rock materials. In addition, the  $K_d$ 's generally decrease with increasing atomic number across the REE suite (Benedict et al., 1997). Consequently, REEs have more chances to be absorbed by carbonate rocks or materials than by volcanic rocks or materials. HREEs have a weaker affinity for aquifer rock surface than the LREEs in both the carbonate- and felsic volcanic-rock aquifers of southern Nevada.

Finally, mixing of groundwaters from different aquifers also modifies REE concentrations, signatures, and REE fractionations. For example, two NCEWDP wells (1S and 9S) are typical volcanic groundwaters with strong negative Eu anomalies. However, groundwaters from several zones of two wells (1S Zone1 and 9S Zone2 - 4) exhibit strongly enriched in HREE. These fractionations may be due to the contribution of groundwaters from the carbonate (limestone) aquifer or groundwaters interacting with carbonate materials (including alluvium composed of fragments of these carbonate rocks). Another example is the groundwater from Cane Spring on the NTS, which mainly demonstrates REE signatures of "limestone" groundwaters with a negative Ce anomaly and HREE enrichment. However, groundwater in Cane Spring has much higher REE



concentrations (Table 3.3) and a less negative Ce anomaly than other carbonate groundwaters. Located between Tippipah and Topopah Springs and the Spring Mountains, Cane Spring waters are likely a mixture of volcanic groundwaters from Tippipah and Topopah springs and carbonate groundwaters from the Spring Mountains. Stetzenbach and others (2001) also suggested that Cane Spring waters are a mixture of predominantly regional carbonate groundwater and a lesser amount of local volcanic waters based on the PCA study on trace elements in these groundwaters.

### 3.5. Conclusions

Comparisons of the REE concentrations and behaviors in both groundwaters and aquifer rocks demonstrate that the shale-normalized REE patterns of the carbonate groundwaters and those of the volcanic rock groundwaters resemble the shale-normalized REE patterns of the respective rock types through which they flow. Carbonate groundwaters can be further distinguished into “dolomite” groundwaters discharging from the Lower Paleozoic carbonate (dolomite or dolomitic limestone) aquifer and “limestone” groundwaters discharging from the Upper Paleozoic carbonate (limestone) aquifer. Groundwaters from Army Well and Furnace Creek, from the Spring Mountains, and from Tippipah and Topopah springs represent the end-members of groundwaters from dolomite, limestone, and volcanic rock aquifer, respectively. REE signatures in groundwaters mimic those in the aquifer rocks with which these groundwaters interacted. Mixing of groundwater from different aquifers in various percentages also resulted in the modifications of REE signatures in groundwaters from springs and wells in southern

Nevada. Comparing and normalizing REE signatures in groundwater to those in the local aquifer rocks provide direct information for tracing groundwater sources and for understanding changes of REE signatures during rock/water interactions. The negative Ce and Eu anomalies are also correlative between groundwaters and aquifer rocks. In other words, these anomalies reflect the relative Ce and Eu concentration of the whole-rock samples.

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## CHAPTER 4

### RARE EARTH ELEMENT GEOCHEMISTRY OF SECONDARY MINERALS OCCURRING IN FRACTURES WITHIN AQUIFERS IN SOUTHERN NEVADA

#### 4.1. Abstract

A total of 26 secondary mineral samples (mainly calcite) were collected from the western Pahute Mesa-Oasis Valley (WPM-OV) and from underground tunnels (ESF and ECRB) at Yucca Mountain, southern Nevada. These samples were analyzed for their rare earth element (REE) concentrations using both ICP-MS and LA-ICP-MS. Different REE patterns in secondary minerals, along with other geological and geochemical data (such as petrographic, mineralogical, stable isotope, and fluid inclusion), suggest that the fracture-coating minerals were precipitated from groundwaters that originated from different sources over a long interval of geologic time. Such secondary minerals in fractures can precipitate either from groundwater percolating through the unsaturated zone, or from upwelling groundwater (both shallow perched and deep aquifer groundwater) with hydrothermal fluid influences, or a combination of these two origins. Mineral samples from different depths in the same borehole may have different origins. A comparative study was performed using ICP-MS and LA-ICP-MS to analyze the same mineral sample for its REE concentrations. The good correlation of the REE results

obtained from the two different analytical methods shows a great potential for LA-ICP-MS in high-precision spot analysis of rocks and minerals.

#### 4.2. Introduction

Secondary minerals precipitate from groundwater flowing through fractures, in both the unsaturated and saturated zones. The origin of fracture-coating minerals, mainly secondary calcite and silica, at the Nevada Test Site (NTS) has been debated for the past several years. Two competing hypotheses have been proposed to explain the origin of these secondary minerals. Based on extensive isotopic and mineralogical studies, one proposal indicates that the secondary minerals (mainly calcite and silica) in the unsaturated zone formed from meteoric water infiltrating through and dissolving components from the carbonate- and silica-rich soils and from the rocks along fracture flow paths (e.g., Szabo and Kyser, 1990; Peterman et al., 1992; Vaniman and Whelan, 1994; Whelan et al., 1994, 1998, 2002; Vaniman and Chipera, 1996; Marshall et al., 1998; Paces et al., 1998, 2001; Wilson et al., 2003). However, on the basis of fluid inclusions in calcite coatings, an alternative proposal attributes these secondary minerals to upwelling hydrothermal fluids that occasionally rose far above the normal water table, flooding the unsaturated zone, and even discharging at the surface (Hill et al., 1995; Dublyansky and Szymanski, 1996; Stuckless et al., 1998; Hill and Dublyansky, 1999; Dublyansky et al., 2001). These fluid inclusion studies have indicated that the depositional temperatures of calcite coatings ranged from 35 to 85<sup>0</sup>C, which is higher than modern ambient temperatures at Yucca Mountain. Meanwhile, numerous studies

have demonstrated that secondary minerals exhibit a variety of distinctly different chemical and isotopic signatures which are generally correlated to different zones in the hydrostratigraphic column (e.g., Peterman et al., 1992; Whelan and Stuckless, 1992; Vaniman, 1993, 1994; Paces et al., 1996; Denniston et al., 1997; Rose et al., 1998; Vaniman et al., in press). For example, calcite in the upper unsaturated zone may have a different signature than those in the deep saturated zone, with regard to minor and trace elements and isotopic ratios. Therefore, it is not impossible for secondary minerals within fractures or cavities in different zones to have different origins.

Whether the secondary minerals in fractures formed from percolating meteoric water or from upwelling groundwater or hydrothermal fluid, they record geochemical changes and the history that occurred in the paleo-groundwater that flowed through the fractures (Wallin and Peterman, 1999; Lee et al., 2003). Therefore, further study of the origins of these secondary minerals at Yucca Mountain and elsewhere in southern Nevada will provide crucial information for evaluating hydrogeologic changes and the fate of the future nuclear waste repository.

Rare earth elements (REEs), a special group of trace elements, and some other trace elements may play an important role in tracing groundwater flow. With their unique and chemically coherent property, REEs have spawned considerable interest in their behavior in geologic processes. Because of their size and valance, REEs exhibit distinctive chemistry as compared to their nearest neighbors (barium and hafnium) in the periodic table. Also, the systematic decrease in ionic radius with increasing atomic number, within the lanthanide suite, imparts predictable chemical differences that can

record subtle geochemical processes in natural systems. Consequently, REEs have been used extensively as sensitive tracers of geochemical processes in rock and seawater studies (e.g., Hanson, 1980; Elderfield and Greaves, 1982; DeBaar et al., 1983; Cullers and Graf, 1984). Recent studies of trace elements and REEs in groundwater systems (e.g., Smedley, 1991; Fee et al., 1992; Gosselin et al., 1992; Stetzenbach et al., 1994, 1999, 2001; Kreamer et al., 1996; Hodge et al., 1996, 1998; Johannesson et al., 1997, 1999, 2000; McCarthy et al., 1998) have shown promising results in the tracing of groundwater sources and the prediction of groundwater flow paths. These studies indicate that groundwaters and some surface waters can inherit their REE and trace element signatures from the rocks or aquifer materials with which they interact. Therefore, understanding the geochemistry of REEs and other trace elements in groundwaters is important not only for tracing groundwater flow, but also for investigating water/rock interactions.

Previous studies have indicated that REE and other trace elements in fractured zones can be changed with the hydrogeochemical state of the groundwater. The chondrite- and local rock-normalized REE patterns can be used as a good indicator of groundwater environment changes in fractured rock systems (aquifers) (Johannesson et al., 2000; Lee et al., 2003). REE and other trace element geochemical analyses in individual samples of secondary minerals from Yucca Mountain and adjacent areas (Pahute Mesa) will greatly help us understand the origin of these secondary minerals, including the source of the mineral-precipitating water, water chemistry, water/rock interaction, crystallization mechanism, and mineral growth phases. When combined with other geochemical studies, such as isotopic and fluid inclusion studies, REE and other

trace element analyses of secondary minerals also provide geochemical evidence of the paleohydrologic history and the history of groundwater movement in the region, which is critical information for risk assessments of radioactive waste at the NTS and Yucca Mountain.

#### 4.3. Hydrogeologic Setting

Geologically, the study area belongs to the Basin and Range Province. The geology of the study area contains more than 11,000 m of sedimentary rocks ranging from Precambrian through Paleozoic, which were mainly formed in marine environments. Overlying the Precambrian and Paleozoic rock interval are approximately 4000 m of Tertiary volcanic rocks of the Timber Mountain-Oasis Valley caldera complex. The volcanic rocks are overlain by Quaternary basin-fill alluvial and lacustrine deposits (Winograd and Thordarson, 1975). The complete rock and sediment sequence with 29 formations in southern Nevada has been grouped into 10 hydrogeologic units, including 6 aquifers and 4 aquitards (Winograd and Thordarson, 1975). The lower Paleozoic (i.e., Cambrian through Devonian) regional carbonate aquifer (locally up to 4600 m thick) and the basin-fill aquifer have the widest areal distribution and are the two principal aquifers in the region (Winograd and Thordarson, 1975; Dudley and Larson, 1976; Winograd and Pearson, 1976; Claassen, 1985). These units are the focus of this study. The Tertiary volcanic aquifers, which mainly occur in the NTS and the Yucca Mountain region, and the upper Paleozoic (Pennsylvania through Permian) carbonate aquifer are also identified as important groundwater-bearing units in some areas

(Winograd and Thordarson, 1975; Dettinger, 1989; Peterman et al., 1992; Fridrich et al., 1994; Stuckless and Dudley, 2002). Groundwater is stored and transmitted in these aquifers chiefly through secondary openings developed along fractures.

Many hydrogeologic and geochemical studies suggest that groundwaters of the lower carbonate aquifer of southern Nevada represent complex mixtures of groundwaters recharged in different regions and through different aquifers, including through-flow of the regional carbonate aquifer as far north as the mountain ranges of central Nevada (Winograd and Thordarson, 1975; Dettinger et al., 1995; Davisson et al., 1999), recharge from the Spring Mountains, and recharge from Tertiary volcanic rocks on the NTS (Winograd and Friedman, 1972; Winograd and Thordarson, 1975; Dudley and Larson, 1976; Winograd and Pearson, 1976; Cowart, 1979; Osmond and Cowart, 1982; Dettinger, 1989; Farmer, 1996; Thomas et al., 1996; Stuckless and Dudley, 2002). Figure 4.1 is a schematic, hydrogeologic cross-section of the NTS/Yucca Mountain region showing the major three aquifers and the general groundwater flow directions in southern Nevada (from Stetzenbach et al., 2001).

#### 4.4. Methodology

##### 4.4.1. Sample Collection

A total of twenty-six secondary mineral samples were collected and analyzed for this study. Of them, seventeen samples were collected from archived cores and cuttings of eleven different drill holes (PM-2, PM-3, UE-18t, U-19AR, U-20AS, ER-EC-4, ER-EC-6, ER-EC-8, ER-18-2, ER-30-1, and ER-OV-3a) on the western Pahute Mesa-Oasis

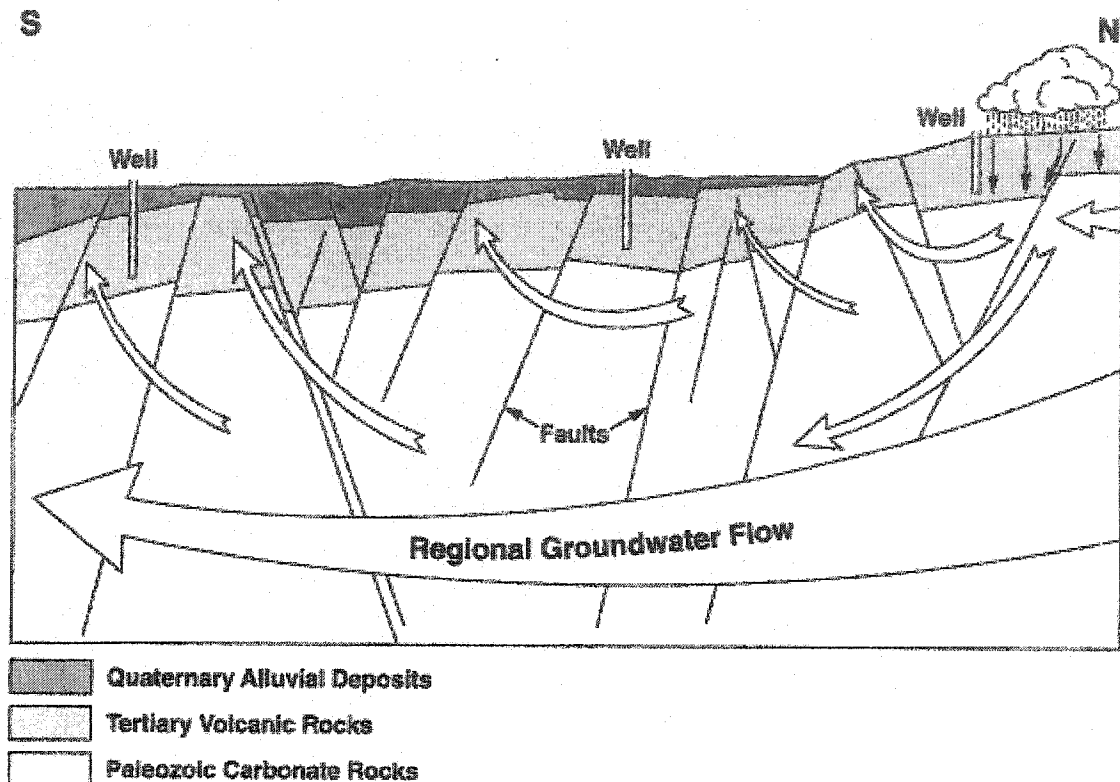


Fig. 4.1. Schematic hydrogeologic cross-section showing three aquifers (basin-fill, volcanic, and regional carbonate) in southern Nevada (from Stetzenbach et al., 2001).

Valley (WPM-OV) region, and nine samples were collected from eight locations of the Exploratory Studies Facilities (ESF) and the enhanced characterization of the repository block (ECRB) cross drift at Yucca Mountain, Nevada (ESF28+81, ESF59+87, ESF60+52.5, ESF 74+03, ESF78+05.2, ESF 78+41, ECRB07+40.5, and ECRB12+90). The sample locations for this study are shown in Figure 4. 2.

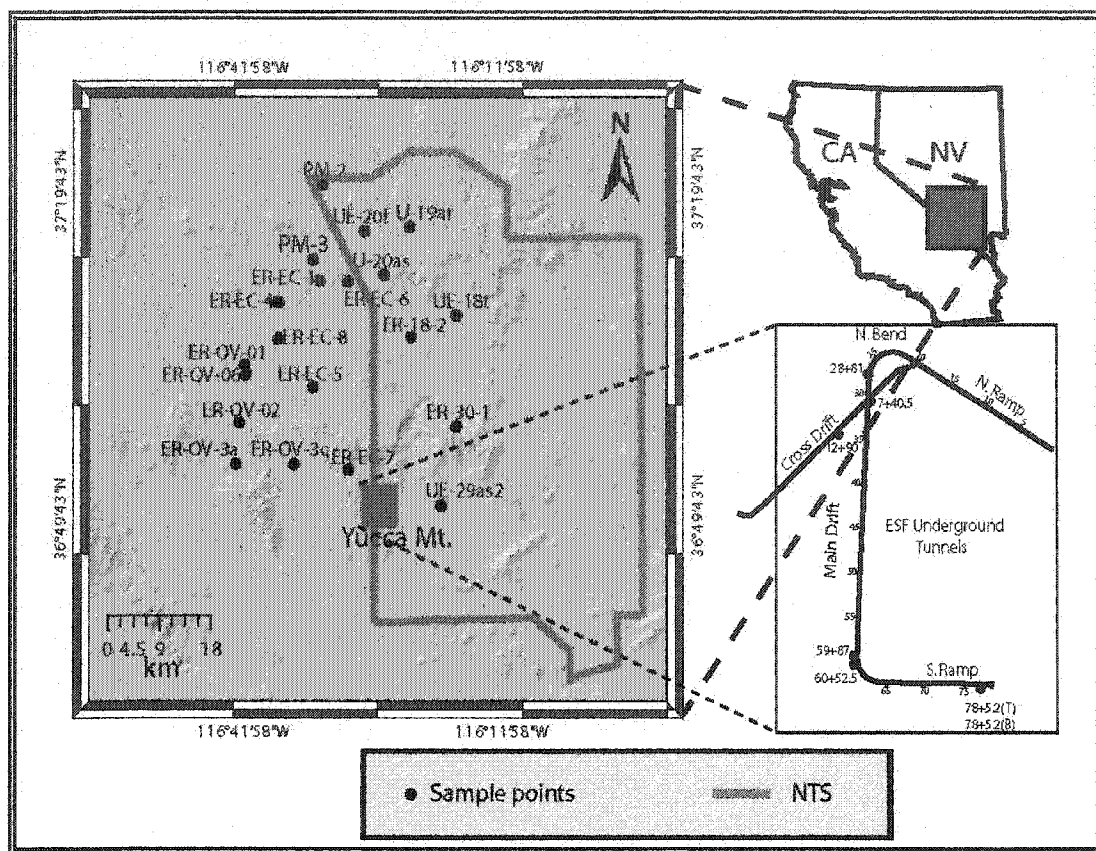


Fig. 4.2. Map of southern Nevada showing the study area and the sample locations in the western Pahute Mesa and Oasis Valley (WPM-OV) and in the ESF and ERCB at Yucca Mountain.

The mineral sampling depth in eleven boreholes in the WPM-OV varies from the upper unsaturated zone (~ 170 ft) to the deep saturated zone (> 8000 ft). Sample information, including drill hole identification, depths to groundwater tables, sampling intervals, lithostratigraphic units, hydrostratigraphic units, and brief sample descriptions, are summarized in Table 4.1. In addition, detailed petrographic descriptions and isotopic analyses of these samples can be found in technical reports by IT Corporation (1998) and



Table 4.1. Descriptions of the secondary mineral samples collected from the WPM-OV and Yucca Mountain, Nevada.

Drill Hole	Standing Water Level (ft below ground surface)	Depth Intervals Sampled (ft below ground surface)	Lithostratigraphic Unit	Hydrostratigraphic Unit	Characteristic Mineral Assemblage
PM-2	852	320	Thirsty Canyon Group	Timber Mountain Aquifer	calcite and botryoidal
			Spearhead Tuff	Vitric tuff aquifer	opaline silica
		5893	Volcanics of Quartz Mountain	Basal Aquifer	quartz, calcite, chlorite,
			Rhyodacite to Dacite Flows	lava flow aquifer	illite/smectite, and hematite
		8050	Volcanics of Quartz Mountain	Basal Aquifer	quartz, calcite, feldspar,
			Rhyodacite to Dacite Flows	lava flow aquifer	chlorite, epidote, and pyrite
PM-3	1457	1790-1810	Basalt of U-19ac	Upper paintbrush Confining Unit	calcite
		2860-2870	Basaltic Lavas of UE-19e	Calico Hills Confining Unit	calcite
UE-18t	916	1378	Timber Mountain Group	Timber Mountain Aquifer	calcite with a mixture of
			Ammonia Tanks Tuff	Vitric tuff aquifer	smectite and opaline silica
		2020	Timber Mountain Group	Timber Mountain Aquifer	calcite with weakly
U-19ar	2119		Rainier Mesa Tuff	Welded tuff aquifer	iron-stained clay
		173	Thirsty Canyon Group	Timber Mountain Aquifer	calcite as fine grained
			Pahute Mesa Tuff	Vitric tuff aquifer	disseminations
		1560	Timber Mountain Group	Timber Mountain Aquifer	calcite as fine grained
			Pool Member	Vitric tuff aquifer	disseminations

Table 4.1. (continued)

U-20as	2010	290-330	Timber Mountain Group Ammonia Tanks Tuff	Timber Mountain Aquifer Vitric tuff aquifer	calcite as cement-like impregnations
		1150-1160	Trachyte of Ribbon Cliff	Basal Aquifer lava flow aquifer	chalcedony, clays, calcite
ER-EC-4	749	2210-2220	Timber Mountain Group Ammonia Tanks Tuff	Timber Mountain Aquifer Welded tuff aquifer	chachedony, Mn-Fe- oxides, with minor smectite
ER-EC-6	1426	3420-3440	Pahute Mesa lobe of Topopah Spring Tuff	Timber Mountain Aquifer Welded tuff aquifer	smectite, chlorite, chachedony
ER-EC-8	323	1850-1870	Timber Mountain Group Mafic-poor Ammonia Tanks Tuff	Timber Mountain Aquifer Welded tuff aquifer	REE-bearing carbonate calcite and quartz
ER-EC-18-2	1213	2050-2080	Timber Mountain Group Mafic-rich Ammonia Tanks Tuff	Timber Mountain Aquifer Welded tuff aquifer	calcite and Fe-Mn-oxides
ER-30-1	451	750-760	Rhyolite of Chuker Canyon	lava flow aquifer	calcite
ER-OV-3a	57	20	Alluvium	Alluvial Aquifer	calcite
ESF28+81					Early Stage: calcite (anhedral crystals and stubby blades)
ESF59+87			Paintbrush Group:		Intermediate Stage: calcite
ESF60+52.5	1600 ~ 2300	950 ~ 1000	Tiva Canyon Tuff PTn	Welded tuff aquifer	and less opal
ESF78+05.2(T)					Late Stage: clear and sparry
ESF78+05.2(B)			Topopah Spring Tuff		calcite and opal
ECRB07+40.5					
ECRB12+90					

Note: Data from IT Corporation (1998) and Benedict and others (2000).

Benedict and others (2000).

The ESF at Yucca Mountain is a 7.6 m (24.5 ft) diameter, 7.8 km (4.8 miles) long C-shaped tunnel. It was excavated through the Tiva Canyon Tuff, PTn, and Topopah Spring Tuff to allow direct studies on the volcanic stratigraphy. The ECRB at Yucca Mountain, approximately 15 m (50 ft) above the repository horizon, is a smaller and 2.7 km (1.7 miles) long side tunnel. It was constructed to further examine the Topopah Spring Tuff and the Solitario Canyon fault zone. The unsaturated zone at Yucca Mountain extends from the surface to depths of 500 to 700 m (1600 to 2300 ft), where the water table is encountered and the saturated zone begins. The future repository horizon is approximately 300 m (985 ft) below the surface and 200 to 400 m (650 to 1300 ft) above the water table.

Unlike archived cores and cuttings, the mineral samples at Yucca Mountain were directly collected from the underground tunnels. Starting in 1995, more than 300 secondary mineral samples were collected from the ESF and ECRB tunnels to help reconstruct the Quaternary paleohydrology of the unsaturated zone. Detailed studies of fluid inclusions within secondary minerals in the unsaturated zone at Yucca Mountain were recently conducted by researchers at the Department of Geoscience at the University of Nevada, Las Vegas (UNLV) and the U.S. Geological Survey (USGS) (Whelan et al., 2002; Wilson et al., 2003).

#### 4.4.2. Analysis of REEs Using ICP-MS

The REEs were measured in 24 (not in ESF 77+03 and ESF 78+41) secondary

mineral samples using inductively coupled plasma mass spectrometry (ICP-MS) (Perkin-Elmer® Elan 5000). The sample preparations and the analytical methods are similar to those used for rock analysis (Johannesson and Zhou, 1999). Briefly, minerals in the veins and fracture coatings were separated from the host rock using dental tools and picks. The mineral samples were cleaned using distilled water and ground with a mortar and pestle. Approximately 0.25 grams of each mineral (i.e., powder) sample were placed in ultraclean Teflon®-lined microwave digestion bombs, followed by 5 mL of ultrapure HF (Seastar, Inc. double sub-boiling, distilled in Teflon®) and 5 mL of ultrapure HNO<sub>3</sub> (Seastar, Inc. double sub-boiling, distilled in quartz). The Teflon®-lined microwave digestion bombs were then sealed and placed in a microwave oven (CEM Corporation MDS-2100) and heated to 190°C and pressurized to  $8.62 \times 10^5$  Pa (125 p.s.i.) for 25 minutes. After 25 minutes, the samples were allowed to cool before 50 mL of a saturated boric acid solution was added to each sample. The samples were subsequently heated again in the microwave for 5 minutes at 70°C and  $6.9 \times 10^3$  Pa -  $1.38 \times 10^4$  Pa (1 - 2 p.s.i.). The dissolved rock samples were then decanted into clean polyethylene bottles and diluted by a factor of 2 - 50 before analysis using ICP-MS. In this case, a series of 5 standards of known concentration (i.e., 0.01 µg/kg, 0.05 µg/kg, 0.25 µg/kg, 0.5 µg/kg, and 1.0 µg/kg) were prepared and routinely monitored during analysis in order to calibrate the instrument, check the calibration, and calculate the trace element concentrations of these samples. The U.S. Geological Survey rock standard W-2 (diabase) was included as a check standard during the analysis; our measurements never deviated from the standard by more than 10%. A duplicate sample and a method blank

were analyzed for quality control of the analyses.

#### 4.4.3. Analysis of REEs Using LA-ICP-MS

Three mineral samples from Yucca Mountain, including ESF 60+52.5, ESF 77+03, and ESF 78+41, were selected for REE analysis using the laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) at the Analytical Laboratory of Nevada Bureau of Mines and Geology at the University of Nevada, Reno. Sample ESF 60+52.5 was analyzed by both ICP-MS and LA-ICP-MS. The mineral samples were prepared as polished 100  $\mu\text{m}$  thick thin sections without covers. With the unique operating conditions, such as wavelength, energy, laser repetition frequency, ablation duration, and laser beam size ( $\sim 100 \mu\text{m}$  in diameter), the LA-ICP-MS system makes it possible to quantify trace element concentrations (including REEs) at specific spots or growth zones of rock and mineral samples (Poitrasson et al., 2000). A total of 15 spots within the mineral growth zones in three mineral samples were analyzed for their REE concentrations, including 5 spots (Spots 1 - 5) in ESF 78+41, 4 spots (Spots 6 - 9) in ESF 77+03, and 6 spots (Spots 10 - 15) in ESF 60+52.5. The National Institute of Standards and Technology standard (NIST SRM 612-1), a homogenized glass matrix (3 mm wafer) spiked with up to sixty-one trace elements at known concentrations, was used to calculate REE concentrations at those spots. Prior to final calculations of trace element concentrations at each spot, instrumental errors were eliminated by subtracting intensity counts for trace elements in the samples with corresponding intensity counts in the instrument blanks. A second NIST standard (NIST SRM 612-2) was analyzed as a check

standard; most of our measurements were within  $\pm 20\%$  of this standard.

## 4.5. Analytical Results

### 4.5.1. Rare Earth Elements Analyzed by ICP-MS

We analyzed the concentrations (ppm) of REEs in 24 secondary mineral samples by ICP-MS in this study, along with chondrite-normalized Nd/Yb ratios, shale-normalized Yb/Nd ratios, and Ce/Ce\* and Eu/Eu\* ratios. The results are presented in Table 4.2. REE abundances are commonly evaluated after normalizing the measured REE concentrations to the concentration in an average chondritic meteorite (in the case of igneous rocks or magmatic processes) or average shale (in the case of sedimentary rocks or weathering processes) (e.g. Evensen et al., 1978). This step smoothes out the atomic-number-dependent variations in the absolute abundances of the REE and facilitates the assessment of the processes under consideration. Because the geologic environment recorded in the samples from WPM-OV drill samples and from the Yucca Mountain tunnels was complex and reflected overlapping hydrothermal and weathering processes, both chondrite- and shale-normalized REE plots are presented. Chondrite-normalized REE patterns for the 24 samples are shown in Figure 4.3, while shale-normalized REE patterns for the same samples are shown in Figure 4.4.

Table 4.2. REE concentrations (ppm) of the secondary mineral samples collected from Southern Nevada for this study.

Analytical Method: ICP-MS. CN = chondrite-normalized, SN = shale-normalized.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Nd/Yb) <sub>CN</sub>	(Yb/Nd) <sub>SN</sub>	Ce/Ce*	Eu/Eu*
PM-2/320	0.54	0.41	0.11	0.43	0.08	0.01	0.08	0.01	0.05	0.01	0.03	0.00	0.02	0.00	6.46	0.56	-0.39	-0.25
PM-2/5893	75.34	109.69	12.56	39.89	8.51	4.87	8.00	1.21	5.11	0.85	2.09	0.27	1.58	0.23	8.41	0.43	-0.07	0.40
PM-2/8050	31.58	62.24	6.78	21.88	2.97	0.70	3.09	0.36	1.56	0.29	0.84	0.11	0.69	0.10	10.51	0.34	0.02	-0.01
PM-3/1790	8.97	29.45	2.50	8.16	3.30	0.22	3.08	0.57	2.99	0.60	1.70	0.26	1.64	0.25	1.66	2.18	0.18	-0.53
PM-3/2860	22.56	42.23	5.14	19.07	6.18	2.27	6.82	1.02	5.38	1.19	3.53	0.53	3.38	0.57	1.88	1.92	-0.02	0.17
UE-18V/1378	7.28	0.36	2.62	10.50	3.04	0.11	2.86	0.42	2.01	0.39	1.00	0.13	0.71	0.11	4.93	0.73	-1.70	-0.79
UE-18V/2020	20.20	28.19	3.39	11.06	2.76	1.79	3.44	0.64	3.48	0.65	1.54	0.19	1.01	0.15	3.63	0.99	-0.09	0.39
U-19AR/173	51.01	90.46	10.52	34.57	7.77	1.56	7.29	1.08	5.39	1.12	3.43	0.51	3.29	0.52	3.5	1.03	-0.02	-0.05
U-19AR/1560	17.78	36.91	4.92	18.35	4.86	0.78	4.49	0.73	3.91	0.82	2.45	0.36	2.28	0.36	2.68	1.35	-0.02	-0.15
U-20AS/290	41.55	83.93	8.40	25.47	5.56	0.87	5.16	0.78	4.01	0.88	2.71	0.40	2.68	0.42	3.16	1.14	0.04	-0.16
ER-EC-4a	1.83	0.44	0.92	4.68	1.17	0.27	1.29	0.22	1.30	0.27	0.77	0.10	0.55	0.07	2.86	1.26	-1.11	-0.02
ER-EC-4b	1.91	2.77	0.50	2.02	0.38	0.11	0.47	0.09	0.59	0.14	0.46	0.07	0.37	0.04	1.84	1.97	-0.16	0.02
ER-EC-6	21.25	53.08	10.98	34.56	16.79	2.60	19.73	3.97	16.07	4.36	10.70	1.36	7.51	0.87	1.53	2.35	-0.10	-0.22
ER-EC-8	31.10	0.64	8.93	24.55	5.75	0.31	5.08	0.69	3.19	0.60	1.58	0.20	1.10	0.14	7.44	0.48	-2.03	-0.62
ER-18-2	20.44	22.68	3.57	12.39	2.70	1.59	3.26	0.66	4.20	0.89	2.55	0.37	2.27	0.36	1.82	1.98	-0.19	0.35
ER-30-1	32.59	57.16	7.42	19.94	4.06	0.63	3.84	0.56	3.01	0.62	1.91	0.29	1.93	0.28	3.44	1.05	-0.05	-0.16
ER-OV-3a	40.33	84.10	9.88	26.46	5.60	0.99	5.12	0.74	4.00	0.78	2.30	0.35	2.34	0.35	3.77	0.96	0.01	-0.10
ESF28+81	6.54	0.23	1.77	6.79	1.77	0.07	2.15	0.34	1.80	0.35	0.86	0.10	0.59	0.09	3.84	0.94	-1.78	-0.80
ESF59+87	19.56	10.47	7.33	22.34	6.44	0.09	7.57	1.16	6.67	1.46	3.90	0.46	2.15	0.28	3.47	1.04	-0.68	-1.28
ESF60+52.5	2.54	0.58	1.17	5.39	1.66	0.04	2.42	0.45	2.93	0.73	2.17	0.29	1.35	0.18	1.33	2.72	-1.11	-1.13
ESF78+05.2(T)	0.46	0.36	0.07	0.16	0.03	0.01	0.04	0.01	0.07	0.03	0.02	0.00	0.02	0.00	3.28	1.10	-0.31	0.05
ESF78+05.2(B)	9.75	0.70	2.59	8.88	2.04	0.04	1.89	0.27	1.30	0.25	0.66	0.09	0.52	0.08	5.68	0.64	-1.47	-1.08
ECRB07+40.5	1.59	0.24	0.50	2.15	0.67	0.03	0.87	0.15	0.97	0.22	0.66	0.09	0.57	0.09	1.25	2.89	-1.18	-0.73
ECRB12+90	4.38	0.58	1.48	5.89	1.58	0.06	2.04	0.38	2.55	0.63	1.97	0.29	1.71	0.28	1.15	3.14	-1.26	-0.82

$$\text{Ce/Ce}^* = \log \{ 2\text{Ce}_{\text{SN}} / [\text{La}_{\text{SN}} + \text{Pr}_{\text{SN}}] \}.$$

$$\text{Eu/Eu}^* = \log \{ 2\text{Eu}_{\text{SN}} / [\text{Sm}_{\text{SN}} + \text{Gd}_{\text{SN}}] \}.$$

#### 4.5.1.1 Chondrite-normalized REE Patterns

Most secondary mineral samples from the WPM-OV and the Yucca Mountain tunnels exhibit REE concentration enrichments relative to chondrite (Sample/Chondrite > 1) (Fig. 4.3), except for PM-2/320 and ESF 78+05.2 (T). They all are enriched in the light rare earth elements (LREE) relative to the heavy rare earth elements (HREE) on a chondrite-normalized plot. Four types of REE patterns are observed in the chondrite-normalized plots shown in Figure 4.3.

(1) Type (1c) pattern:

[Samples: PM-2 (320 ft), UE-18t (1378 ft), ER-EC-4a (1150-1160 ft), ER-EC-8 (1850-1870 ft), ESF28+81, ESF59+87, ESF60+52.5, ESF78+05.2 (T), ESF78+05.2 (B), ECRB07+40.5, and ECRB12+90]

Type (1c) is characterized by moderate to strong LREE enrichment, with strong negative Ce and Eu anomalies (Fig. 4.3). The chondrite-normalized Nd/Yb ratios for these samples vary from 1.15 in ECRB 12+90 to 7.44 in ER-EC-8 (1850-1870 ft). The Ce/Ce\* ratios for these samples vary from -0.31 in ESF78+05.2 (T) to -2.03 in ER-EC-8 (1850-1870 ft) and the Eu/Eu\* ratios from -0.02 in EC-EC-4a (1150-1160 ft) to -1.28 in ESF 59+87 (Table 4.2). It is notable that the sample ESF 78+05.2 (T) has much lower REE concentrations with a positive Eu/Eu\* ratio (0.05) and positive Dy and Ho anomalies (Fig. 3d). These results may be caused by analytical errors. Hence, the sample ESF 78+05.2 (T) is still categorized into Type (1c) based on its strong LREE enrichment and a strong negative Ce anomaly. This pattern is typical of near-surface (pedogenic)



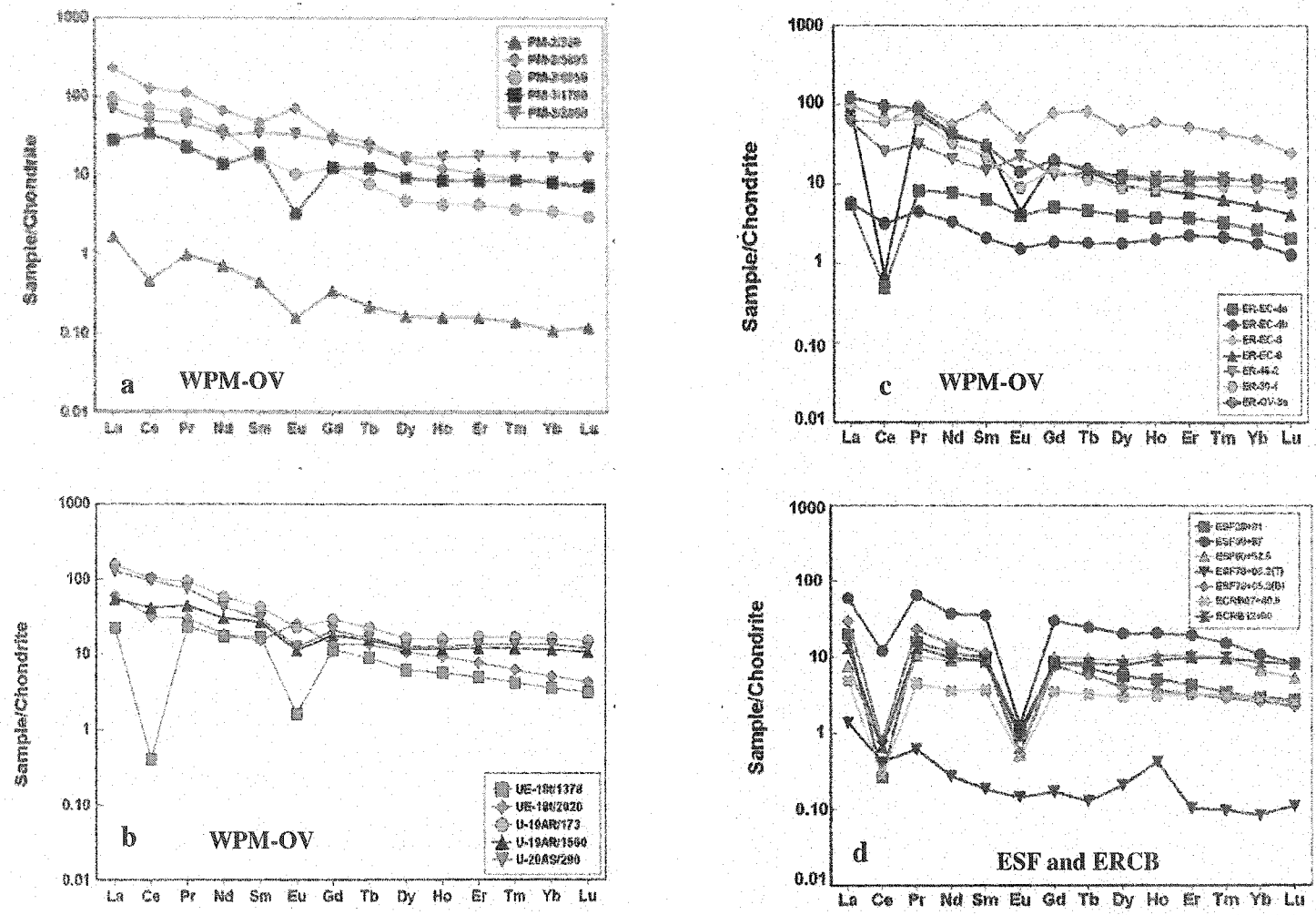


Fig. 4.3. Chondrite-normalized REE patterns of 24 secondary mineral samples collected from the western Pahute Mesa–Oasis Valley (WPM-OV) (a, b, c) and the ESF and ERCB at Yucca Mt. (d), southern Nevada. REEs were analyzed using ICP-MS.

processes (Denniston et al., 1997; Zhou et al., 1999b) and is also observed in samples from the upper saturated zone. The REE patterns suggest that these samples were precipitated from downward-flowing waters originating from the unsaturated zone. The calcite  $\delta^{18}\text{O}$  values for these samples are generally consistent with this interpretation (IT Corporation, 1998; Benedict et al., 2000; Whelan et al., 2002). The strong negative Ce and Eu anomalies result from the decreased solubility that accompanies the oxidation of Ce and Eu in a shallow depositional environment (Vaniman and Chipera, 1996).

(2) Type (2c) pattern:

[Samples: PM-3 (1790 ft), U-19AR (173 ft), U-19AR (1560ft), U-20AS (290 ft), ER-EC-6 (3420-3440 ft), and ER-30-1 (750-760 ft)]

Type (2c) is defined by a moderate to strong LREE enrichment accompanied by very weak Ce and moderate negative Eu anomalies (Fig. 4.3). The chondrite-normalized Nd/Yb ratios for these samples vary from 1.53 in ER-EC-6 (3420-3440 ft) to 3.50 in U-19AR (173 ft). The Ce/Ce\* ratios for these samples range from -0.10 in ER-EC-6 (3420-3440 ft) to 0.18 in PM-3 (1790 ft) and the Eu/Eu\* ratios from -0.05 in U-19AR (173 ft) to -0.53 in PM-3 (1790 ft) (Table 4.2). This pattern is associated with samples from both the saturated zone [PM-3 (1790 ft), ER-EC-6 (3420-3440 ft), and ER-30-1 (750-760ft)] and the unsaturated zone [U-19AR (173 ft), U-19AR (1560ft), and U-20AS (290 ft)]. It is very similar to the chondrite-normalized REE patterns for felsic volcanic rocks and perched volcanic groundwater at the Nevada Test Site [Johannesson et al., 1997, 2000; Zhou et al., 1999a]. Although the calcite samples U-19AR (173 ft) and U-20AS (290 ft)

are from the shallow unsaturated zone, the geochemical data for these samples suggest that they may have originated from upwelling groundwater (Benedict et al., 2000).

(3) Type (3c) pattern:

[Samples: PM-2 (5893 ft), PM-3 (2860 ft), UE-18t (2020 ft), and ER-18-2 (2050-2080 ft)]

Type (3c) is characterized by moderate LREE enrichment with a weak negative Ce anomaly and a strong positive Eu anomaly (Figs. 4.3a - c). The chondrite-normalized Nd/Yb ratios for these samples vary from 1.82 in ER-18-2 (2050-2080 ft) to 8.41 in PM-2 (5893 ft). The Ce/Ce\* ratios for these samples range from -0.02 in PM-3 (2860 ft) to -0.19 in ER-18-2 (2050-2080 ft) and the Eu/Eu\* ratios from 0.17 in PM-3 (2860 ft) to 0.40 in PM-2 (5893 ft) (Table 3.2). This pattern is only observed in four samples from the saturated zone. The positive Eu anomaly is reminiscent of those reported for hydrothermal fluids from mid-ocean ridges [Klinkhammer et al., 1994], and may imply a hydrothermal origin for this sample. This conclusion is consistent with independent evidence from the mineral oxygen isotope compositions and the coexisting vein mineral assemblage (Rose et al., 1998; IT Corporation, 1998). However, the  $\delta^{18}\text{O}$  value for ER-18-2 (2050-2080 ft) suggests only a moderate depositional temperature (43°C) (Benedict et al., 2000). Hence, if this sample was of hydrothermal origin, it would probably be deposited in a cooler part of the geothermal system. The calcite  $\delta^{13}\text{C}$  value (-0.9‰) for ER-18-2 (2050-2080 ft) is within the accepted range of values for a deep carbon source originating from Paleozoic bedrock.

(4) Type (4c) pattern:

[Samples: PM-2 (8050 ft), ER-EC-4b (2210-2220 ft), and ER-OV-3a (20 ft)]

The type (4c) pattern is defined by a moderate to strong LREE enrichment with no or weak Ce and Eu anomalies (Figs. 4.3a, c). The chondrite-normalized Nd/Yb ratios for these samples vary from 1.84 in ER-EC-4b (2210-2220 ft) to 10.51 in PM-2 (8050 ft). The Ce/Ce\* ratios for these samples vary from -0.16 to 0.01 and the Eu/Eu\* ratios from -0.10 to 0.02 (Table 2). The sample PM-2 (8050 ft) (Fig. 4.3a) and ER-EC-4b (2210-2220 ft) (Fig. 4.3c), both from the deep saturated zones, do not show strong negative anomalies for either Ce or Eu. Although the calcite sample from ER-OV-3a (20 ft) (Fig. 4.3c) is from the shallow unsaturated zone, the geochemical data for this sample suggest it may have originated from upwelling groundwater (Benedict et al., 2000). This pattern is correlative to the chondrite-normalized REE patterns in the Lower Paleozoic carbonate rocks and in the carbonate groundwater in southern Nevada (Zhou et al., 1999a; Johannesson et al., 1997, 1999). It is notable that the three samples displaying this type of pattern have an approximate order of magnitude difference in their REE concentrations.

#### *4.5.1.2 Shale-normalized REE Patterns*

Shale-normalized REE patterns for 24 secondary mineral samples are shown in Figure 4.4. The composite shale data used to normalize the mineral sample data are from Sholkovitz (1988, Table 5.1). Ce and Eu anomalies (negative or positive) in the shale-normalized REE patterns are similar to those in the chondrite-normalized REE patterns for the same mineral sample. Most samples analyzed in this study exhibit equivalent

order of magnitude REE concentrations as shale (sample/shale  $\equiv$  1 in a logarithmic scale) (Fig. 4.4). Four samples, including PM-2 (320 ft), ER-EC-4a (1150 – 1160 ft), ER-EC-4b (2210 – 2220 ft), and ESF 78+05.2 (T), are depleted relative to shale (sample/shale < 1 in a logarithmic scale) and exhibit low REE concentrations. The samples are subdivided into three types on the basis of the shale-normalized patterns and the shale-normalized Yb/Nd and Er/Nd ratios (Table 4.3, Fig. 4.4): (1s) enriched LREE with small shale-

Table 4.3. Shale-normalized REE patterns of the samples examined in this study.

Shale-Normalized REE Pattern	Sample	(Yb/Nd) <sub>SN</sub>	(Er/Nd) <sub>SN</sub>
<b>Type (1s): LREE Enrichment</b>	PM-2/8050	0.34	0.39
	PM-2/5893	0.43	0.53
	ER-EC-8	0.48	0.65
	PM-2/320	0.56	0.76
	ESF78+05.2(B)	0.64	0.75
	UE-18t/1378	0.73	0.97
<b>Type (2s): Flat with a slight HREE enrichment</b>	ESF28+81	0.94	1.28
	ER-OV-3a	0.96	0.88
	UE-18t/2020	0.99	1.41
	U-19AR/173	1.03	1.01
	ESF59+87	1.04	1.77
	ER-30-1	1.05	0.97
	ESF78+05.2(T)	1.10	1.28
	U-20AS/290	1.14	1.08
	ER-EC-4a	1.26	1.66
	U-19AR/1560	1.35	1.35
<b>Type (3s): Strong HREE enrichment</b>	PM-3/2860	1.92	1.88
	ER-EC-4b	1.97	2.30
	ER-18-2	1.98	2.09
	PM-3/1790	2.18	2.11
	ER-EC-6	2.35	3.14
	ESF60+52.5	2.72	4.07
	ECRB07+40.5	2.89	3.10
	ECRB12+90	3.14	3.39

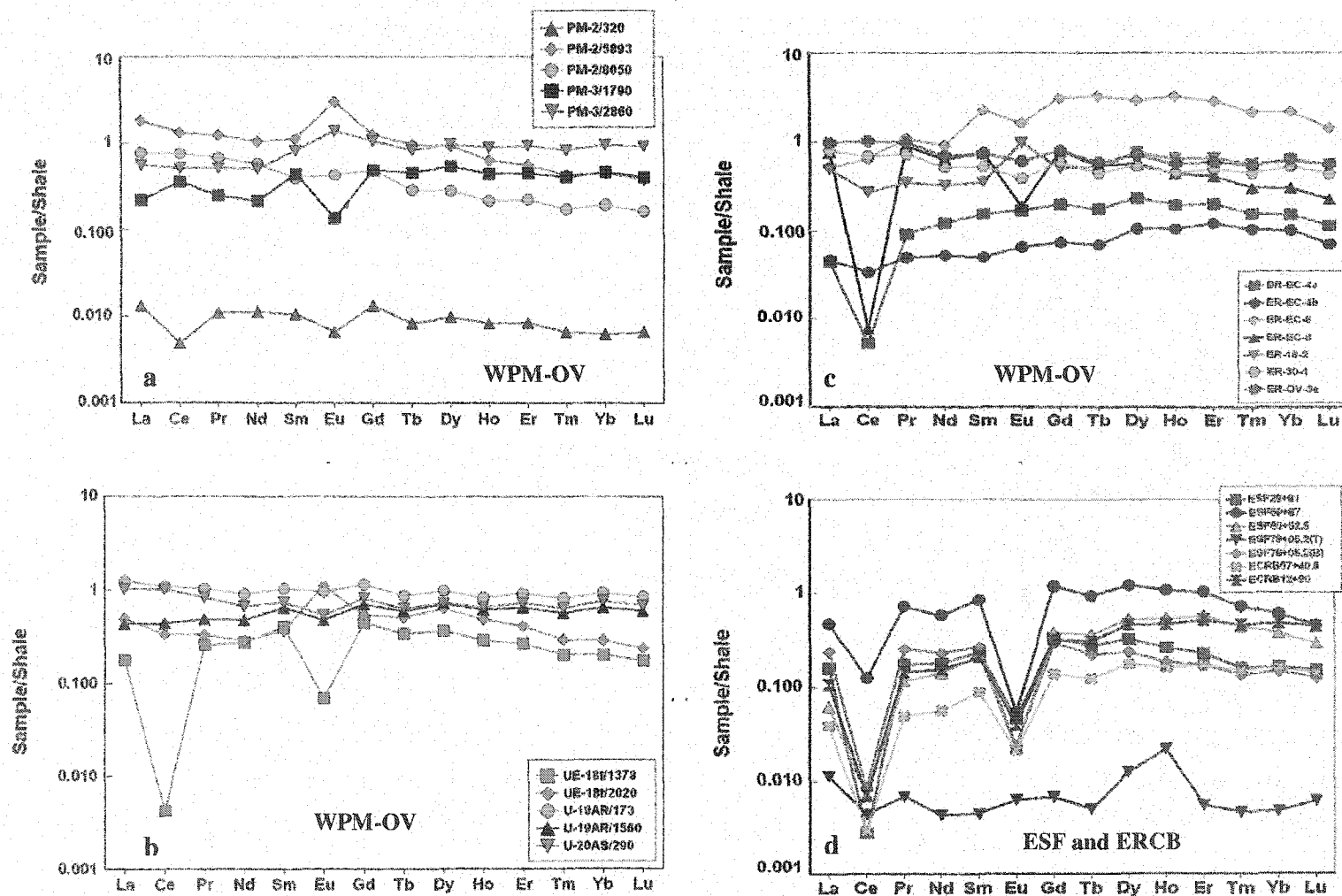


Fig. 4.4. Shale-normalized REE patterns of 24 secondary mineral samples collected from the western Pahute Mesa–Oasis Valley (WPM-OV) (a, b, c) and the ESF and ERCB at Yucca Mt. (d), southern Nevada. REEs were analyzed using ICP-MS.

normalized Yb/Nd and Er/Nd ratios  $[(Yb/Nd)_{SN} < 0.73, (Er/Nd)_{SN} < 0.97, SN = \text{shale-normalized}]$ ; (2s) flat shale-normalized patterns with a slight HREE enrichment. Shale-normalized Yb/Nd and ER/Nd ratios are near to slightly larger than 1; (3s) strong HREE enrichment with larger  $(Yb/Nd)_{SN}$  and  $(Er/Nd)_{SN}$  ratios (between approximately 2 and 3).

#### 4.5.2. Rare Earth Elements Analyzed by LA-ICP-MS

Concentrations (ppm) of the REEs in 3 secondary mineral samples analyzed by LA-ICP-MS in this study, along with chondrite-normalized Nd/Yb ratios, shale-normalized Yb/Nd ratios, and Ce/Ce\* and Eu/Eu\* ratios, are presented in Table 4.4. The data include REE concentrations at a total of 15 spots in 3 samples (ESF 78+41, ESF 77+03, and ESF 60+52.5) (Fig. 4.5). Chondrite- and shale-normalized REE patterns from 15 spots in 3 samples are shown in Figure 4.6. The average REE concentrations for the sample ESF 60+52.5 are also calculated and presented in Table 4 based on the REE data at spots 10 - 15. The average REE data obtained from LA-ICP-MS are compared with the data analyzed by ICP-MS for the same sample (ESF 60+52.5).

**ESF 78+41 (Spots 1 - 5):** Chondrite-normalized REE patterns (Fig. 4.6a) from Spots 1 - 5 in sample ESF 78+41 are generally characterized by moderate to strong LREE enrichment, with strong negative Ce and Eu anomalies. The  $(Nd/Yb)_{CN}$  (CN = chondrite-normalized) ratios for 5 spots vary from 1.57 to 10.79, the Ce/Ce\* ratios from -0.63 to -1.68, and the Eu/Eu\* ratios from -0.43 to -1.07 (Table 4.4).

Shale-normalized REE patterns (Fig. 4.6d) for the same sample show a LREE enrichment at Spots 1 - 3  $[(Yb/Nd)_{SN}$  ratios varying from 0.33 to 0.93 (Table 4.4)] and a

Table 4.4. REE concentrations (ppm) of three secondary mineral samples collected from southern Nevada for this study.  
Analytical Method: LA-ICP-MS. CN = chondrite-normalized, SN = shale-normalized.

Sample	Spot	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Nd/Yb) <sub>CN</sub>	(Yb/Nd) <sub>SN</sub>	Ce/Ce*	Eu/Eu*
ESF 78+41	Spot1	21.53	0.58	1.02	5.20	1.73	0.08	0.90	0.11	0.44	0.08	0.22	0.03	0.16	0.03	10.79	0.33	-1.65	-0.57
	Spot2	13.16	0.54	0.83	3.78	1.16	0.06	1.12	0.12	0.73	0.14	0.39	0.05	0.28	0.05	4.47	0.81	-1.49	-0.61
	Spot3	11.59	0.41	0.83	3.96	1.25	0.08	1.71	0.24	1.36	0.26	0.60	0.06	0.34	0.06	3.88	0.93	-1.57	-0.62
	Spot4	55.31	1.77	7.23	34.11	14.22	0.29	15.36	2.30	13.02	3.13	7.28	0.69	3.55	0.62	3.20	1.13	-1.68	-1.07
	Spot5	3.48	1.15	0.34	2.00	0.74	0.07	0.87	0.12	0.83	0.22	0.71	0.10	0.42	0.07	1.57	2.29	-0.63	-0.43
ESF 77+03	Spot6	2.83	1.49	0.93	5.08	1.71	0.07	2.72	0.42	2.72	0.69	1.93	0.22	1.09	0.17	1.56	2.31	-0.65	-0.86
	Spot7	0.15	0.01	0.00	0.03	0.03	0.00	0.03	0.01	0.01	0.00	0.01	0.00	0.02	0.01	0.45	8.01	-1.25	-0.20
	Spot8	0.14	0.00	0.00	0.01	0.02	0.00	0.02	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.37	9.65	-1.63	-0.38
	Spot9	0.16	0.01	0.00	0.03	0.04	0.01	0.03	0.00	0.01	0.00	0.01	0.00	0.01	0.01	0.82	4.39	-1.45	-0.09
	Spot10	14.10	1.74	0.34	2.03	0.67	0.11	0.72	0.20	0.44	0.11	0.24	0.03	0.27	0.04	2.48	1.45	-0.95	-0.18
ESF 60+52.5	Spot11	6.40	0.47	0.10	0.59	0.17	0.12	0.20	0.03	0.14	0.09	0.09	0.01	0.08	0.02	2.33	1.55	-1.16	0.43
	Spot12	3.68	0.75	0.05	0.17	0.08	0.02	0.06	0.01	0.04	0.01	0.03	0.01	0.03	0.01	1.64	2.20	-0.72	-0.03
	Spot13	6.92	0.65	1.66	7.59	2.63	0.17	2.65	0.41	2.80	0.55	1.79	0.23	1.51	0.28	1.68	2.15	-1.33	-0.57
	Spot14	3.55	1.13	0.28	1.17	0.56	0.03	0.50	0.09	0.51	0.12	0.46	0.07	0.42	0.07	0.94	3.84	-0.63	-0.66
	Spot15	7.44	0.05	0.98	5.44	1.60	0.08	2.06	0.34	2.17	0.51	1.80	0.21	1.47	0.25	1.23	2.92	-2.41	-0.71
AveREE		7.02	0.80	0.57	2.83	0.95	0.09	1.03	0.18	1.01	0.23	0.73	0.09	0.63	0.11	1.50	2.35	-1.20	-0.29

$$\text{Ce/Ce}^* = \log \{ 2\text{Ce}_{\text{SN}} / [\text{La}_{\text{SN}} + \text{Pr}_{\text{SN}}] \}.$$

$$\text{Eu/Eu}^* = \log \{ 2\text{Eu}_{\text{SN}} / [\text{Sm}_{\text{SN}} + \text{Gd}_{\text{SN}}] \}.$$



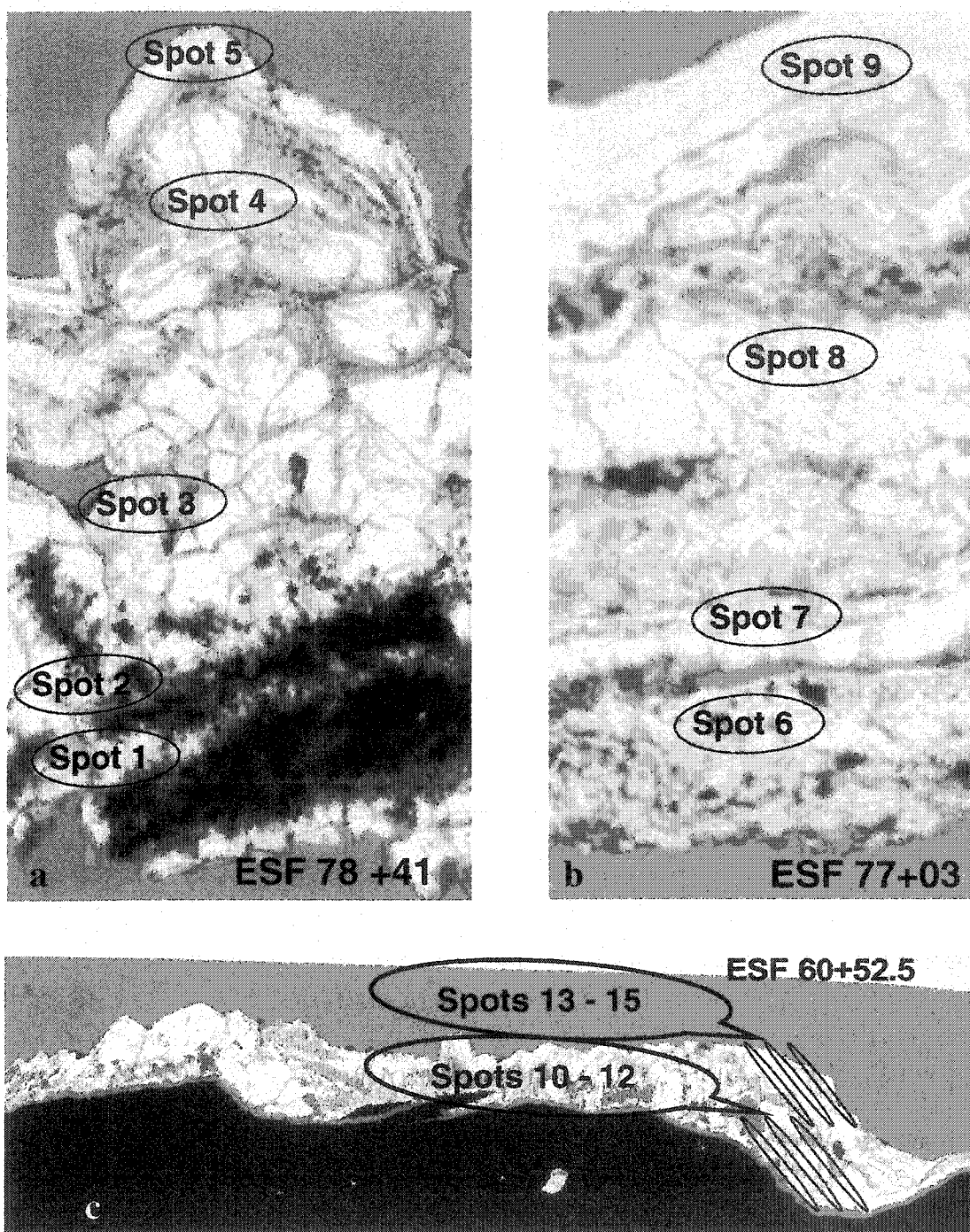


Fig. 4.5. Photographs of thin sections from three samples showing the specific spots where REE concentrations were determined by LA-ICP-MS. (a) Spot 1 - 5 in ESF 78+41, (b) Spots 6 - 9 in ESF 77+03, and (c) Spots 10 - 15 in ESF 60+52.5.

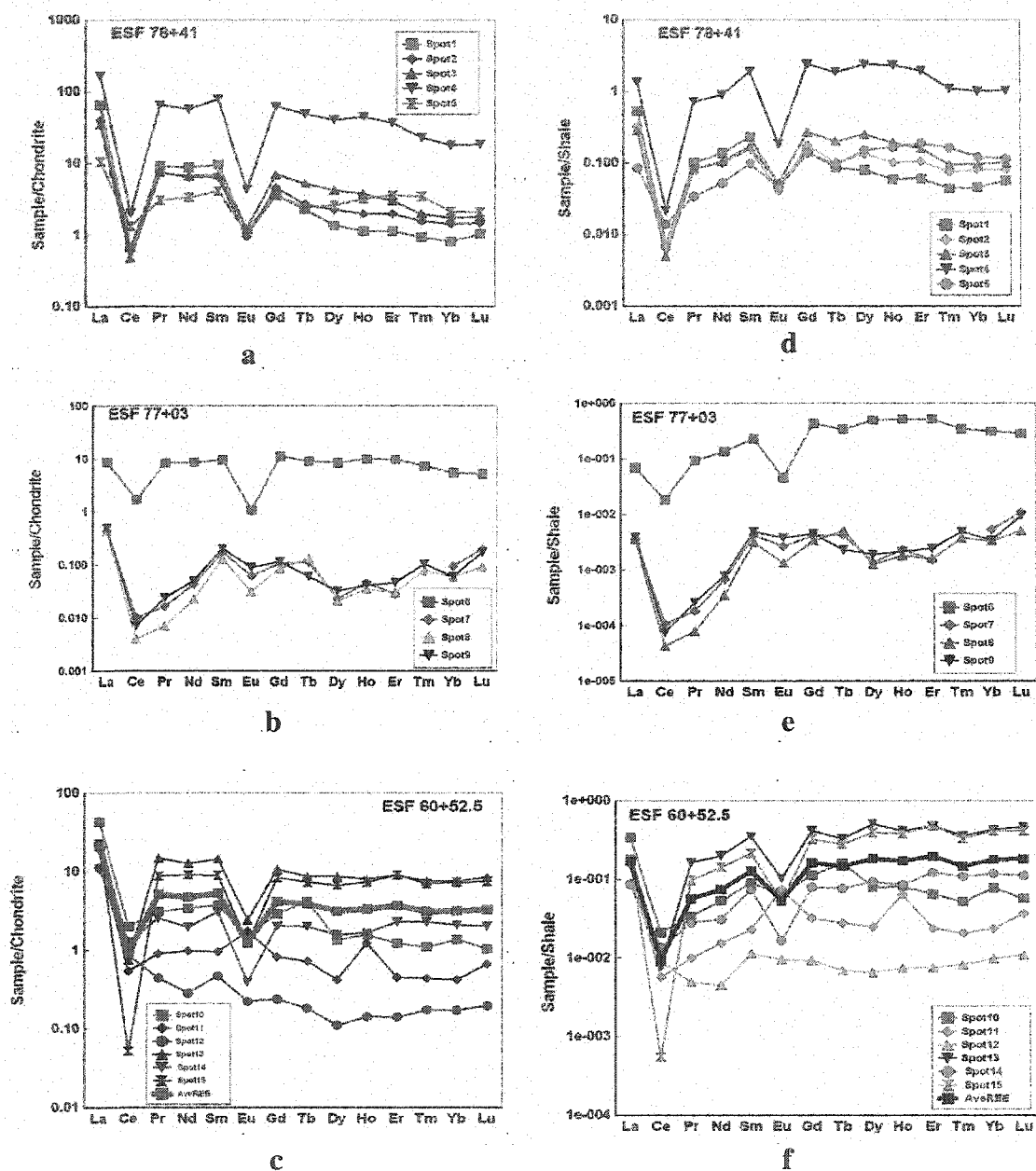


Fig. 4.6. Chondrite- and shale-normalized REE patterns for three secondary mineral samples from Yucca Mountain. (a) chondrite-normalized REE pattern at Spots 1 - 5 in ESF 78+41, (b) chondrite-normalized REE pattern at Spots 6 - 9 in ESF 77+03, (c) chondrite-normalized REE pattern at Spots 10 - 15 in ESF 60+52.5, the thicker black line represents the average chondrite-normalized pattern of Spots 10 - 15; (d) shale-normalized REE pattern at Spots 1 - 5 in ESF 78+41, (e) shale-normalized REE pattern at Spots 6 - 9 in ESF 77+03, (f) shale-normalized REE pattern at Spots 10 - 15 in ESF 60+52.5, the thicker black line represents the average shale-normalized pattern of Spots 10 - 15.

HREE enrichment at Spots 4 and 5  $[(Yb/Nd)_{SN}]$  ratios varying from 1.13 to 2.29 (Table 4.4)], with strong negative Ce and Eu anomalies.

From bottom to top (or inner to outer) within a fracture (Fig. 4.5a), Spots 1 - 5 represent different stages (early to late) of secondary mineral growth (Wilson et al., 2003). Although their chondrite-normalized REE patterns are similar, there are still some differences from spot to spot. Spot 1 shows the strongest LREE enrichment  $[(Nd/Yb)_{CN} = 10.79]$ . Spot 5 displays the weakest LREE enrichment  $[(Nd/Yb)_{CN} = 1.57]$ , less negative Ce and Eu anomalies, and an enrichment from Tb to Tm. Spots 2 - 4 have a similar and moderate LREE enrichment  $[(Nd/Yb)_{CN}]$  ranging from 3.20 to 4.47]. However, Spot 4 has much higher REE concentrations with stronger negative Ce and Eu anomalies (Fig. 4.6a). These differences are also shown in shale-normalized REE patterns (Fig 4.6d). It is notable that all spots have a strong enrichment from Pr to Sm, and most spots have a depletion from Gd to Lu, except for Spot 5.

Similar to Type (1c) described above (Fig. 4.3), this pattern is typical of near-surface (pedogenic) processes and is also observed in samples from the upper saturated zone. The samples were precipitated from the percolating waters originating from the vadose zone. The strong negative Ce and Eu anomalies result from the decreased solubility that accompanies the oxidation of Ce and Eu in a shallow depositional environment (Vaniman and Chipera, 1996).

**ESF 77+03 (Spots 6 - 9):** Spots 6 - 9 in sample ESF 77+03 (Fig. 4.5b) show two different types of chondrite-normalized REE patterns (Fig. 4.6b). Spot 6 is characterized by a weak LREE enrichment  $[(Nd/Yb)_{CN} = 1.56]$ , with strong negative Ce and Eu

anomalies ( $Ce/Ce^* = -0.65$ ,  $Eu/Eu^* = -0.86$ ). REE concentrations are a magnitude higher than those at other spots in the same sample. Spots 7 - 9 have a similar chondrite-normalized pattern, which is strongly enriched in HREE  $[(Nd/Yb)_{CN}]$  varying from 0.37 to 0.82] with a strong negative Ce anomaly ( $Ce/Ce^*$  from -1.25 to -1.63) and a weak negative Eu anomaly ( $Eu/Eu^*$  from -0.09 to -0.38). There is an elevation between Pr and Sm and a depletion between Sm and Dy.

Shale-normalized REE patterns (Fig. 4.6e) at Spots 6 - 9 in the same sample also distinguish Spot 6 from Spots 7 - 9, even though they all show HREE enrichment and a strong negative Ce anomaly. Spot 6 has much higher REE concentrations and much less HREE enrichment  $[(Yb/Nd)_{SN} = 2.31]$  than Spots 7 - 9  $[(Yb/Nd)_{SN}]$  ratios varying from 4.39 to 9.65].

Spots 6 - 9 in sample ESF 77+03 are located in different mineral growth zones (Fig. 4.5b) and represent different stages (early to late) of mineral growth (Wilson et al., 2003). The differences in their REE patterns suggest that they were precipitated from groundwaters originated from different sources at different times. Obviously, Spots 7 - 9, with similar REE patterns and REE concentrations, were formed by groundwaters from geochemically similar sources during the later stage. Spot 6, with a REE pattern similar to Type (1c), represents a near-surface (pedogenic) calcite precipitation during the earlier stage.

**ESF 60+52.5 (Spots 10 - 15):** Chondrite-normalized REE patterns (Fig. 4.6c) from Spots 10 - 15 in sample ESF 60+52.5 can be grouped into two different types. Spots 10 - 12 are generally characterized by strong LREE enrichment with a strong negative Ce

anomaly and a weak negative or positive Eu anomaly. The  $(\text{Nd/Yb})_{\text{CN}}$  ratios for the three spots vary from 1.64 to 2.48, the  $\text{Ce/Ce}^*$  ratios from -0.72 to -1.16, and the  $\text{Eu/Eu}^*$  ratios from -0.03 to 0.43. The La concentrations at Spots 10 - 12 are much higher than are other REEs. Spot 11 shows positive anomalies for both Eu and Ho. Spots 13 - 14 display a similar chondrite-normalized REE pattern, which is generally enriched in LREE [ $(\text{Nd/Yb})_{\text{CN}}$  ratios from 0.94 to 1.68] with strong negative Ce and Eu anomalies ( $\text{Ce/Ce}^*$  from -0.63 to -2.41,  $\text{Eu/Eu}^*$  from -0.57 to -0.71).

Shale-normalized REE patterns (Fig. 4.6f) for the same sample show a moderate HREE enrichment [ $(\text{Yb/Nd})_{\text{SN}}$  from 1.45 to 2.20] with negative Ce and negative or positive Eu anomalies at Spots 10 - 12 and a strong HREE enrichment [ $(\text{Yb/Nd})_{\text{SN}}$  from 2.15 to 3.84] with strong negative Ce and Eu anomalies at Spots 13 - 15.

The normalized REE patterns at Spots 10- 12 are overall similar although they have some differences, such as a positive Eu anomaly at Spot 11. Located at the bottom of the secondary calcite crust (Fig. 4.5c) with a similar REE pattern, the three spots represent the earlier stage of calcite precipitation, which may represent precipitation from similar groundwaters. The positive Eu anomaly at Spot 11 may record the influence of thermal fluids during calcite precipitation. The normalized REE patterns for Spots 13 - 14 are almost identical, suggesting that they were precipitated from groundwaters with similar geochemical signatures. Again, the strong negative Ce and Eu anomalies are due to the oxidation of Ce and Eu in a shallow depositional environment (Vaniman and Chipera, 1996). Thus, this REE pattern indicates that this late stage calcite (Spots 13 - 15) was precipitated from percolating waters originating in the vadose zone.

#### 4.6. Discussion

Secondary minerals (mainly calcite) from fractures and cavities in unsaturated and saturated zone rocks around the NTS and Yucca Mountain exhibit distinct chemical and isotopic signatures that correlate to different zones in the hydrostratigraphic column (Peterman et al., 1992; Whelan and Stuckless, 1992; Vaniman, 1993, 1994; Vaniman and Chipera, 1996; Paces et al., 1996; Denniston et al., 1997; Rose et al., 1998; Zhou et al., 1999b; Benedict et al., 2000; Whelan et al., 2002; Wilson et al., 2003). These previous studies showed that the stable isotope values of calcite generally reflect the origin of the groundwater from which the mineral forms, as well as its depositional temperature. However, later diagenetic processes can alter the isotopic signatures in the minerals. Therefore, it may not always be possible to use stable isotope data to delineate the groundwater sources from which secondary minerals were precipitated. As a unique group of trace elements, rare earth elements (REE) in secondary calcite can provide additional insight into the origin of the fluid from which calcite forms. In addition, the data may potentially be used in conjunction with groundwater REE data to evaluate water-rock interaction processes and paleohydrologic history.

##### 4.6.1. REE Concentrations and Patterns

The secondary mineral samples from the WPM-OV wells and the underground tunnels at Yucca Mountain all exhibit some degree of REE fractionation. In general, there are remarkable distinctions in REE fractionation between upper unsaturated zone minerals and deep saturated zone minerals. This suggests that solution characteristics at

the time of deposition played an important role in the REE composition of the mineral being deposited in fractures. In general, the calcite is strongly enriched in REE relative to chondrite (Sample/Chondrite  $\gg 1$ ) (Figs. 4.3a - d) and exhibits REE concentrations comparable to average shale (Figs. 4.4a - d). LREE enrichments are generally observed for all samples on the chondrite-normalized plot (Fig. 4.3). However, samples exhibiting modest LREE enrichments on the chondrite-normalized plot show weak to moderate HREE enrichments on the shale-normalized plot (Fig. 4.4). This is due to differences in the relative abundances of LREE vs. HREE for the average chondrite and shale compositions.

There are at least four different chondrite-normalized REE patterns from the secondary mineral samples analyzed by ICP-MS: Type (1c) moderate to strong LREE enrichment with strong negative Ce and Eu anomalies; Type (2c) moderate to strong LREE enrichment accompanied by very weak Ce and moderate negative Eu anomalies; Type (3c) moderate LREE enrichment with a weak negative Ce anomaly and a strong positive Eu anomaly; and Type (4c) moderate to strong LREE enrichment with no or weak Ce and Eu anomalies. Type (1c) represents a REE pattern that results from typical near-surface (pedogenic) processes. Most unsaturated zone samples [except for sample UE-18t(1378)] from the WPM-OV and all samples from the ESF and ECRB at Yucca Mountain show Type (1c) REE pattern. Type (2c), occurring in both unsaturated and saturated zone samples, is very similar to the REE patterns in the felsic volcanic rocks and in the perched volcanic groundwater from the Nevada Test Site (Johannesson et al., 1997). Type (3c) and Type (4c) patterns are mostly from the deep saturated zone samples,

with the exception of ER-OV-3a (20 ft). They do not show strong negative anomalies for either Ce or Eu. Instead, positive Eu anomalies (Type 3c) are observed in several samples [PM-2 (5893 ft), PM-3 (2860 ft), UE-18t (2020 ft), and ER-18-2 (2050-2080 ft)] from the upper saturated zone. The hydrothermal origin for these secondary minerals indicates that fluids with elevated temperatures intruded the open fractures in the study area at one time in the geologic past. It is not impossible that this geological process can be repeated in the future, which would pose a potential risk for the radioactive waste repository at Yucca Mountain. Type (4c), from a deep saturated zone mineral [PM-2(8050) and ER-EC-4b (2210-2220 ft)], is similar to the REE patterns in the Lower Paleozoic carbonate rocks and in the carbonate groundwater in southern Nevada (Zhou et al., 1999; Johannesson et al., 1997, 1999; this study). The sample ER-EC-4b (2210-2220 ft) has  $\delta^{18}\text{O}$  values that indicate precipitation at a temperature below the regional geothermal gradient, also suggesting locally deep circulation of cooler groundwater (Benedict et al., 2000). Although the calcite sample from ER-OV-3a (20 ft) is from the shallow unsaturated zone, it also shows Type (4c) REE pattern. Well ER-OV-3a is located at the lower portion of Oasis Valley (Fig. 4.2), with a surface elevation 3844 ft and a shallow groundwater table (57 ft) (Benedict et al., 2000). Therefore, it is possible for groundwater to upwell to this level (20 ft from the surface and 37 ft from the groundwater table) and to precipitate calcite. A radiocarbon analysis on the sample ER-OV-3a (20 ft) yielded a  $^{14}\text{C}$  age of 26,650 years (Benedict et al., 2000). The results of stable isotope and REE analyses for this sample suggest that the calcite precipitated from evaporating regional groundwater at a time when the water table was elevated relative to its current position.



With two exceptions, the REEs always occur in the  $3^+$  valence state in nature. Since their outer electron structures are so similar, the REEs show very similar chemical properties, and they generally occur as a group in nature (Krauskopf, 1979). However, the effective ionic radius for the  $3^+$  oxidation state progressively decreases from 1.03 Å in  $\text{La}^{3+}$  to 0.86 Å in  $\text{Lu}^{3+}$  (for sixfold coordination; data from Shannon, 1976). As a result, there is a tendency for the light REE (LREE; La through Nd) to be partitioned from the heavy REE (HREE; Er through Lu) during mineral growth from a liquid. In the case of calcite ( $\text{CaCO}_3$ ), the  $\text{Ca}^{2+}$  ions are in sixfold coordination with oxygens of the  $(\text{CO}_3)^{2-}$  groups, with an effective ionic radius of 1.00 Å. This is similar to the ionic radius of the LREE, implying the LREE may be preferentially incorporated into the calcite crystal structure relative to the HREE, in the absence of other competing effects. In addition, anomalous variations in the distribution of Ce and Eu reflect changes in the oxidation state of these elements ( $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$  and  $\text{Eu}^{3+}$  to  $\text{Eu}^{4+}$ ). Hence, these elements provide useful indicators of redox conditions at the time of mineral deposition.

It is notable, however, that mineral/solution partitioning of REE may also influence the LREE to HREE distribution. Preferential ion substitution of LREE for  $\text{Ca}^{2+}$  in the calcite structure was previously noted. In addition, Wood (1990) showed that HREE solubility is enhanced relative to LREE in the presence of carbonate species at elevated pH values. As noted above, moderate to weak LREE enrichments in the chondrite-normalized plots (Fig. 4.3) correlate with HREE enrichments in the shale-normalized plots (Fig. 4.4). This pattern is observed in several samples, including PM-3 (1790), ER-EC-4a, ER-EC-4b, ER-EC-6, ER-18-2, ESF 60+52.5, ECRB 07+40.5, and

ECRB 12+90. Wood (1990) noted that the solubility of LREE is enhanced relative to HREE in the presence of elevated dissolved sulfate concentrations. Sulfate has been identified as one of the dominant anions in groundwater from the volcanic aquifers in southern Nevada (e.g. Thomas et al., 1999; Chapman and Lyles, 1993; Zhou et al., 2000). However, bicarbonate ion concentrations always exceed those of sulfate, and the extent to which these competing ion effects influence REE solubilities remains an open question.

#### 4.6.2. Ce and Eu Anomalies and Other Geochemical Evidence

Anomalous variations in the distribution of Ce and Eu are observed for many of the samples, and are related to redox conditions at the time of calcite deposition. In general, the most pronounced Ce and Eu depletions are observed in samples from shallow saturated zone fractures [such as samples with Type (1c) REE pattern]. This is consistent with oxidation being a more influential process in the near-surface environment. However, some “near-surface” samples show relatively weak redox anomalies [e.g., ER-OV-3a (20 ft) and ER-30-1 (750-760 ft)], indicating that proximity to the weathering zone is not the sole factor influencing redox conditions. Calcite deposition temperatures obtained from  $\delta^{18}\text{O}$  results do not correlate with LREE/HREE enrichments, nor do they correlate with the presence of Ce and Eu anomalies (Benedict et al., 2000). However, the higher temperature sample [such as ER-EC-6 (3420-3440 ft)] does show a higher REE concentrations (Fig. 4.3c and Fig. 4.4c), implying enhanced solubility at elevated temperatures. As previously noted, the positive Eu anomaly in several samples may be

indicative of hydrothermal conditions. However, correlations between calcite  $\delta^{18}\text{C}$  results and REE patterns were not observed.

In general, it is not yet possible to clearly link specific REE patterns and concentrations to specific processes or environments. A combination of factors influence the observed patterns, including groundwater chemistry, host rock REE abundances, redox conditions, temperature, and stratigraphic position. The limited data obtained during this study do not permit the relative importance of each factor to be evaluated. However, the fact that significant variations in REE fractionation and total REE concentrations exist suggests that additional analytical work may help link certain REE patterns to specific processes.

#### 4.6.3. Comparison of REE Results from ICP-MS and LA-ICP-MS

ICP-MS has been widely used for trace element analysis in geologic materials, such as rocks and minerals. With a high resolution and low detection limits, it has been used to quantify trace element (including REEs) concentrations in groundwater at the parts-per-trillion level since 1990's (i.e., Stetzenbach et al., 1994). However, using ICP-MS for solid material analysis requires completely digesting samples into solutions with acids. It needs a certain amount (i.e., 0.25 grams) of sample for digestion, which is not available occasionally. In addition, this method only analyzes trace element concentrations of a whole rock or mineral sample. It can't provide trace element concentrations at a specific portion of the sample (such as different mineral growth

zones), which is crucial to address some fundamental questions such as rock and mineral sources, geological processes, diagenetic alterations, and paleohydrologic history.

LA-ICP-MS has been developed to meet these requirements since the early of 1990's (Chenery and Cook, 1993; Poitrassion et al., 2000). With unique operating conditions and a laser beam with small diameter ( $\sim 100 \mu\text{m}$ ), LA-ICP-MS can determine trace elements in single mineral grains in a specific mineral (i.e., calcite) growth zone. The analysis can be performed directly on a thin section or hand specimens. The method allows us to study geochemical variations of trace elements in different mineral growth zones. The variations of trace element chemistry of these minerals, which were precipitated from groundwater flowing through the preexisting fractures, will help us understand the geochemical history of groundwater flows during a specific geologic interval.

Three secondary mineral samples from ESF and ERCB at Yucca Mountain were analyzed for their REE concentrations using LA-ICP-MS in this study. One sample (ESF 60+52.5) was analyzed for its REE concentrations using both ICP-MS and LA-ICP-MS. As discussed above, REE concentrations and patterns determined by LA-ICP-MS vary from Spot 10 to Spot 15 that represents different mineral growth zones (Figs. 4.6c, f). However, although REE concentrations from ICP-MS are generally higher than those from LA-ICP-MS, chondrite- and shale-normalized REE patterns obtained by averaging REE concentrations at Spots 10 - 15 in ESF 60+52.5 are very similar to those that are plotted using the REE data from ICP-MS for the same sample (Figs. 4.7a, b). Higher REE concentrations from ICP-MS analysis may be due to the impurity of the bulk

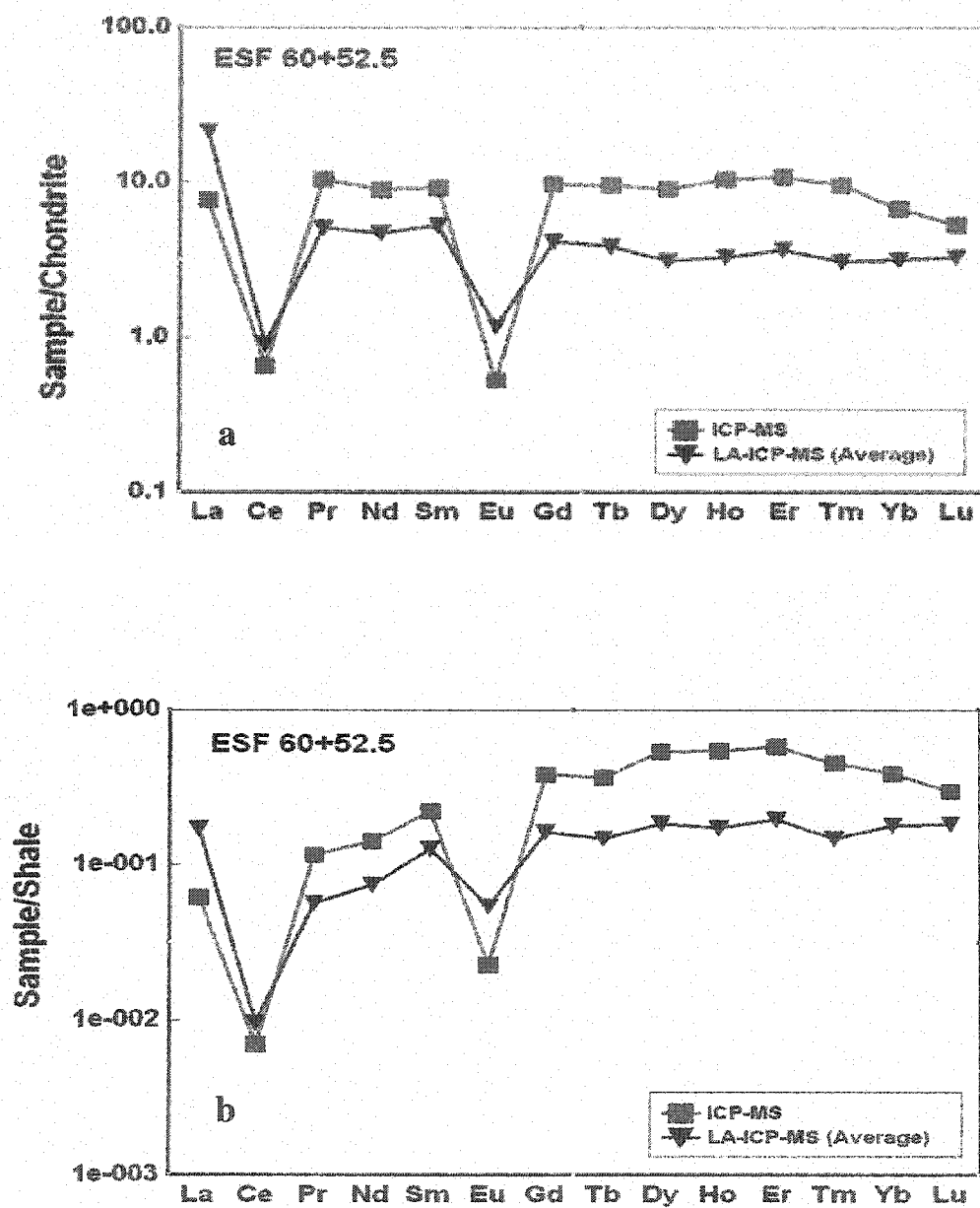


Fig. 4.7. Chondrite- and shale-normalized REE patterns obtained from both ICP-MS and LA-ICP-MS in the sample ESF 60+52.5. The average REE concentrations from Spots 10 - 15 in ESF 60+52.5 were used for the plots [LA-ICP-MS (Average)]. (a) chondrite-normalized REE plot, (b) shale-normalized REE plot.

mineral sample. For example, Fe and Mn oxides and clays coated on the mineral samples, with intergrown trace minerals (particularly apatite and crandallite), can greatly elevate REE concentrations of the samples. This comparison study shows LA-ICP-MS can be a useful alternative to ICP-MS for analyzing the samples for their trace elements on a microscopic scale. Future research will benefit tremendously from advances in high-resolution spot analysis by LA-ICP-MS.

#### 4.7. Conclusions

REE signatures in secondary minerals can be used to determine alteration processes and groundwater sources from which the minerals were precipitated. Anomalous variations in Ce and Eu concentrations, related to changes in oxidation state ( $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$  and  $\text{Eu}^{3+}$  to  $\text{Eu}^{4+}$ ), are useful indicators of redox conditions at the time of mineral deposition. Different REE patterns in secondary minerals, along with other geological and geochemical data (such as from petrographic, mineralogical, stable isotope, and fluid inclusion analyses), suggest that the fracture-coating minerals in southern Nevada may have precipitated from groundwaters that originated from different sources during geologic history. These secondary minerals in fractures can be formed either by groundwaters percolating through unsaturated zones, or from upwelling groundwaters (both shallow perched and deep aquifer groundwaters) with hydrothermal fluid influences, or a combination of these two origins. The mineral samples from different depths in the same borehole may have different origins.

However, it is not yet possible to unequivocally link specific patterns to specific processes due to the relatively small REE data set. Future investigations of REE patterns in calcite samples should continue to focus on linking the observed patterns to other physicochemical parameters (e.g. depositional temperature, host rock REE concentrations, and water chemistry). In addition, comparative studies with groundwater REE data are needed to determine the applicability of these data for constraining reactive flow and transport geochemical models.

The correlation of the REE results of the same sample using both ICP-MS and LA-ICP-MS shows a great promise for LA-ICP-MS in high-precision spot analysis for rocks and minerals. In addition, LA-ICP-MS requires much less sample preparations and less analytical time. One of the challenges in LA-ICP-MS analysis is the selection of high-quality standards that directly affect the accuracy of the analytical data. However, it can be improved with more sample and standard analyses using this method.

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## CHAPTER 5

### RARE EARTH ELEMENT SIGNATURES FROM BATCH LEACH TESTS

#### 5.1. Introduction

Rare earth elements (REE) have been used extensively to study petrological and mineralogical processes, as well as trace element cycling in the oceans since the late 1970's and early 1980's (e.g., Hanson, 1980; Elderfield and Greaves, 1982; DeBaar et al., 1983; Cullers and Graf, 1984). More recently, with the improvement of analytical instrumentation, REEs can be readily measured at the low parts-per-trillion level, in natural waters using, for example, inductively coupled plasma mass spectrometry (ICP-MS; Stetzenbach et al., 1994; Graham et al., 1996; Halicz et al., 1999). One consequence of the improvements in analytical instrumentation is the increase in the numbers of investigations of the REEs in groundwaters (Smedley, 1991; Fee et al., 1992; Gosselin et al., 1992; Halicz et al., 1999). Many of these studies indicate that groundwaters commonly have REE patterns that closely mimic the REE patterns of the rocks through which they flow. The similarities between groundwater and aquifer rock REE patterns suggest that the REEs may be useful tracers of groundwater-aquifer rock interactions. Many investigations have already demonstrated the utility of the REEs as chemical tracers of numerous geochemical weathering processes and possibly biogeochemical

redox processes (Hanson, 1980; Moffett, 1990, 1994). Although previous studies have demonstrated that in many cases the REE concentrations observed in groundwaters mimic those of rocks through which they flowed, quantitative, controlled investigations of the REE signatures aqueous solutions acquire by reacting with different types of rocks at low temperatures have not been completed. In order to gain a better understanding of how different rock types can affect the concentrations of REEs in aqueous solutions that react with the rocks and to obtain the baseline information concerning REE behavior during rock-water reactions, we conducted a series of batch reactor experiments involving compositionally different rock types, and two aqueous solutions, distilled deionized water and an acidic solution.

## 5.2. Analytical Methods

### 5.2.1. Rock Sample Collection

We chose the Paleozoic stratigraphic section at Frenchman Mountain near Las Vegas, Nevada (Fig. 3.1) as our major sampling location because: 1) the stratigraphic sequence in this section is very similar to the lower part of the regional carbonate aquifer of southern Nevada (e.g., Winograd and Thordarson, 1975); and 2) information gained by studying the REE signatures of these rocks and their resulting leachate solutions can be applied to our studies of REEs in groundwaters from this aquifer (e.g., Stetzenbach et al., 1994; Johannesson et al., 1997). In addition, the stratigraphic section is exposed on the eastern edge of the city of Las Vegas, which allows for easy access and detailed sampling. The Paleozoic strata exposed at the site consist of shales, sandstones, and

especially abundant carbonate rocks (e.g., dolomite, dolomitic limestone, and limestone) that range in age from Cambrian up to Permian (Rowland, 1987; Rowland et al., 1990). Ordovician and Silurian rocks are, however, missing from this section. Sixteen out of 19 rock samples used for the batch tests in this study were collected from the lower portion of the Frenchman Mountain section, including samples from the Tapeats Sandstone (Tapeats1), Bright Angel Formation (shale or sandstone) [BAS(SS)1, BAS(SL)2, BAS3, and BAS6], and Bonanza King Formation (dolomite) (BKD1, BKD2, BKD3, BKD4, BKD5, BKD6, BKD7, BKD8, BKD9, BKD10, and BKD11). On the other hand, one sample (FR8Oaal) was collected from the Aysees Member of the Lower Ordovician Antelope Valley Limestone at Fossil Ridge, 20 miles northwest of Las Vegas, Nevada (see Johannesson et al., 2000a). One rhyolitic rock sample (Surprise1) was also examined in the batch tests. Therefore, the samples used in the batch tests represent five different rock types, including shale [BAS(SL)2, BAS(SL)3, BAS6], fine- and medium-grained sandstone (BAS(SS)1, Tapeats1], limestone (FR8Oaal), dolomite (BKD1 through BKD11), and felsic volcanic rock (Surprise1).

### 5.2.2. Batch Tests

#### 5.2.2.1. *Preparation and leachates*

Approximately 5 - 10 kg of rock was collected from each sample location. Rock samples were subsequently broken into 0.5-1.0 cm size fragments using a sledge hammer. Fragments without weathering rinds, calcite veins, and obvious signs of possible alteration were carefully selected, until approximately 500 to 1000 grams of fragmental

material were obtained for each rock sample. The fragmental rock samples were further crushed to ~ 70-mesh in size, which were subsequently used in three batch tests employing different solutions and variable reaction times (Table 5.1). In addition, an

Table 5.1. Parameters used for three batch tests.

Parameters	Batch Test 1	Batch Test 2	Batch Test 3
<b>Rock Types</b>	shale, sandstone, limestone, dolomite, rhyolite	shale, sandstone, dolomite	shale, sandstone, limestone, dolomite, rhyolite
<b>Solutions</b>	distilled-deionized water	distilled-deionized water	acidic water solution
<b>Sample Weight (g)</b>	30	75 - 82	50
<b>Solution Weight (g)</b>	60	200 - 220	100
<b>Solution/Sample Weight Ratio</b>	2 : 1	3 : 1	2 : 1
<b>pH (starting)</b>	7	7	4
<b>Temperature (<math>^{\circ}</math>C)</b>	~ 25	~ 25	~ 25
<b>Reaction Time (days)</b>	40	67	42

aliquot of each crushed rock sample was preserved for REE analysis of the bulk rock (see below). For Batch Tests 1 and 2, 60 to 220 g of distilled-deionized water (pH=7; 18 m $\Omega$ ) was added to between 30 g to 80 g of each of the crushed rock samples within acid-washed, high-density linear polyethylene bottles (mass ratio of solution to rock sample ranged from 2:1 to 3:1; Table 5.1). The crushed rock samples and distilled-deionized

water was allowed to react at room temperature ( $\sim 25^{\circ}\text{C}$ ) for 40 days (Batch Test 1) and 67 days (Batch Test 2), respectively. In Batch Test 3, a dilute nitric acid solution ( $\text{pH}=4$ ) was prepared from ultrapure  $\text{HNO}_3$  (Seastar, Inc. double sub-boiling, distilled in quartz) and distilled-deionized water, and subsequently reacted with the crushed rock samples for 42 days at room temperature ( $\sim 25^{\circ}\text{C}$ ; Table 5.1). During each batch test period, all sample bottles containing the crushed rock - leaching solution mixtures were agitated for 5 minutes each day to allow a complete reaction between rock sample and leaching solution. Following completion of the reaction period, the leachate solutions were separated from the crushed rock using a centrifuge, and then filtered through  $0.45\ \mu\text{m}$  Nuclepore® filters (Johannesson and Zhou, 1999).

#### 5.2.2.2. REE analysis of leachates

All leachate samples were acidified using ultra-pure nitric acid (Seastar, Inc. double sub-boiling, distilled in Teflon®), and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Perkin-Elmer® Elan 5000) with ultrasonic nebulization. The ultrasonic nebulization increased the analytical sensitivity and decreased the potential interferences from oxide formation in the plasma stream. Due to the small amount of leachate from each batch test, no pre-concentration by cation-exchange has been done. The following REE isotopes were selected for analysis since they have no or less elemental isobaric interferences:  $^{139}\text{La}$ ,  $^{140}\text{Ce}$ ,  $^{141}\text{Pr}$ ,  $^{146}\text{Nd}$ ,  $^{149}\text{Sm}$ ,  $^{151}\text{Eu}$  and  $^{153}\text{Eu}$  (mean value),  $^{157}\text{Gd}$ ,  $^{159}\text{Tb}$ ,  $^{163}\text{Dy}$ ,  $^{165}\text{Ho}$ ,  $^{166}\text{Er}$ ,  $^{169}\text{Tm}$ ,  $^{172}\text{Yb}$ , and  $^{175}\text{Lu}$ . During ICP-MS analysis, a series of 5 standards of known concentrations (i.e.,  $0.1\ \mu\text{g/kg}$ ,  $0.5\ \mu\text{g/kg}$ ,  $1.0\ \mu\text{g/kg}$ ,  $5.0\ \mu\text{g/kg}$ , and  $10.0\ \mu\text{g/kg}$ ) were prepared and routinely monitored in order to

calibrate the instrument, check the calibration, and calculate the sample REE concentrations. The REE values determined in the Method Blanks were subtracted from the leachate solutions to obtain the leachate concentrations.

### 5.2.3. Analysis of REE in Rock Samples

The REEs were measured in 17 rock samples using ICP-MS (Perkin-Elmer® Elan 5000) as discussed in Johannesson and Zhou (1999). Briefly, approximately 0.25 grams of each rock (i.e., powder) sample were placed in precleaned Teflon®-lined microwave digestion bombs, followed by 5 mL of ultrapure HF (Seastar, Inc. double sub-boiling, distilled in Teflon®) and 5 mL of ultrapure HNO<sub>3</sub> (Seastar, Inc. double sub-boiling, distilled in quartz). The Teflon®-lined microwave digestion bombs were then sealed and placed in a microwave oven (CEM Corporation MDS-2100) and heated to 189°C and pressurized to  $8.62 \times 10^5$  Pa (125 p.s.i.) for 25 minutes. After 25 minutes, the samples were allowed to cool before 30 mL of a saturated boric acid solution was added to each sample. The samples were subsequently heated again in the microwave for 5 minutes at 100°C and  $6.9 \times 10^4$  Pa -  $1.38 \times 10^5$  Pa (10 - 20 p.s.i.). The dissolved rock samples were then decanted into clean polyethylene bottles and diluted by a factor of 180 before analysis by ICP-MS. The U.S. Geological Survey rock standard W-2 (diabase) was included as a check standard during the analysis from which our measurements never deviated by more than 10% (Guo, 1996).



### 5.3. Analytical Result

#### 5.3.1. REE Concentrations of Southern Nevada Rocks

The REE concentrations (in ppm) for 16 different sedimentary rock samples and one rhyolite (Surprise 1) examined in this study are presented in Table 5.2. Again, these same rock samples were used in the different batch leach tests of this study. The chondrite-normalized REE patterns for these rock (both silicate and carbonate rocks) samples are plotted in Fig. 5.1. The chondrite-normalizing factor that was employed for the normalization calculations is that tabulated by Hanson (1980).

The silicate rocks (Fig. 5.1a) have REE concentrations that are on average about a factor of 10 greater than the carbonate rocks examined in the study (Fig. 5.1b; Table 5.2). Moreover, every rock analyzed exhibits an enrichment in the light REEs (LREE) over the heavy REEs (HREE) compared to chondrite (Fig. 5.1). The chondrite-normalized Nd/Yb ratios  $[(Nd/Yb)_{CN}]$ , where CN = chondrite-normalized) range from 1.7 for one of the Bonanza King dolostone samples, up to 5.6 for sample BAS6 from the Bright Angel Formation (Table 5.2). All of the carbonate rocks have chondrite-normalized negative Ce anomalies, whereas the silicate rocks exhibit both negative and positive Ce anomalies (Fig. 5.1). When the rock samples are normalized to Average Shale, they exhibit relatively flat patterns (not shown) as demonstrated by their  $(Yb/Nd)_{SN}$  ratios (where SN = shale-normalized), which are generally close to 1 (Table 5.2). The Average Shale values used to calculate these shale-normalized ratios is the composite "Average Shale" previously used by oceanographic researchers (e.g., Elderfield and Greaves, 1982; DeBaar et al., 1983; Sholkovitz, 1988), and in our previous investigations (Johannesson

Table 5.2. Concentrations of rare earth elements (ppm) in aquifer materials (rocks) used for batch tests.

CN = chondrite-normalized, SN = shale-normalized.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Nd/Yb) <sub>CN</sub>	(Yb/Nd) <sub>SN</sub>	Ce/Ce*	Eu/Eu*
BAS(SS)1	13.15	47.62	4.22	18.74	5.49	1.31	6.79	1.12	6.22	1.29	3.52	0.48	2.97	0.46	2.10	1.72	0.19	-0.04
BAS(SL)2	37.84	79.41	10.85	41.63	7.95	1.52	6.80	1.08	5.93	1.29	3.84	0.58	3.99	0.62	3.48	1.04	-0.02	-0.05
BAS6	57.72	97.01	13.70	48.50	8.15	1.50	6.76	1.01	5.35	1.07	3.11	0.45	2.86	0.43	5.65	0.64	-0.07	-0.06
Tapeats 1	11.02	31.26	2.80	10.41	1.96	0.39	1.74	0.24	1.19	0.23	0.69	0.11	0.70	0.11	4.97	0.73	0.14	-0.05
Surprise 1	18.74	39.84	4.89	17.66	3.82	0.61	3.50	0.57	3.22	0.66	1.84	0.28	1.81	0.27	3.25	1.11	0.01	-0.15
FR8Oaal	2.32	5.05	0.54	2.11	0.40	0.10	0.41	0.07	0.34	0.08	0.22	0.03	0.18	0.03	3.85	0.94	0.04	0.01
BKD1	1.09	1.50	0.14	0.53	0.09	0.02	0.09	0.01	0.08	0.01	0.05	0.00	0.04	0.00	4.96	0.73	-0.05	-0.11
BKD2	0.61	1.23	0.14	0.52	0.09	0.02	0.11	0.01	0.10	0.02	0.06	0.01	0.05	0.00	3.69	0.98	0.02	-0.13
BKD3	3.22	7.00	0.81	3.07	0.62	0.15	0.60	0.11	0.66	0.15	0.47	0.07	0.47	0.07	2.18	1.66	0.03	0.01
BKD4	3.42	7.51	0.94	3.60	0.72	0.15	0.69	0.11	0.66	0.13	0.39	0.06	0.37	0.06	3.26	1.11	0.01	-0.04
BKD5	6.93	14.73	1.77	6.65	1.36	0.25	1.28	0.21	1.24	0.26	0.78	0.11	0.72	0.11	3.07	1.18	0.01	-0.10
BKD6	2.48	4.46	0.47	1.83	0.35	0.06	0.34	0.05	0.35	0.07	0.23	0.03	0.21	0.03	2.88	1.25	0.00	-0.10
BKD7	1.09	2.01	0.25	0.92	0.16	0.04	0.16	0.03	0.14	0.03	0.08	0.01	0.08	0.01	4.04	0.89	-0.02	0.07
BKD8	3.90	8.18	1.02	3.79	0.71	0.15	0.68	0.11	0.62	0.13	0.41	0.05	0.37	0.05	3.40	1.06	0.00	-0.03
BKD9	5.93	12.80	1.57	6.13	1.36	0.30	1.36	0.24	1.57	0.35	1.12	0.18	1.19	0.19	1.71	2.11	0.01	-0.02
BKD10	2.98	5.35	0.62	2.28	0.38	0.08	0.38	0.05	0.32	0.07	0.19	0.02	0.17	0.02	4.53	0.80	-0.02	-0.04
BKD11	4.86	9.92	1.19	4.49	0.98	0.19	0.86	0.15	0.88	0.19	0.55	0.09	0.56	0.09	2.87	1.26	0.01	-0.30

$$\text{Ce/Ce}^* = \log \{ 2\text{Ce}_{\text{SN}} / [\text{La}_{\text{SN}} + \text{Pr}_{\text{SN}}] \}.$$

$$\text{Eu/Eu}^* = \log \{ 2\text{Eu}_{\text{SN}} / [\text{Sm}_{\text{SN}} + \text{Gd}_{\text{SN}}] \}.$$

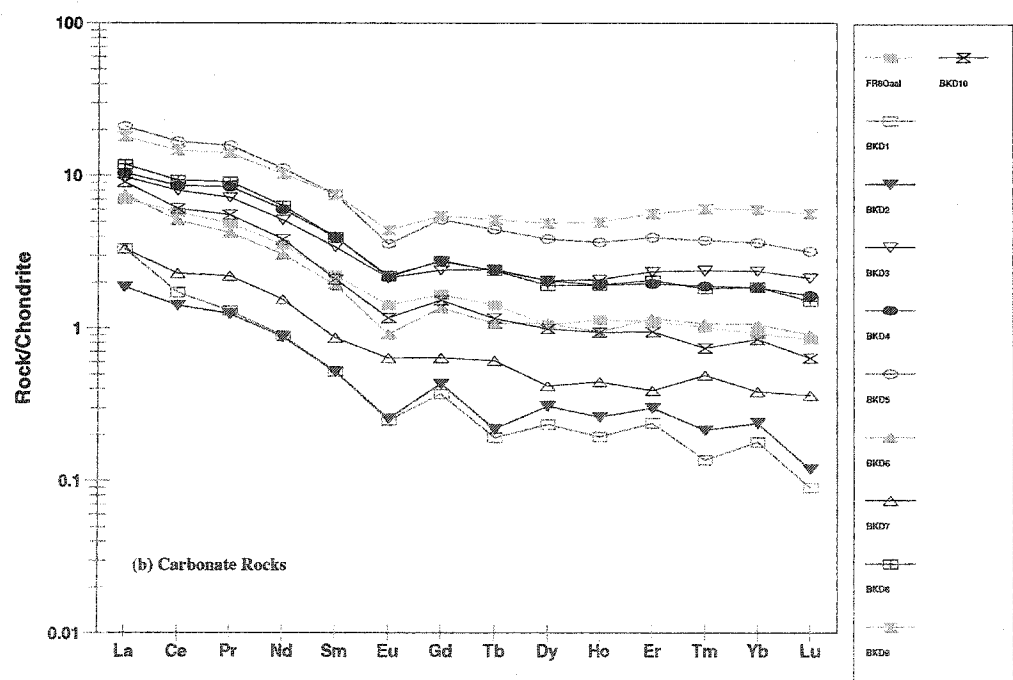
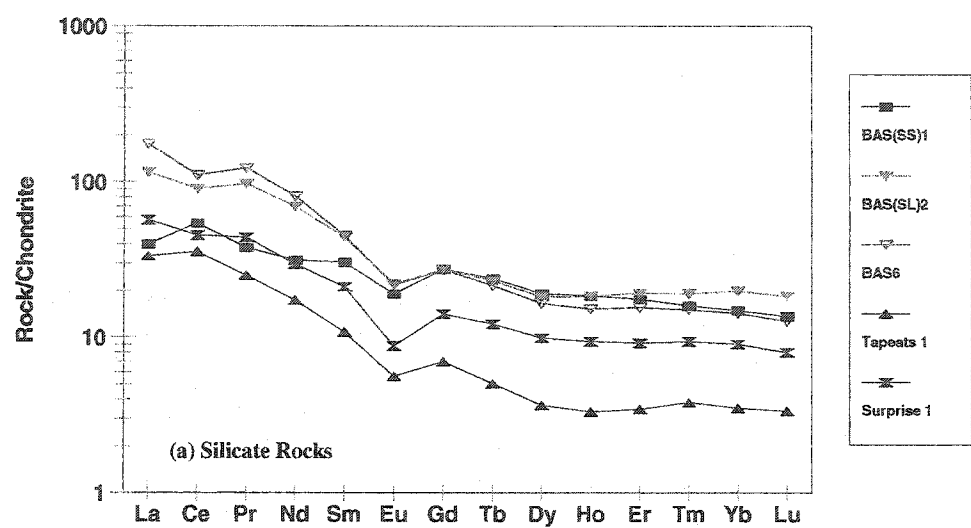


Fig. 5.1. Chondrite-normalized REE patterns for (a) silicate rocks, and (b) carbonate rocks from Frenchman Mountain near Las Vegas and Fossil Ridge in southern Nevada. These rock samples were prepared and used for our batch leach tests.

et al., 1997, 2000).

The chondrite-normalized REE patterns for the silicate and carbonate rocks of southern Nevada demonstrate that the carbonate rocks contain lower abundances of all of the REEs than the silicate rocks (Fig. 5.1). The spiky HREE patterns exhibited by some of the carbonate rocks (i.e., BKD1 and BKD2) reflect the difficulty encountered in quantifying the HREEs in these two rock samples using the digestion and analytical methods employed in this study. Many of the HREE for BKD1 and BKD2 approach or are below the method detection limits for our ICP-MS using the above described digestion techniques (e.g., Guo, 1996).

### 5.3.2. REEs of the Leach Solutions

#### *5.3.2.1. Leachable fraction using distilled water*

The REE data for each batch test are presented in Table 5.3. The data shows that individual REE concentrations in the leachate solutions from Batch Test 1 are very low, ranging from 1.4 pmol/kg to 2,570 pmol/kg (Table 5.3). In Batch Test 1, the solution that reacted with rhyolitic pumice (Surprise1) had the highest REE concentrations, whereas the solutions that reacted with Ordovician limestone (FR8Oaal), and with Cambrian dolomite (BKD3) exhibit the lowest REE concentrations (Table 5.3).

Rare earth element concentrations for each of the leachate solutions from Batch Test 1 are plotted in Fig. 5.2, where each leachate has been normalized to the REE concentrations determined in the respective rock with which each reacted. All of the leach solutions from Batch Test 1 have substantially lower REE concentrations than the

Table 5.3. Concentrations of rare earth elements (pmol/kg) in leachates from three batch tests. RN = rock-normalized.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Yb/Nd) <sub>RN</sub>	Ce/Ce*	Eu/Eu*
<b>Batch Test 1</b>																	
BKD3	179.3	135.6	18.1	78.7	19.9	43.9	19.0	1.4	11.5	1.5	4.5	0.0	5.3	0.0	0.52	-0.30	0.97
Surprise 1	1594.6	2574.2	320.8	1201.8	216.1	95.1	232.1	30.0	174.2	37.7	117.5	18.7	124.1	19.8	1.21	-0.07	0.40
BAS(SL)2	185.0	464.6	59.7	226.4	47.1	26.5	50.3	7.2	38.0	6.3	20.1	3.5	18.7	3.4	1.04	0.05	0.41
BAS(SS)1	199.4	498.1	56.3	270.0	98.7	50.0	145.3	21.1	116.9	21.0	50.9	7.3	39.5	5.0	1.10	-0.13	0.28
FR8Oaal	194.4	28.0	6.6	17.6	1.5	4.3	3.2	0.0	1.7	0.0	0.0	0.0	1.8	0.0	1.44	-0.93	0.87
<b>Batch Test 2</b>																	
Tapeats 1	122.5	213.7	22.1	79.6	21.9	146.3	15.4	2.0	8.8	2.1	6.9	1.4	2.1	0.7	0.48	-0.14	1.57
BAS6	506.5	475.8	77.2	341.7	72.5	27.6	91.2	12.3	58.3	9.9	33.6	3.0	36.7	5.3	2.18	-0.17	0.21
BKD1	43.9	120.4	11.2	54.9	22.1	22.1	24.5	4.2	22.9	2.8	9.6	1.8	7.1	0.9	2.31	0.13	0.71
BKD2	41.4	51.1	5.2	21.8	7.4	56.0	8.0	0.6	2.4	0.5	2.4	0.4	1.5	0.2	0.91	-0.10	1.61
BKD4	15.5	19.7	3.1	12.6	3.3	7.9	4.8	0.4	4.2	0.6	1.7	0.5	1.0	0.2	0.95	-0.17	0.96
BKD5	22.3	34.0	5.3	15.1	3.9	23.7	4.9	0.5	2.1	0.9	2.3	0.8	3.7	0.4	2.74	-0.13	1.45
BKD6	28.0	20.7	3.2	8.9	2.8	15.3	1.7	0.0	2.7	0.6	0.7	0.5	0.5	0.1	0.58	-0.29	1.56
BKD7	17.4	26.1	4.1	12.5	6.2	8.5	2.4	0.2	3.3	0.2	1.6	0.5	1.3	0.3	1.54	-0.10	0.85
BKD8	20.0	16.1	1.6	7.0	2.8	18.2	2.7	1.0	0.9	0.5	1.1	0.5	0.9	0.4	1.53	-0.23	1.48
BKD9	28.5	39.2	4.9	15.7	6.2	19.5	4.4	0.3	5.7	0.2	1.7	0.3	1.6	0.2	0.62	-0.11	1.22
BKD10	20.4	29.7	3.6	12.1	4.3	12.7	2.8	1.3	2.9	0.7	0.9	1.3	3.1	0.9	4.18	-0.06	1.22
BKD11	399.2	821.6	104.3	392.0	77.2	27.4	67.9	10.5	60.1	12.2	29.8	4.3	29.3	4.4	0.72	-0.01	0.27
<b>Batch Test 3</b>																	
FR8Oaal	221.7	245.5	43.5	183.7	37.2	15.0	37.5	6.6	24.7	5.8	22.3	1.4	11.4	1.4	0.86	-0.26	0.22
BAS6	334.0	1829.1	67.1	242.0	80.5	60.6	76.9	10.3	42.4	14.5	20.7	4.7	29.9	5.7	2.51	0.55	0.57
BKD1	138.9	2635.6	56.8	153.2	13.9	27.8	36.2	3.8	16.8	1.8	16.2	0.0	12.8	1.4	1.49	0.83	0.77
Tapeats 1	63.7	1513.0	16.1	88.7	11.0	223.1	19.7	0.0	4.8	0.0	2.1	0.0	3.0	0.0	0.61	0.92	1.82

$$\text{Ce/Ce}^* = \log \{2\text{Ce}_{\text{RN}}/[\text{La}_{\text{RN}} + \text{Pr}_{\text{RN}}]\}.$$

$$\text{Eu/Eu}^* = \log \{2\text{Eu}_{\text{RN}}/[\text{Sm}_{\text{RN}} + \text{Gd}_{\text{RN}}]\}.$$

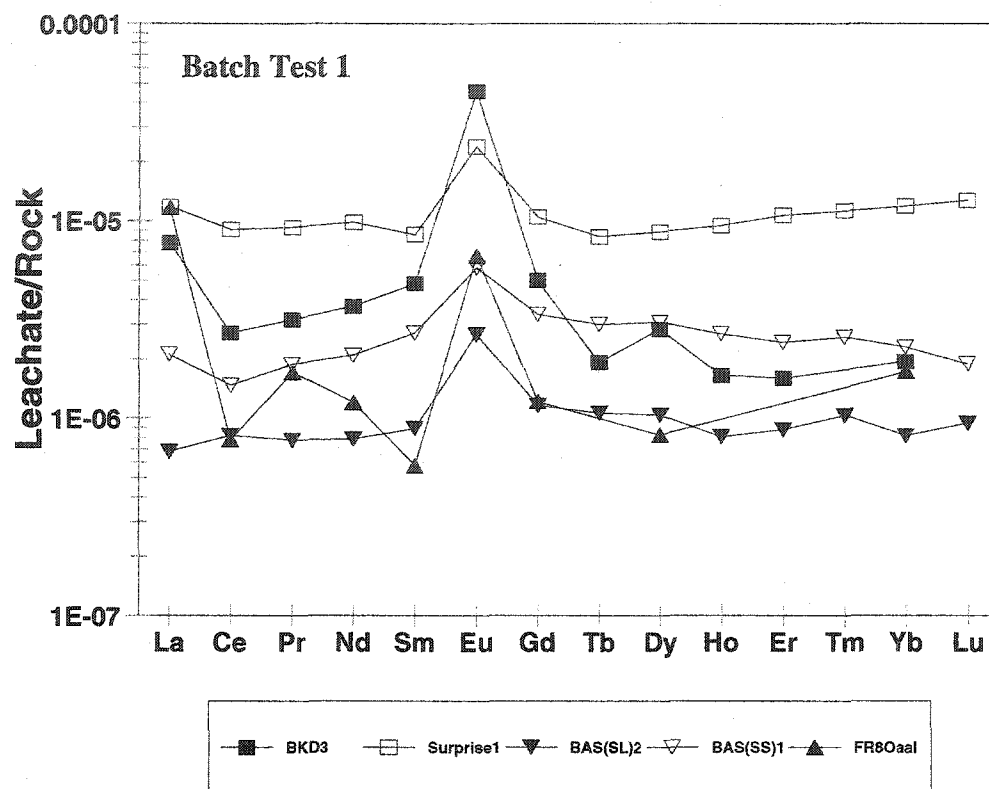


Fig. 5.2. Rock-normalized REE patterns of the leachate solutions from Batch Test 1.

respective rocks (e.g., between a factor of  $10^5$  to  $10^6$  lower). Interestingly, except for Eu in each case, and La for the leachates that reacted with BKD3 and FR8Oaal, the rock-normalized REE patterns for the leachate are relatively flat (Fig. 5.2). This flat rock-normalized pattern is best developed for the leachates that reacted with the rhyolitic rock sample, Surprise 1, with shale BAS(SL)2, and with fine sandstone BAS (SS)1 [(Yb/Nd)<sub>RN</sub> = 1.21, 1.04, 1.10, respectively; Table 5.3]. These flat patterns indicate that REEs were leached from these rocks in essentially the same relative proportions at which

they occur in their respective rock samples. There is evidence for a slight enrichment in the HREEs in the Surprise 1 leach solutions, as the rock-normalized pattern for this leach solution exhibits a shallow positive slope between Tb and Lu (Fig. 5.2). There may also be some enrichment in the HREEs of the leachate solution that reacted with FR8Oaal, however, insufficient data exists for the HREEs in this leachate (e.g., only Dy and Yb were quantified by our method). On the other hand, the leachates that reacted with dolomite (BKD3) and the sandstone [BAS(SS)1] may have slight enrichments in the middle REEs (MREE) compared to their respective rocks. The Batch Test 1 leachates have variously enriched and depleted Ce concentrations. The leachate that reacted with BAS(SL)2 exhibits weak positive Ce anomaly ( $Ce/Ce^* = 0.05$ ; Table 5.3), whereas Surprise 1, BKD3, FR8Oaal, and BAS(SS)1 have negative Ce anomalies ( $Ce/Ce^* = -0.07, -0.30, -0.93, -0.07$ , respectively; Table 5.3). On the other hand, the Eu concentration in each leachate is higher than expected based on the rock-normalized values for Sm and Gd ( $0.28 \leq Eu/Eu^* \leq 0.97$ ; Table 5.3).

Table 5.3 contains rare earth element concentrations for each of the leachate solutions from Batch Test 2. The solutions that reacted with one of the Cambrian dolomites (BKD11), and the shale (BAS6) had the highest REE concentrations, whereas the solutions that reacted with other Cambrian dolomites (e.g. BKD4 and BKD8) exhibit the lowest REE concentrations (Table 5.3). The chief differences in Batch Test 2, compared to Batch Test 1, were the greater solution/rock sample ratio (by weight, 3:1 vs. 2:1, respectively; Table 5.1), and the greater duration at Batch Test 2 (67 days vs. 40 days for Batch Test 1; Table 5.1).

Figure 5.3 is a rock-normalized REE plot of the leachate solutions from Batch Test 2, where each leach solution has been normalized to the respective rock with which it reacted. In general, the shapes of these rock-normalized leachate patterns resemble those from Batch Test 1 in that they are all relatively flat, and have large positive Eu anomalies ( $0.21 \leq \text{Eu}/\text{Eu}^* \leq 1.61$ ; Table 5.3). Only two leachate samples do not exhibit the same degree of positive enrichment in Eu compared to Sm and Gd; BAS6 and

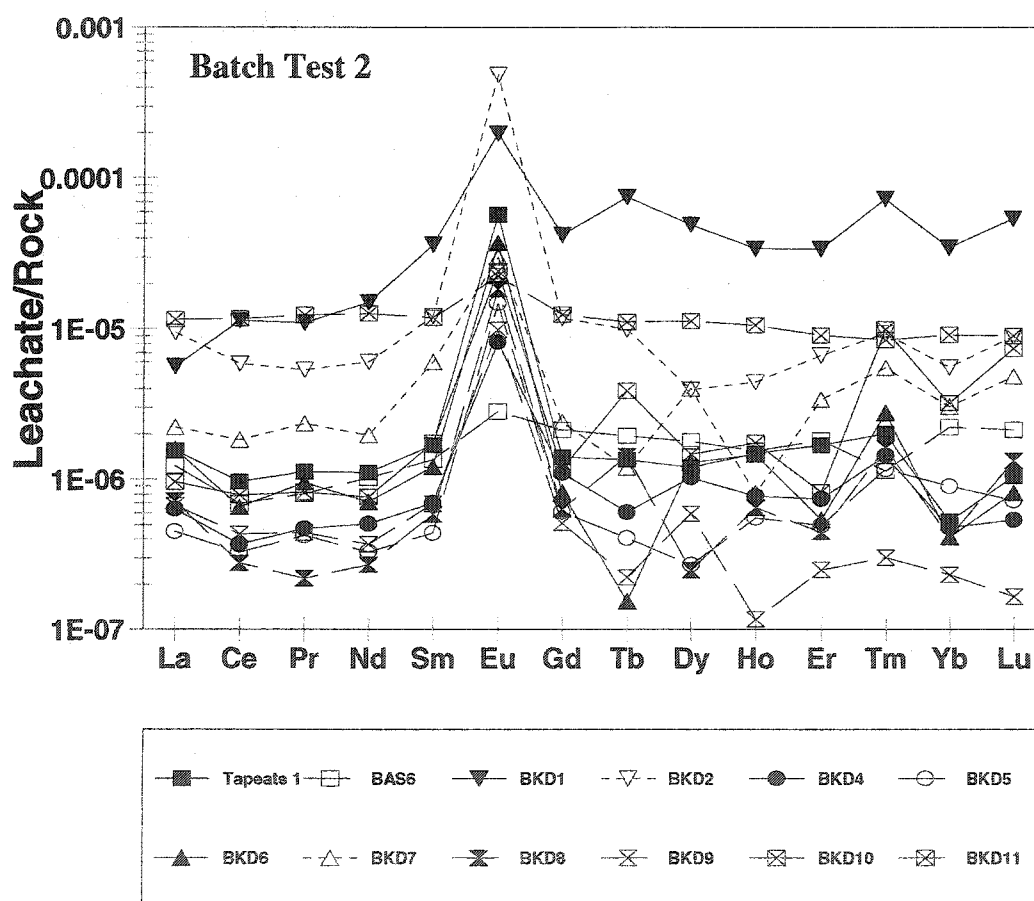


Fig. 5.3. Rock-normalized REE patterns of the leachate solutions from Batch Test 2.



BKD11 have  $\text{Eu}/\text{Eu}^*$  of 0.21 and 0.27, respectively (Table 5.3). These leachates also exhibit weak negative Ce anomalies ( $-0.29 \leq \text{Ce}/\text{Ce}^* \leq -0.01$ ), except for the leachate that reacted with BKD1 ( $\text{Ce}/\text{Ce}^* = 0.13$ ; Table 5.3). The chief differences between the results of these two batch tests are the smoother LREE patterns and more variability in the HREE patterns of the Batch Test 2 leachates compared to the Batch Test 1 leachates.

#### 5.3.2.2. *Leachable fraction using acidic water solution*

Table 5.3 also lists the REE concentrations of leach solutions from Batch Test 3, in which crushed rock samples were reacted with a weak nitric acidic solution ( $\text{pH} = 4$ ) for 42 days. Similar to the other batch tests, the REE concentrations of these leachates are very low, ranging from 1.1 pmol/kg to 2,630 pmol/kg (Table 5.3). The solution that reacted with Cambrian dolomite (BKD1) had the highest REE concentrations, whereas the solution that reacted with Tapeats Sandstone (Tapeats1) had the lowest REE concentrations (Table 5.3).

Rock-normalized REE ratios of these weak nitric acid leach solutions are plotted in Fig. 5.4. Because these leachates have similar (i.e., order of magnitude) REE concentrations to those of Batch Test 1 (Table 5.3), they also exhibit similar rock-normalized ratios. Again, all of the leachates of Batch Test 3 exhibit positive Eu anomalies which range from a low of  $\text{Eu}/\text{Eu}^* = 0.22$  up to  $\text{Eu}/\text{Eu}^* = 1.82$  (Table 5.3). In addition, all but the leachate that reacted with the Ordovician Limestone (i.e., FR8Oaal) have large positive Ce anomalies (Fig. 5.4). The leachate that reacted with FR8Oaal instead exhibits a small negative Ce anomaly ( $\text{Ce}/\text{Ce}^* = -0.26$ ; Table 5.3). Neglecting the Ce and Eu anomalies, the leachates that reacted with FR8Oaal, BAS6, and Tapeats1,

have relatively flat rock-normalized REE patterns. However, the rock-normalized REE pattern for the leachate that reacted with BKD1 exhibits an irregular shape (Fig. 5.4).

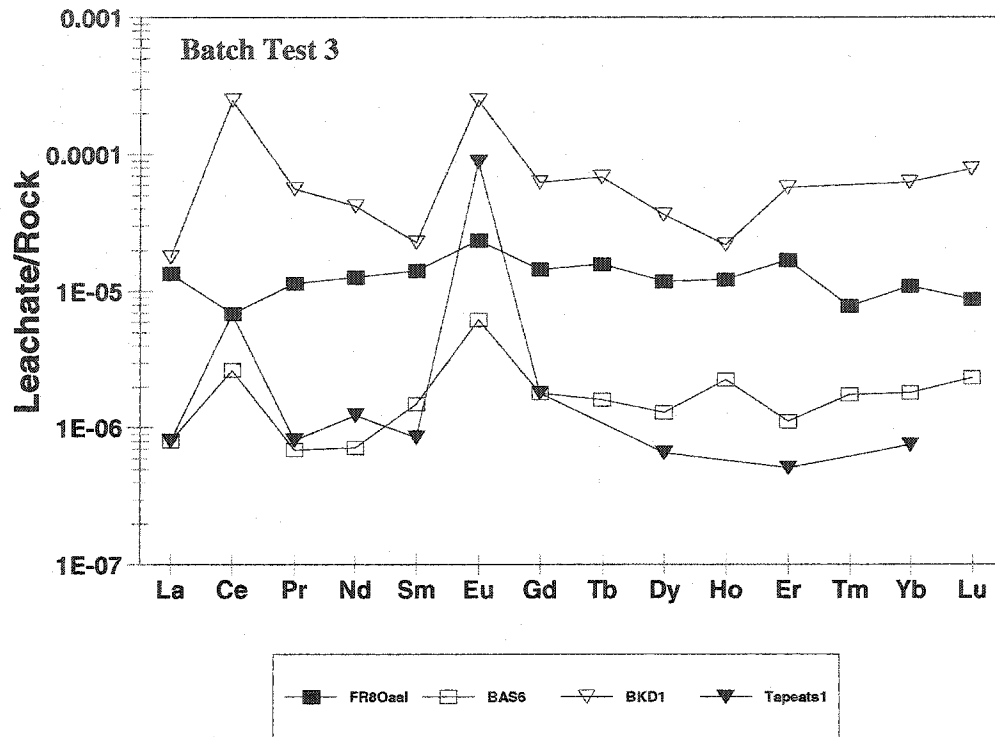


Fig. 5.4. Rock-normalized REE patterns of the leachate solutions from Batch Test 3.

## 5.4. Discussion

### 5.4.1. REE Signatures of Leachates

Many of the leachate solutions have REE signatures that are not substantially fractionated compared to the rock samples with which they reacted, and hence, the source of the dissolved REEs in the leachates (Figs. 5.2 - 5.4). The similarities in the relative proportions of REEs between the rock samples and the leachates are especially apparent for the distilled-deionized water leachates (i.e., Batch Tests 1 and 2; Figs. 5.2 and 5.3).

These data indicate that, in general, the REEs in these rocks must be in readily leachable sites. Although overall the distilled-deionized water leachates exhibit relatively flat REE patterns when normalized to their respective rock sample, there are some subtle deviations that suggest minor fractionation of the REEs during the leaching process. For example, the leachate with perhaps the flattest rock-normalized pattern (i.e., Surprise 1, rhyolite) also exhibits a smooth increase in rock-normalized HREE values with increasing atomic number (Fig. 5.1). This smooth increase between Tb and Lu suggests that either (1) heavier REEs are located within progressively more readily leachable sites within the source rocks than the LREEs, or (2) solution complexation reactions in the distilled-deionized leachate become important as the water reacts with the rocks leading to preferential leaching and stabilization of HREEs within solution. Many investigators have argued that during the weathering process, LREEs released are subsequently captured by secondary clay minerals formed by weathering reactions, whereas the HREEs are preferentially liberated from the rock and removed from the site of weathering by solution complexation reactions involving inorganic and/or organic ligands (Nesbitt, 1979; Duddy, 1980; Schau and Henderson, 1983; Braun et al., 1993). It is well known that stability constants for REE complexes with carbonate ions increase with increasing atomic number (Cantrell and Byrne, 1987; Lee and Byrne, 1993). Moreover, productions of bicarbonate and carbonate ions are a common product of weathering reactions involving silicate rocks and dissolution of carbonate rocks, respectively (e.g., Garrels and MacKenzie, 1967; Langmuir, 1971). Bicarbonate ions were likely produced in our Batch Test 1 and 2 as distilled-deionized water reacted with

the crushed rock samples.

Some of the leachates from the dolomites (Batch Test 2; Fig. 5.2) also exhibit enrichments in the HREEs relative to the LREEs, although the same, relatively smooth progressive increase in rock-normalized values reported for the Surprise 1 leachate is not observed. Instead, some of these dolostone leachates have a step-like rock-normalized REE pattern, with relatively lower LREE normalized values that step up to higher values between Nd and Sm, and are relatively constant from Tb through Lu (BKD1, Fig. 5.3).

Another subtle fractionation pattern of the rock-normalized leachate profiles is slight enrichments in the middle REEs. This subtle fractionation is only observed in leachates that reacted with the clastic sedimentary rock samples of the Bright Angel Formation [i.e., BAS(SS)1, BAS(SL)2; Fig. 5.2]. Johannesson and Zhou (1999) reported similar, albeit more pronounced, rock-normalized MREE enriched patterns for strong acid leach solutions that reacted with clastic sedimentary rocks containing Fe-Mn oxide/oxyhydroxide phases. Moreover, using a leach solution that specifically targets Fe-Mn oxide/oxyhydroxide phases (i.e., 0.04 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% (v/v)  $\text{CH}_3\text{COOH}$ ), these authors reported MREE enriched, rock-normalized REE patterns for those leachates that reacted with the clastic sedimentary rocks containing petrographically identifiable Fe-Mn oxide/oxyhydroxide phases. Johannesson and Zhou (1999) suggested that the MREE enriched patterns of the leachates reflected the distribution of the REEs in the Fe-Mn oxide/oxyhydroxide phases within these rocks. Others have shown that such oxide phases commonly exhibit MREE enrichments (Gosselin et al., 1992). Consequently, the slight MREE enrichments of the distilled-deionized water leachates for the two Bright

Angel Formation samples compared to their respective rocks may reflect the presence of Fe-Mn oxide/oxyhydroxide phases within these clastic sedimentary rocks that supply MREEs to the leachate solutions. Further investigation may involve leaching these rocks with a hydroxylamine hydrochloride solution to specifically examine the possible contributions of Fe-Mn oxide/oxyhydroxide phases to their readily leachable REE fractions.

Interestingly, the distilled-deionized water leachate of Batch Test 1 that reacted with BKD3 exhibits higher rock-normalized LREE values than observed for the HREEs (Fig. 5.2). The REE pattern of this leach solution suggests that the LREEs occur in sites in BKD3 that are more readily leached by distilled-deionized water than the HREEs, or alternatively, the LREEs are preferentially leached from the rock owing to the formation of preferentially stronger LREE complexes of some ligand with the LREEs than the HREEs. It is difficult to identify a ligand that could occur in distilled-deionized water that more strongly complexes the LREEs in solution than the HREEs. Because BKD3 is a dolomite, carbonate ions are expected to increase in the distilled-deionized water leachate as a result of reacting the dolomite with the neutral pH solution. As a consequence, we would expect that the HREEs would be more stable in the leachate than LREEs owing to complexation of the REEs with carbonate ions. Therefore, the enrichment of the LREEs in this leachate likely reflects that the LREEs occur in more easily leached sites than the HREEs in BKD3.

The most interesting feature of Batch Test 3 is that all of the leachates except for the one that reacted with the Ordovician limestone, FR8Oaal, exhibit positive, rock-

normalized Ce anomalies (Fig. 5.3). Batch Test 3 involved reacting each of the rock samples with a weak nitric acid solution ( $\text{pH} = 4$ ), and hence was different than the other batch tests where distilled-deionized water ( $\text{pH} \approx 7$ ) was used. Instead, the Tapeats Sandstone has an enrichment in Ce relative to La and Pr when normalized to chondrite. Consequently, the positive Ce anomaly of the leachate sample that reacted with the Tapeats Sandstone indicates that the weak nitric acid leachate preferentially liberated Ce from the Tapeats Sandstone compared to both La and Pr. The same preferential leaching of Ce from the rocks can be argued for both BAS6 and BKD1 as a result of reacting these rocks with the weak acid solution (Fig. 5.4). Relatively more Ce must have been leached from the Tapeats Sandstone, however, for the leachate solution to be enriched in Ce with respect to La and Pr when normalized to the Ce enriched Tapeats Sandstone (compare Figs. 5.1 and 5.4). The difference in the behavior of Ce between the distilled-deionized leachate solutions and the weak nitric acid solutions indicates that a Ce enriched mineral of amorphous phase, which is susceptible to the weak acid leach but not the distilled-deionized water solutions, is present in these southern Nevada sedimentary rocks.

As mentioned above, all of the leachates exhibit positive Eu anomalies when normalized to their respective rocks. These positive Eu anomalies may reflect either  $\text{BaO}^+$  interference on the two naturally occurring Eu isotopes (i.e.,  $^{151}\text{Eu}$  and  $^{153}\text{Eu}$ ) during mass quantification by ICP-MS (i.e., Jarvis et al., 1989), or simply the fact that the rocks are depleted in Eu with respect to their chondrite-normalized Sm and Gd values (Fig. 5.1; Table 5.2). We believe that for the vast majority of the leachates, the large positive Eu anomalies reflect Ba interference during quantification (i.e., false positive).

For groundwater samples, the majority of the Ba is removed from the sample by extraction using diethylhexylphosphoric acid (Cerrai and Ghersini, 1966; Hodge et al., 1998). Typically, at least a 500 mL aliquot of each groundwater sample is required to quantify Eu after Ba is extracted from the sample. Unfortunately, insufficient leachate volumes were recovered during the batch tests in the current study (Table 5.1) to conduct the diethylhexylphosphoric acid extraction of Ba from these solutions, and subsequently measured dissolved Eu concentrations.

Nonetheless, it is important to point out that for some of the leachate solutions, the Eu data suggests that false positives during mass quantification from Ba interferences may not be responsible for the positive Eu anomalies. These leachate solutions include those that reacted with BAS(SL)2, BAS(SS)1 of Batch Test 1, BAS6, BKD11 of Batch Test 2, and FR8Oaal and BAS6 of Batch Test 3. For the case of these leachate solutions, the positive Eu anomalies that are characteristic of the leachates are likely due, in part, the large negative Eu anomalies of the rocks. In other words, because of the depletion in Eu (i.e., negative Eu anomalies) that is characteristic of these sedimentary (and felsic igneous) rocks of southern Nevada, normalization of leachate Eu values to the rock values leads, in part, to the positive rock-normalized Eu anomalies of the leachates. For example, the Eu concentration of the leachate that reacted with Surprise 1 rhyolitic pumice (i.e., 95.1 pmol/kg) is substantially lower than either the Sm or Gd concentrations (216 pmol/kg and 232 pmol/kg, respectively) in the leachate. Indeed, the Eu concentration of this leachate is 2.3 times lower than the corresponding Sm value, and 2.4 times lower than the Gd concentration. Moreover, the Eu concentration of the rhyolitic

source rock is a factor of 6.3 lower than Sm, and 5.7 times lower than the Gd concentrations in this rock (Table 5.2). Hence, because the Eu concentration of the leachate is substantially lower than the corresponding Sm and Gd concentrations, the positive Eu anomaly of the rock-normalized leachate probably reflects the large Eu depletion of the rhyolitic rock, Surprise 1.

#### 5.4.2. Implications of Batch Tests

The results of our batch leaching tests are in general agreement, in terms of the similarities between the REE distributions of the leachates and the rock samples, with previous field investigations that reported groundwaters with REE signatures that closely mimicked the REE signatures of the aquifer rocks through which they flowed (e.g., Smedley, 1991; Gosselin et al., 1992; Fee et al., 1992; Leybourne et al., 2000). In addition, the measured REE concentrations in the leachates from our batch tests are grossly similar, in magnitude, to those reported for groundwaters, including groundwaters from southern Nevada (Johannesson et al., 1997; 2000a). Consequently, the batch test data suggest that aquifer rocks are the primary source of REEs to groundwaters, and more importantly, REEs are leached from aquifer rocks by aqueous solutions in proportions similar to those found in the rock/aquifer materials. Consequently, the similarities between the results of our batch leach tests (i.e., REE concentrations and rock-normalized patterns) and reported observations of REE concentrations and patterns in actual groundwater-aquifer systems strongly suggests that groundwaters can inherit aquifer-rock like REE signatures via leaching reactions with the aquifer rocks without incurring



significant fractionation of the REEs during the process.

It is generally well accepted that the acquisition of REEs by natural terrestrial waters from rock weathering reactions depends upon many factors including (1) the distribution and abundance of REE-bearing minerals within the rocks (2) the chemical composition of the natural water/weathering solution (e.g., major solute concentrations, pH, pe, concentrations of inorganic and organic complexing ligands, temperature), (3) the solubility of the REE-bearing minerals in the rocks with respect to the composition of the natural water/weathering solution, and (4) the ability of secondary minerals formed during water-rock reactions to accept REEs leached from the primary minerals of the unweathered rock (Humphris, 1984; Braun et al., 1990; Johannesson and Zhou, 1999). Moreover, previous investigators have examined REE fractionation as a function of chemical weathering of different types of parent rocks (e.g., Balashov et al., 1964; Ronov et al., 1967; Ludden and Thompson, 1978, 1979; Nesbitt, 1979; Duddy, 1980; Schau and Henderson, 1983; Humphris, 1984; Middelburg et al., 1988; Braun et al., 1990, 1993, 1998). Many of these studies indicate that weathered residual materials become enriched in LREEs and depleted in the HREEs compared to the parent rock during water-rock reactions owing, in part, to preferential mobilization of the HREEs (Balashov et al., 1964; Ronov et al., 1967; Nesbitt, 1979; Duddy, 1980). More specifically, LREEs are obtained by secondary clay minerals formed by water-rock reactions, whereas HREEs are preferentially removed from the reaction site by solution complexation reactions involving inorganic and/or organic ligands (e.g.,  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ , humic and/or fulvic acids) that are present in natural waters, including groundwaters (Nesbitt, 1979; Duddy, 1980;

Schau and Henderson, 1983; Braun et al., 1993; Johannesson and Zhou, 1999).

Therefore, solution and surface (i.e., adsorption) complexation can play an important role in fractionating REEs during water-rock reactions by enriching the aqueous solutions in the HREEs, and preferentially concentrating the LREEs in the residual phases (e.g., clay minerals). On the other hand, in the absence of important inorganic and organic complexing ligands, the REEs exhibit greater tendencies to sorb to surface sites as a function of increasing atomic number (e.g., Roaldset, 1974; Aagaard, 1974).

The fact that the leachates resulting from the batch leach tests do not exhibit significant fractionation of the REEs compared to the aquifer rocks suggests that solution and surface complexation reactions involving these heavy metals were not important in the batch tests. More importantly, the observations reporting that many groundwaters have similar REE signatures to the aquifer rocks through which they flow implies that, at least in some cases, REEs are not fractionated during the weathering/leaching process whereby groundwater acquire their REE signatures. The results of our batch leaching tests and the reported REE patterns of actual groundwaters appear to contradict the observations and models of the behavior of REEs during the weathering process which argue for enrichment of the HREEs in the weathering solutions, and hence fractionation of the REEs. In other words, our batch tests along with studies of real groundwaters that during the of acquisition of these elements by groundwaters from the host aquifer rocks, their does not appear to be preferential removal of HREEs, compared to the LREEs, from the site of groundwater-aquifer rock interaction by strong ligands. Instead, these leachates and real groundwaters inherit REE distributions that closely resemble the source (i.e.,

aquifer) rocks.

However, more recent investigations have reported groundwaters with highly fractionated REE patterns compared to the aquifer/aquitard patterns (Johannesson et al., 1999; Johannesson and Hendry, 2000; Leybourne et al., 2000). For example, groundwaters from a shallow, basin-fill aquifer in southern Nevada, a till and clay-rich aquitard in Saskatchewan, and a rhyolitic aquifer in central México, all exhibit large enrichments in HREEs compared to LREEs when normalized to the REE concentration in their respective aquifer materials (Johannesson et al., 1999, 2000; Johannesson and Hendry, 2000). The fractionation of REEs in these groundwaters is consistent with the formation of carbonato and dicarbonato complexes in solution. More specifically, the LREE exhibit a greater affinity to sorb to aquifer/aquitard materials than the HREEs because they chiefly occur in these circumneutral pH groundwaters as positively charged solution species (i.e.,  $\text{LnCO}_3^+$ ,  $\text{Ln}^{3+}$ ,  $\text{LnSO}_4^+$ ), whereas the HREEs occur as negatively charged dicarbonato species (Johannesson and Hendry, 2000). Consequently, solution and surface complexation reactions do exert controls on REEs in groundwater-aquifer systems. Therefore, it is conceivable that during the initial weathering of aquifer rocks by relatively acidic aqueous solutions (e.g., meteoric waters augmented by soil-zone  $\text{CO}_2$ ), the REEs are leached from aquifer rocks in roughly the same proportion with which they occur in the rock. However, with flow within the aquifer and as more rock is weathered, solution complexation becomes progressively more important (e.g., production of  $\text{HCO}_3^-$  during weathering raises the pH and increases the significance of carbonate complexes) leading to strong fractionation of the REEs (Johannesson et al., 2000b, in review).

Although the current batch study shows some interesting results of REEs in the leachates during rock/water interactions, more leaching tests with systematic designs are needed to better constrain the leaching processes. The design parameters, such as pH values of solutions, particle sizes of crushed rock samples, water-rock batch contact time, and amount ratios of solution to rock sample, have to be carefully controlled for our future leaching studies. The systematic leaching studies using different types of rocks and solutions will help us to understand the relationship between aquifer rock and groundwater REE signatures, the leaching mechanisms and kinetics of REEs during water/rock interaction, and the controlling factors on REE signatures and fractionation in natural waters.

### 5.5. Conclusions

Laboratory batch tests were conducted in order to study the affect that compositionally different rocks have on the behavior and concentration of rare earth elements (REEs) in low-temperature aqueous solutions. Different rock types (i.e., shale, sandstone, limestone, dolomite, and rhyolitic pumice) were reacted with distilled deionized water (pH=7; 18 MΩ), and/or acidic aqueous solutions (pH=4). Rock samples were crushed to about 70 mesh in size. Different amounts of distilled deionized water or acidic aqueous solutions were mixed with 20 to 80 grams of individual crushed rock samples within acid-washed, pre-clean polyethylene bottles (mass ratio of aqueous solution to rock sample ranged from 2:1 to 3:1). The crushed rock samples and aqueous solutions were allowed to react for 40 to 65 days at room temperature (~ 25°C). The

sample slurry was subsequently centrifuged and the supernatant filtered (0.45  $\mu\text{m}$  polycarbonate membrane) before quantification of dissolved REEs by ICP-MS.

Concentrations of REEs in the leachate solutions are low, ranging from 0.05 pmol/kg to 2,570 pmol/kg. Solutions that reacted with rhyolitic pumice exhibit the highest REE concentrations, whereas the solutions that reacted with Ordovician limestone, and especially with Cambrian dolomite, have the lowest REE concentrations. When the leachates are normalized to the respective rock with which they reacted, they exhibit relatively flat REE patterns, except for large positive Eu anomalies. Interestingly, the solution that reacted with the pumice sample is slightly enriched in HREE, and the solution leached from Cambrian sandstone shows a weak MREE enrichment. These batch studies suggest that different types of rocks can play important roles in imparting REE signatures to natural waters, and in particular, groundwaters where rock/water ratios are high.

The results of our batch tests using aquifer materials and solutions allowed us to characterize REE signatures released from rock samples to leachates and to determine the easily soluble fractions of REEs during water/rock interaction under standard conditions. Moreover, this study provides information that may be applicable to REE behavior during low-temperature water/rock interaction in general. However, we should apply these batch test results to real groundwater systems with great cautions since other factors, such as filter size used, possible secondary minerals in rock samples and variations of laboratory conditions, could also affect REE patterns of the leachate solutions. More and systematic batch tests are needed to better control the leaching

processes during rock/water interactions.

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## CHAPTER 6

### CONCLUSIONS

Systematic studies on major ion and rare earth element (REE) geochemistry of different components of groundwater flow systems in southern Nevada and eastern California were conducted in this study. These studies characterize the major ion and REE geochemistry of groundwaters, aquifer rocks, and secondary minerals in the study area, compare REE signatures from both groundwater and aquifer materials (rocks and minerals), investigate the origins of secondary minerals in the unsaturated and saturated zones, and perform the leaching experiments using different aquifer materials and solutions.

Major ion geochemical data of groundwaters from 78 springs and wells in southern Nevada and eastern California, collected and analyzed since 1992, are summarized in this study. The data indicate that chemical and hydrologic processes between water and aquifer materials and mineral compositions of aquifer materials through which groundwaters flow mainly control major ion chemistry of groundwater. Major ion chemistry of groundwater can be used for reconstruction of hydrochemical framework of water and for tracing groundwater flow patterns. Four hydrochemical facies of groundwaters have been classified in the study area based on their major cation and anion compositions. The calcium-magnesium-bicarbonate type (facies) groundwater

has moved only through the lower carbonate aquifer or through valley-fill rich in carbonate detritus. The sodium-potassium-bicarbonate type (facies) groundwater has flowed only through volcanic rocks or through valley-fill deposits rich in volcanic detritus. The calcium-magnesium-sodium-bicarbonate type groundwater represents a mixture of two hydrochemical types of groundwaters mentioned above. It was initially within the lower carbonate aquifer and subsequently entered the volcanic-rock aquifers. Further mixing with different quantities of source waters or mixing with the third hydrochemical facies identified, can form another type of water, such as the sodium-sulfate-bicarbonate type.

Groundwater samples and the representative aquifer rock samples were widely collected in southern Nevada and eastern California and analyzed for their REE concentrations. Characterizations and comparisons of the REE concentrations and behaviors in both groundwaters and aquifer rocks demonstrate that the REE patterns of the carbonate groundwaters and the volcanic rock groundwaters resemble those of the respective rock types through which they flow. Carbonate groundwaters can be further distinguished into “dolomite” groundwaters discharging from the Lower Paleozoic carbonate (dolomite or dolomitic limestone) aquifer and “limestone” groundwaters discharging from the Upper Paleozoic carbonate (limestone) aquifer. Groundwaters from Army well and Furnace Creek, from the Spring Mountains, and from Tippetah and Topopah springs represent the end-members of groundwaters from dolomite, limestone, and volcanic rock aquifer, respectively. Mixing of groundwater from different aquifers resulted in the modifications of REE signatures in groundwaters from springs and wells

in southern Nevada. Comparing and normalizing REE signatures in groundwater to those in the local aquifer rocks provide direct information for tracing groundwater sources and for understanding changes of REE signatures during rock/water interactions.

Precipitated from groundwater flows, secondary minerals in the fractures of the unsaturated and saturated zones preserved crucial information on groundwater geochemistry and paleohydrologic history in southern Nevada. REE signatures in secondary minerals can be used to determine alteration processes and groundwater sources from which the minerals were precipitated. Anomalous variations in Ce and Eu concentrations are useful indicators of redox conditions at the time of mineral deposition. A total of twenty-six secondary mineral samples were collected from the western Pahute Mesa-Oasis Valley (WPM-OV) region and from the underground study tunnels at Yucca Mountain and analyzed for their REE concentrations using both ICP-MS and LA-ICP-MS. Different REE patterns in secondary minerals suggest that these secondary minerals in southern Nevada may be precipitated from groundwaters originated from different sources during geologic history. They can be formed either by groundwaters percolating through unsaturated zones, or from upwelling groundwaters (both shallow perched and deep aquifer groundwaters) with hydrothermal fluid influences, or the combination of two origins. Future investigations of REE patterns in calcite samples should continue to focus on linking the observed patterns to other physiochemical parameters (e.g., depositional temperature, host rock REE concentrations, and water chemistry). The REE results of the same sample using both ICP-MS and LA-ICP-MS agree well. The LA-ICP-MS technique has a great potential in high-precision spot analysis for rocks and minerals.

More REE analyses in rock and mineral samples using LA-ICP-MS are needed.

Finally, three laboratory leaching tests were conducted in order to study the effect that compositionally different rocks have on the behavior and concentration of rare earth elements (REEs) in low-temperature aqueous solutions. Different rock types were reacted with distilled deionized water and acidic aqueous solutions for different reaction times. Both rock samples used for the leaching tests and the leachates were analyzed for their REEs. Concentrations of REEs in the leachate solutions are generally low. Normalizing to the respective rock with which they reacted, most leachates exhibit relatively flat REE patterns, except for large positive Eu anomalies. Solutions that reacted with volcanic rocks (rhyolitic pumice) exhibit the highest REE concentrations and a slight HREE enrichment, whereas the solutions that reacted with carbonate rocks have the lowest REE concentrations and a weak MREE enrichment.

These leaching studies suggest that REE signatures in the leachates are controlled by the types of rocks with which they interacted. The leaching experiments allowed us to characterize REE signatures released from rock samples to leachates and to determine the easily soluble fractions of REEs during water/rock interaction under standard conditions. Moreover, the study results may be applicable to REE behavior during low-temperature water/rock interaction in general. However, we should apply these batch test results to real groundwater systems with great cautions. Other factors, such as filter size, possible secondary minerals in rock samples, and variations of laboratory conditions, should be carefully considered because they could also affect REE patterns of the leachate solutions.

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