

FINGERPRINTING OF GROUND WATER
BY ICP-MS

FINAL REPORT
APRIL 30, 1996

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DOE Cooperative Agreement
No. DE-FC 08-90NV10872

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MASTER

This is the final report for Fingerprinting of Ground Water by ICP-MS. This report contains only major findings and conclusions resulting from this project. Detailed reports of all activities performed for this project were provided to the Project Office every quarter since the beginning of the project.

Included in this report are the ground water chemistry data collected at Ash Meadows, Nevada and Death Valley National Park, California, eight peer reviewed journal articles that have been published or are "in press", one article in review and two interpretations of the regional ground water movement under the Nevada Test Site.

The interpretations and journal articles also relied on data that were collected as part of the Harry Reid Center for Environmental Studies' Sample Verification Project.

**Determining the Origin of Groundwaters from Southern Nevada using
Multivariate Statistical Analysis of Dissolved Trace Element Concentrations**

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Introduction

Geochemical investigations of groundwater sources and mixing have relied heavily on the major solutes (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , $\pm \text{F}^-$, Br^- , PO_4^{3-}), stable isotopes of hydrogen and oxygen (δD and $\delta^{18}\text{O}$), and, occasionally, radionuclides such as tritium (^3H) and carbon-14 (^{14}C). Problems with geochemical interpretations of such analyses arise from the low number of major solutes (typically between 7 and 8 are reported) which results in insufficient information for definitive interpretations. Moreover, isotopic analyses can be very costly. We present an alternative approach using numerous trace elements that occur naturally in all ground waters and that can now be measured rapidly and routinely using the inductively coupled plasma-mass spectrometer (ICP-MS) at the Harry Reid Center for Environmental Studies (HRC) at a fraction of the cost of isotopic analysis. The tremendous number of solutes that can be measured by ICP-MS necessitates the examination of each data set by multivariate statistical techniques that help to reduce the data and illuminate correlations between trace elements and, therefore, ground waters of similar and/or different origins.

Regional Setting

The study region encompasses south-central Nevada and the Death Valley region of California. The principal aquifers include the regionally extensive Paleozoic carbonate aquifer, Tertiary felsic volcanic rock aquifers of the Nevada Test Site (NTS), and aquifers from Quaternary basin-fill deposits. Interbasin groundwater flow within the Paleozoic carbonate aquifer has been suggested to explain the many high volume springs ($>0.4\text{m}^3/\text{min}$) that discharge within Ash Meadows National Wildlife Refuge, Death Valley National Park, and along the Muddy River.

Sampling and Analytical Techniques

Groundwater samples were collected from springs in Ash Meadows National Wildlife Refuge, Death Valley National Park, Pahranaagat National Wildlife Refuge, the Nevada Test Site, and along the Muddy River. Well waters were also sampled from wells on the NTS. Each groundwater sample was filtered through a $0.45\ \mu\text{m}$ filter during collection and immediately acidified to $\text{pH} < 2$ with ultrapure nitric acid. The samples were collected in acid-washed low density polyethylene bottles and double bagged in precleaned plastic bags for transport back to the Harry Reid Center for Environmental Studies at the University of Nevada, Las Vegas.

All trace elements were measured by ICP-MS (Perkin Elmer Elan 5000) with ultrasonic nebulization. Major cations were determined by atomic absorption spectroscopy, and the major anions were measured using ion chromatography.

Principal Component Analysis

The multivariate statistical technique, Principal Components Analysis (PCA), was used to examine the trace element and major solute data of the ground-water samples. PCA is a statistical method that allows for the plotting of data from a two-way contingency table as points in low-dimensional vector spaces. The geometry of the individuals, i.e., the rows in the data table, is related to the geometry of the attributes or

columns in the table and, consequently, there exists a correlation between the rows and columns. In multivariate statistical analysis such as PCA, one is interested in determining the intervariable relationship between attributes and other attributes, individuals and other individuals, and between attributes and individuals. The intervariable relationships are examined graphically by acquiring orthogonal information extracted from the variance-covariance matrix that can be subsequently used to form orthogonal axes from which the correlations between attributes and attributes, individuals and individuals, and attributes and individuals can be graphically displayed.

Pahranagat Valley

The results of the PCA analysis of the four major cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) and the PCA analysis of 39 trace elements from ground waters sampled in the Pahranagat Valley and along the Muddy River are shown in Figures 1 and 2. Inspection of Fig. 1 for the major cations indicates that principal component 1 explains approximately 99% of the variation in the data set, whereas principal component 2 only accounts for 1% of the variation. Consequently, we can only say with confidence that Rogers Spring water differs from the other four springs shown in Fig. 1. On the other hand, examination of Fig. 2 for the trace elements clearly demonstrates that not only does Rogers Spring differ chemically, but the other springs also exhibit significant chemical differences. More precisely, the two Pahranagat Valley springs, Hiko and Crystal, are chemically identical, whereas the other Pahranagat Valley spring, Ash, is significantly different from Hiko and Crystal Springs, and all three are different from Muddy and Rogers Springs. Muddy and Rogers Springs are, in turn, different from each other. Consequently, the trace elements provide significantly more information about these ground waters than do the major cations.

Nevada Test Site/Spring Mountains/Ash Meadows/ Pahranagat Valley

Figures 3 and 4 show the results of the PCA of 25 sites (a duplicate was taken at well ER-30, so 26 cases were actually employed) using the four major cations (Na, K, Ca, Mg) (Fig. 3) and 29 trace elements (Fig. 4). The scattergram for the four major cations shows a cluster for the Ash Meadows springs and the three Pahranagat Valley springs. The Nevada Test Site wells and springs which issue from volcanic rock form another cluster, except Cane Spring, which appears to be similar to the carbonate springs of Ash Meadows and Pahranagat Valley. The Spring Mountain springs are spread across the upper left quadrant. Cold Spring (AM) appears to be an outlier which agrees with previous investigations.

The trace elements produce different clusters than those obtained with the major cations. Again, the Ash Meadows & Pahranagat Valley (except Cold) springs form one cluster. The Spring Mountain springs form another cluster with Willow Spring showing some differences from the other four. The NTS wells and springs show three distinct groups. Wells J-12, J-13, and ER-30 (two samples) form a cluster between the carbonate water of Ash Meadows, Pahranagat Valley, and Spring Mountain. Tippihah and Topopah springs are well removed from the carbonate cluster and Cane falls between them but closer to the carbonates.

Interpretation of Results

The Ash Meadows ground waters are thought to be a mixture of carbonate ground waters from

Spring Mountain recharge, interbasin flow of deep Paleozoic carbonate waters from Pahranaagat Valley and a small component of NTS waters (see Rare earth elements as geochemical tracers of regional groundwater flow). This is reflected in both the trace elements and major cations PCA. The major element PCA shows a strong similarity but two distinct clusters for these waters. The trace elements PCA makes no distinction between these waters, indicating both have derived their trace element "signature" from a similar carbonate source. Only Cold Spring does not fit this pattern, and it is thought to be waters from other Ash Meadows springs that have been recharged and recycled through the alluvium.

The Spring Mountain springs do not form a cluster for the major cation PCA, but the trace elements show a strong chemical relationship between all of them except Willow Spring. Willow Spring differs from the other Spring Mountain springs in that it is located on the southern edge of the mountains and issues from sandstone in Red Rock Canyon.

The NTS wells and springs form a cluster in the major cation PCA which seems to indicate their emergence from the Tertiary felsic rocks of the NTS. However, in the trace element PCA the waters of J-12, J-13, and the two ER-30 samples show a strong chemical relationship to the carbonate waters of Ash Meadows and Spring Mountain. Topopah and Tippihah springs, however, appear to be significantly different from all the other waters. These two springs issue at the base of Shoshone Mountain and most likely represent perched ground waters that have only encountered the Tertiary felsic rocks of the NTS.

The waters of wells J-12, J-13, and ER-30 (which are located in 40-Mile Wash) are also pumped from volcanic rock. This is reflected in the major cation PCA, but the trace element PCA shows a clear relationship between these waters and the waters derived from carbonate sources. We propose that this may be due to upwelling of the regional carbonate waters beneath the NTS.

From a chemistry standpoint the major cations, especially sodium, are significantly more soluble than most of the trace elements. The felsic rocks of the NTS are sodium rich and may impart this "signature" to the water over a relatively short distance or time. The less soluble trace elements, however, are more likely to reflect the rock with which the water has had the longest contact time, namely the Paleozoic carbonates associated with deep interbasin gradual flow.

The last figure (5) shows the trace element relationship between the waters from Pahranaagat Valley, Ash Meadows, Spring Mountain, and the Death Valley/Furnace Creek area. The waters from Ash Meadows appear to be very similar to the waters of the DV-Furnace Creek springs, suggesting that the ground water flow from Ash Meadows continues towards DV and is, at least in part, discharged at the Furnace Creek springs.

**RARE EARTH ELEMENTS AS GEOCHEMICAL
TRACERS OF REGIONAL GROUNDWATER FLOW**

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INTRODUCTION

The unique and chemically coherent behavior of the rare earth elements (REEs) has spawned considerable interest in their occurrence in geologic systems. Because of their size and valence, the REEs exhibit distinct chemistry compared to their nearest neighbors (barium and hafnium) in the periodic table. Moreover, the systematic decrease in ionic radius with atomic number within the lanthanide suite, imparts predictable chemical differences from La through Lu which can record subtle geochemical processes in natural systems. These properties have been used extensively in petrologic studies to examine geochemical processes responsible for solid phase-melt phase fractionation and petrogenesis, in general, as well as the investigation of adsorptive processes and solution complexation in seawater.

Because the REEs in groundwaters are thought to primarily be derived from the rocks through which the water flows (Smedley, 1991; Johannesson et al., 1994), the REEs may be particularly useful for evaluating groundwater - rock interaction and determining groundwater source regions. Here we demonstrate for the first time that the dissolved REE concentrations of the groundwaters reflect water-rock interactions and that the REEs are valuable tracers for evaluating the sources of groundwaters.

PREVIOUS INVESTIGATIONS

Previous investigators sought to identify the source of the numerous large volume springs ($>0.4\text{m}^3/\text{min}$) that issue within Ash Meadows. (The total annual discharge of the springs in Ash Meadows is estimated at $2.1 \times 10^7 \text{ m}^3$ (i.e., 17,000 acre-feet)). Based on the analysis of the conservative tracer deuterium, Winograd and Friedman (1972) concluded that Ash Meadows groundwater is a combination of water recharged in the Spring Mountains, 20 - 30 km to the east, and interbasin groundwater flow from Pahranaagat Valley, 145 km to the northeast. The contribution of through-flow from Pahranaagat Valley to Ash Meadows was determined to be roughly 35% of the total Ash Meadows discharge, whereas the remaining 65% was proposed to originate as recharge in the Spring Mountains (Winograd and Friedman, 1972). These same mixing ratios were supported by the subsequent work of Osmond and Cowart (1982) using uranium-series disequilibrium analyses of the same groundwaters.

SAMPLING AND ANALYSIS

We collected groundwater samples from Ash Meadows, Pahranaagat Valley, and the Spring Mountains by pumping from each spring's source using precleaned, acid-washed teflon tubing, connected to a peristaltic pump. The groundwater samples were pumped through $0.45 \mu\text{m}$ Gelman Sciences in-line groundwater filter capsules and directly into acid-washed low density polyethylene bottles (Stetzenbach et al., 1994). The samples were then immediately acidified with ultra-pure nitric acid and doubled bagged in acid-washed plastic bags for transportation to the laboratory. The REEs were determined by inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer Elan 5000) with ultrasonic nebulization after 50-fold preconcentration by cation-exchange (Stetzenbach et al., 1994).

RESULTS AND DISCUSSION

The origin of the Ash Meadows groundwaters was initially evaluated by simulating mixing using the equations of Langmuir et al. (1978) and the REE concentrations measured in the Spring Mountain, Pahranaagat Valley, and Ash Meadows groundwaters (Fig. 1) (Table 1). Mixing proportions similar to those determined with deuterium and uranium (i.e., 70 - 80% Spring Mountain and 20 - 30% Pahranaagat Valley groundwater), were found to produce shale-normalized REE patterns that closely mimicked the Ash Meadows signature for the middle and heavy REEs (MREE and HREE) (i.e., Eu - Lu) (Fig. 1). However, the resultant mixtures were always depleted in the light REEs (LREE) owing to the shale-normalized LREE depletions of both Spring Mountain and Pahranaagat Valley groundwater (Fig. 1, Table 2, Mixture 1).

Perched groundwaters from felsic volcanic rocks (i.e., rhyolites and quartz latites) of the Nevada Test Site, that overlie the Paleozoic carbonate rocks, are the only likely candidate for an additional groundwater component that could produce LREE concentrations like those of the Ash Meadows groundwaters. Perched groundwaters discharging from two springs at the base of the Shoshone Mountains, which are entirely composed of these felsic volcanic rocks, were sampled (Table 1, Fig. 2). These groundwaters have very different shale-normalized REE patterns than the carbonate waters and display LREE enrichments and negative Eu anomalies (Fig. 2). In addition, the perched groundwaters exhibit substantially larger REE concentrations than the purely carbonate end-member groundwaters as well as the Ash Meadows groundwaters. The perched Nevada Test Site groundwaters have REE concentrations, for example, that are on average 110, 340, and 40 times larger than the REE concentrations of the Spring Mountain, Pahranaagat Valley, and Ash Meadows groundwaters, respectively. The REE patterns of the perched Nevada Test Site groundwater also resemble the REE patterns of the felsic volcanic rocks from which the water issue and, consequently, we propose they are characteristic of an end-member groundwater that has only interacted with felsic volcanic rocks. Incorporating the LREE enriched perched groundwaters into the mixing calculations results in an extraordinary fit to the Ash Meadows data when approximately 1% of this groundwater is added to the Spring Mountain - Pahranaagat Valley mixture (Fig. 3). Moreover, a combination of roughly 54% Spring Mountain, 45% Pahranaagat Valley, and 1.1% of the perched groundwaters was found to most closely approximate the REE concentrations and shale-normalized REE patterns of Ash Meadows (Fig. 3, Table 2). The relatively small proportion of perched Nevada Test Site groundwater required to produce LREE concentration and shale-normalized REE patterns of the groundwater mixture that resemble the Ash Meadows groundwaters is in remarkable agreement with the less than 5% contribution predicted by Winograd and Thordarson (1975) using typically conservative sodium. Moreover, the dominant contribution to Ash Meadows of groundwaters recharged in the Spring Mountains as well as the significance of Pahranaagat Valley groundwaters to the Ash Meadows springs is preserved by our REE mixing model.

SUMMARY AND CONCLUSIONS

In summary, the groundwater sources and mixing ratios determined with dissolved REE concentrations in the regional groundwaters of south-central Nevada are remarkably similar to those determined with the more traditionally accepted conservative tracers deuterium, uranium, and sodium. Our work, therefore, is highly suggestive of the use of REEs as geochemical tools for tracing groundwater source, deciphering mixing proportions of different groundwaters, and, in general, for investigating groundwater-rock interactions.

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Data analysis books entitled, Chemical Analysis of Water from Ash Meadows Springs and Chemical Analysis of Water from Death Valley Springs can be issued upon request. Please call 895-1357 and ask for Sally Hamilton.

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