METHODS TO DIFFERENTIATE BETWEEN GROUNDWATER SOLUTE SOURCES[1]

by

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Abstract: The Robinson district, Ely, Nevada is located in a complex hydrogeological system consisting of 12 distinct provinces each with distinctive background chemistry. To elucidate transport pathways, it was necessary to discriminate between background, marginally impacted, and historic source impacted waters. Standard approaches such as Piper diagrams failed to provide adequate discriminatory power. Therefore, a selected set of pit lakes, waste rock seeps, and surface water/groundwater samples were analyzed for a suite of major, minor and trace elements, rare earth elements (REEs), precious metals, and stable isotopes ($^{16}O/^{18}O$ and D/H). The stable isotopes $^{16}O/^{18}O$ and D/H provide coarse discrimination between the three classes of water. Background waters were found to contain barium above 10 $\mu g/L$, and less in mine-impacted waters due to precipitation of insoluble barium sulfate. Scandium, rhenium, and rubidium in waste rock related seeps and pit lakes, in conjunction with barium allowed clear segregation between the three classes of water.

Introduction

The Robinson Mining District (RMD) has a long history of mining activity, dating back to 1860. Over the last 100+ years, silver ore from the shallow subsurface, gold from oxide overburden, and copper from deeper sulfide units have all been mined from the district. In addition to standard mining techniques, low metal grades in some lithologic units prompted historic attempts (1924 - 1978) to leach waste rock dumps with sulfuric acid (Winters Company 1992). The inefficiencies associated with this technique inevitably resulted in elevated sulfate concentrations in the shallow alluvial aquifer underlying parts of the eastern side of the BHP property. However, the prevalence of limestone subjacent to source areas has neutralized the acidic leachate, resulting in natural attenuation of metals and localized (rather than regional) impacts to the shallow aquifer.

The geology and the associated hydrogeology are complex, due to a myriad of faults that offset blocks, juxtaposing transmissive units against impermeable units (BHP 1996). Consequently, there are clear and distinct hydrologic units that are separable based both on groundwater elevations and on aqueous geochemical classification. In order to identify impacts from historic sources, and separate these effects from the post-1994 era when mining in the district commenced after a hiatus of approximately 10 years, it was necessary to discriminate between the naturally occurring elevated background solute concentrations in the mineralized zone hydrologic unit located in the heart of the district, from those in the peripheral units. Migration pathways from historic source areas to downgradient transport positions were described as part of this investigation.

Groundwater Hydrology

Regional groundwater flow is generally from the high mountain ranges into the basins and valley floors. There is a major groundwater divide separating the BHP property. Groundwater originating in the Egan Range typically flows to the north in Steptoe Valley and to the south in White River Valley (Figure 1).

Local groundwater flow in the RMD is more complex, and is dictated by a variety of structural and hydraulic features. The primary aquifers in the Robinson Mining District are the deeper Paleozoic rocks and the unconsolidated alluvial sediments which typically have higher hydraulic conductivities than other rocks in the region. Groundwater in the Paleozoic carbonate aquifer can be either confined or unconfined, and flow is controlled by mineralization, alteration, faults, the hydraulic conductivity of the carbonates, and the locations of Late Cretaceous intrusions. Groundwater in the alluvial aquifer is unconfined, and flow is controlled by elevation of the water table above mean sea level (amsl) and conductivity differences within the alluvial sediments (Figure 1).

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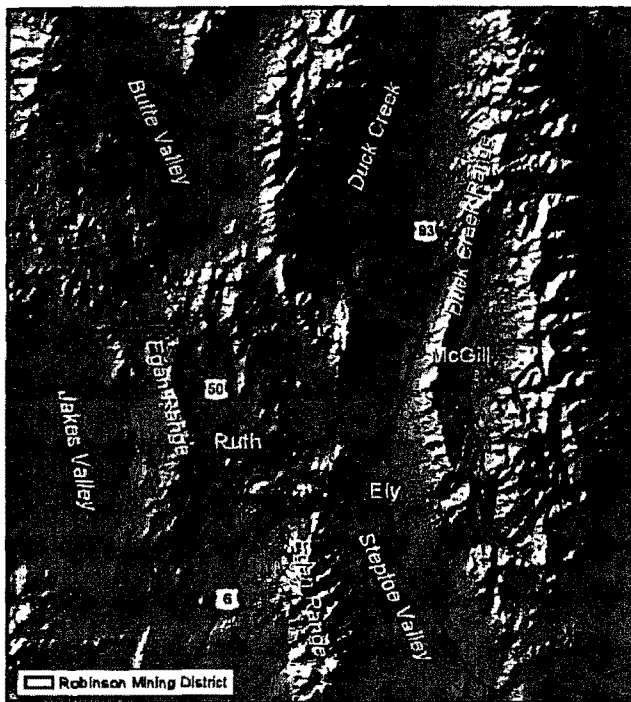
54

Figure 1. Location of Robinson Mining District and regional topography.

Occurrence and Movement of Groundwater

Water levels measured in wells and borings in the mine area range from only a few feet below ground surface (BGS), to several hundreds of feet BGS leading to changes in the hydraulic head of hundreds of feet over a lateral distance of tens of feet. A water-level map for bedrock units in the RMD was constructed from the April 1997 sampling event (Figure 2). Major groundwater hydrology features on the map include the Egan Range that forms a regional groundwater and surface water divide, the Saxton Peak and Jupiter faults that combine to form an east-trending groundwater divide that separates groundwater in the RMD from aquifers that occur to the south, and low-conductivity, outcropping igneous rock units (Weary Flats pluton and a Tertiary rhyolite) that form stratigraphic hydraulic barriers (a groundwater mound) on the northern side of the mineralized block.

Hydrogeological Provinces

Owing to the hydrogeologic description of different groundwater provinces, polygonal shapes were defined that link hydrogeologically similar areas of the RMD together by incorporating characteristics
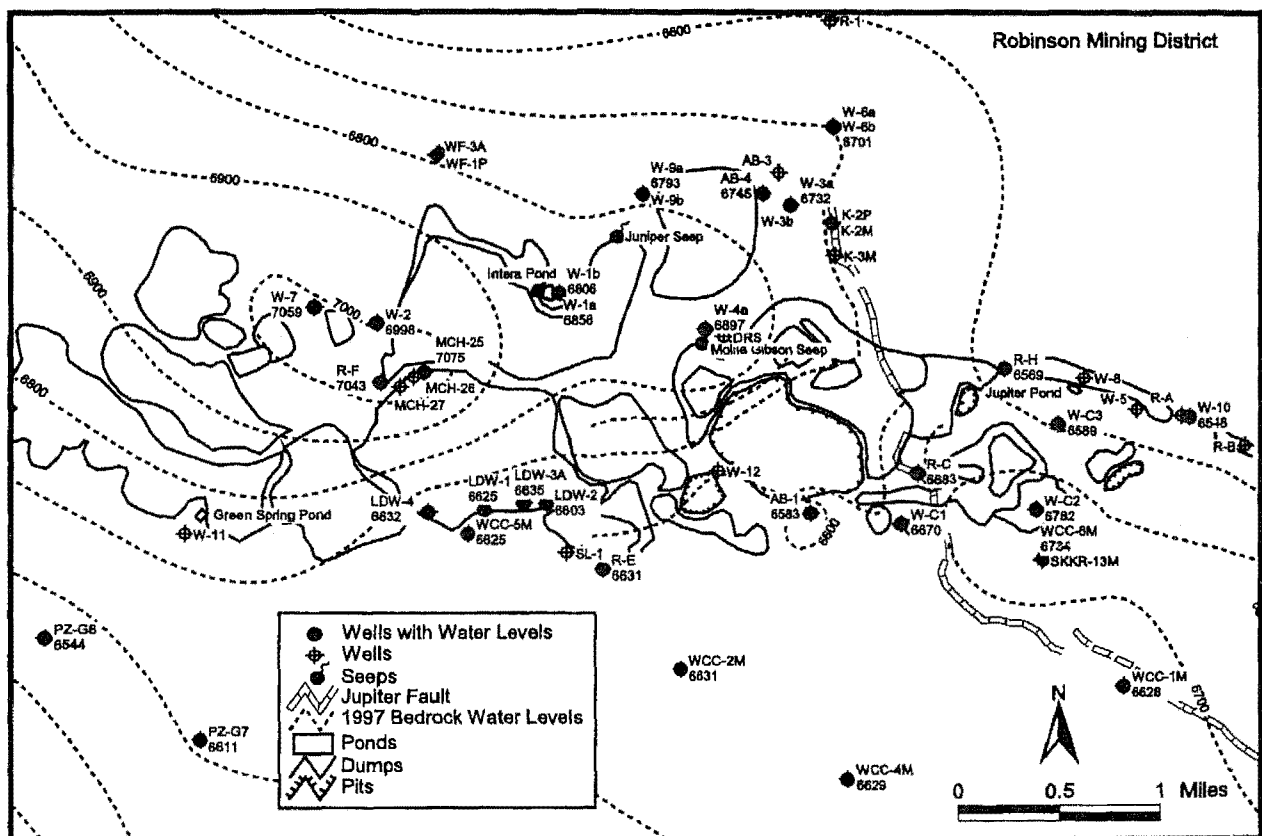

Figure 2. Robinson Mining District, water-level map of bedrock aquifers, April, 1997 monitoring data.
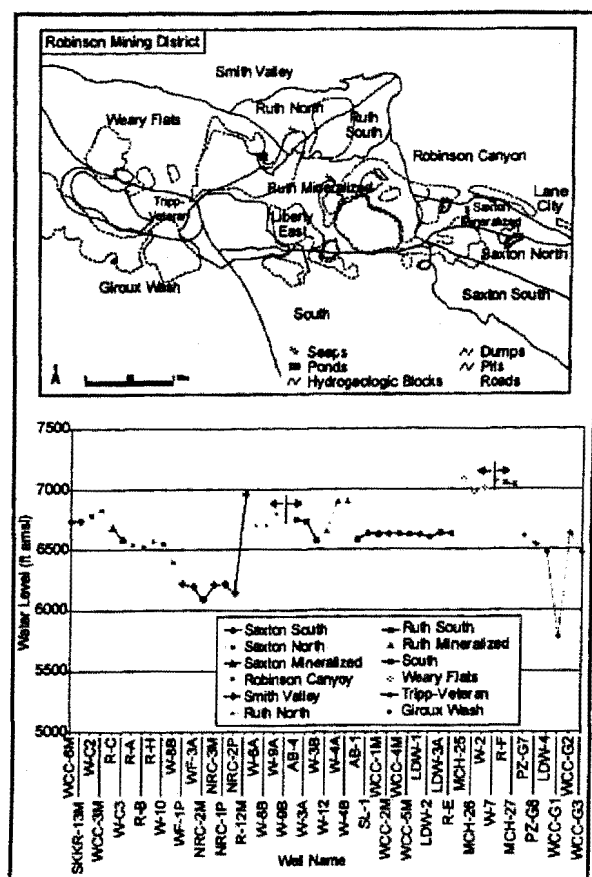
Figure 3. Robinson Mining District, hydrogeological provinces and hydrographs.

in the Smith Valley block, has a head measured nearly 1000 ft higher than the other wells in that block. This difference in head is due to the large areal extent of this hydrogeologic block. Smith Valley encompasses the area north of the RMD, from the Egan Range to the Smith Valley Floor. Monitoring well R-12M was drilled near the crest of the Egan Range, and is located near the groundwater divide formed by this mountain chain, whereas the other wells within this block are located in the valley proper. In the Giroux Wash block, monitoring well WCC-G1 has an observed hydraulic head approximately 800 ft lower than the other monitoring wells sampled in that proposed block. This difference in hydraulic head can be explained because WCC-G1 is on the west side of the hydraulically sealing Giroux Wash fault.

Sampling and Analytical Methods

Sampling and analysis of Robinson district surface water and groundwater was conducted to characterize the chemistry, water quality and geochemical evolution of site waters from potential and known source areas to downgradient locations.

The sampling program analyzed waters from a total of 18 surface water and groundwater locations across the site (Figure 4) consisting of ten surface water locations, including six waste rock seeps/ponds locations, samples from three pit lakes (Ruth, Kimbley and Liberty), and one sample from the Giroux Wash tailings pond. Seven of the eighteen locations were from existing groundwater monitoring wells (R-A, R-C, R-H and R-F), two temporary highway-construction water-supply wells (GQ-1 and GQ-2), and one sample from Deep Ruth Shaft. An additional sample was collected from Murry Spring (the Town of Ely's water supply). The groundwater samples collected from Murry Spring and temporary water-supply wells GQ-1 and GQ-2 are located away from the Robinson district site and are representative of background conditions for non-mineralized groundwater. The surface water and groundwater sample locations were selected because they are representative of locations within major hydrologic provinces at the RMD, and represent strategic locations with respect to potential source areas (e.g., waste rock seeps and pit lakes) and potential groundwater migration pathways.

groundwater flow, stratigraphy, and degree of mineralization. There are 12 hydrogeologic blocks specified in this present interpretation. A major enhancement in the hydrogeologic block designation resulted from incorporation of hydrogeologic data obtained from monitoring wells installed during 1997. Potential solute transport pathways from historic source areas were characterized within the appropriate hydrogeologic provinces.

A hydrograph of water level elevations (ft amsl) vs. wells segregated by blocks shows the inter-relationship of hydraulic heads within the proposed hydrogeologic provinces (Figure 3). Heads typically vary less than 300 ft within the confines of a proposed hydrogeologic block for wells completed in the equivalent stratigraphic interval. Monitoring wells in the area of the RMD range from 40 feet to over 700 feet BGS, total depth. Several monitoring wells in the region are completed deeper than 1000 feet BGS. However there are two exceptions to this general observation. Monitoring well R-12M, located

Seventeen new monitoring wells (W-1a through W-12) were installed consisting of six nested well-pairs and five individual wells. The newly installed monitoring wells were strategically located near potential sources of mine-impacted waters (e.g., Juniper seep), or in areas where horizontal and/or vertical hydrologic control was lacking. New monitoring wells designated with an "a" or

56

Figure 4. Robinson Mining District source anaysis, surface water and groundwater
sampling locations.
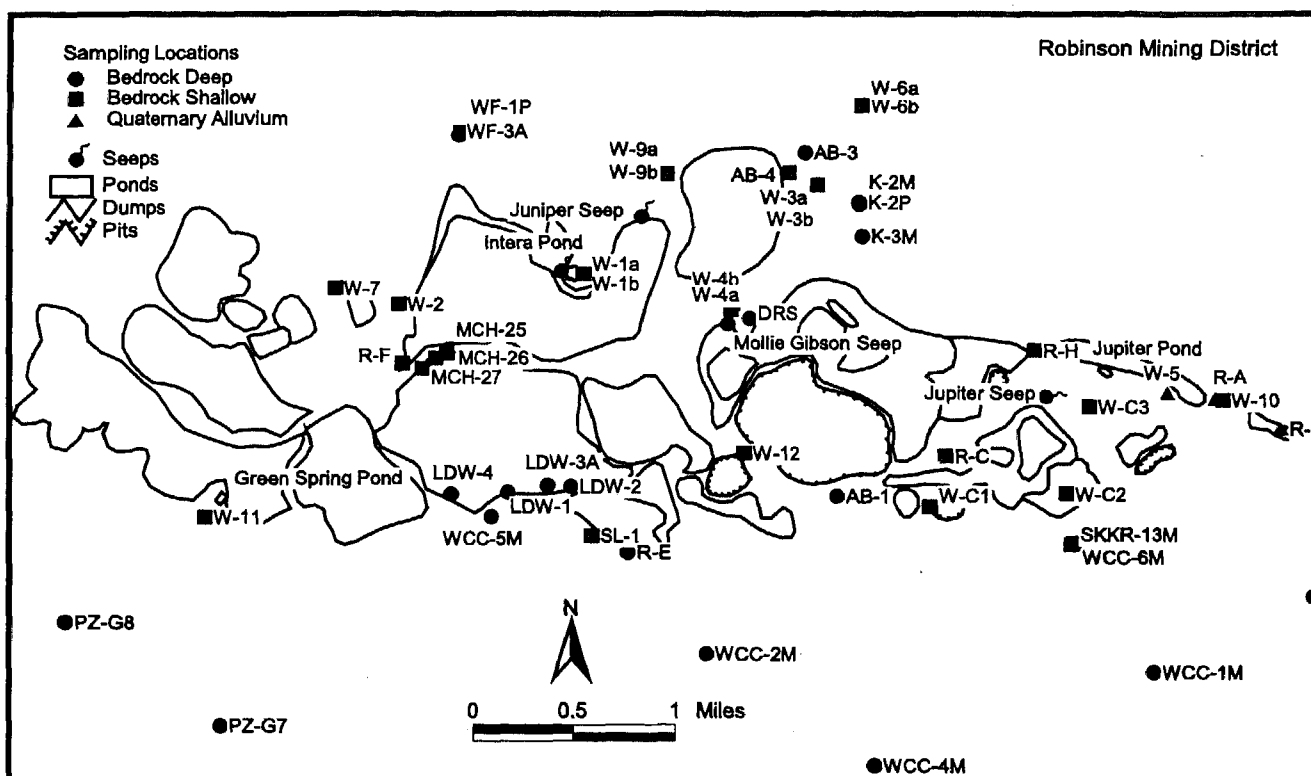
"b" suffix indicate nested well pairs; the "a" suffix
designates a shallow well (well was screened at first water),
and a "b" suffix indicates a "deep" well (well was
completed deeper within the aquifer). These new
monitoring wells were mainly completed in the mineralized
bedrock aquifers.

Analyses for trace and precious metals, rare earth
elements (REEs), and major cations and anions were
conducted at XRAL Laboratories, Toronto, Ontario.
Analyses for metals were performed using inductively
coupled plasma (ICP) and/or inductively coupled plasma-
mass spectroscopy (ICP-MS). Analyses for anions were
undertaken using established ion chromatography, ion
selective electrode or colorometric techniques. Stable
isotopes ($^{18}O/^{16}O$ and deuterium, ^2H) were analyzed by
Geochron Laboratories, Cambridge, Massachusetts.

Results

Geochemical evaluation of the Phase A and B
groundwater and surface water chemical data was
performed to characterize site water quality, and to identify
trace metal and Rare Earth Elements (REE's) that could be
used either as indicator elements or tracers to evaluate the
potential influence of mine-impacted waters along known
and suspected flow pathways.

Trilinear Diagrams

The spatial relationship between selected surface
water and groundwater chemistry is typically interpreted
based on major cation and anion ratios (Figure 5). At
RMD, trilinear diagrams failed to provide the resolution
necessary to fingerprint individual water sources at the
site. However, they do exhibit broad trends in major element
chemistry that contribute to the geochemical evaluation.

For example, pits and seeps have similar ratios of
major cations and anions with subtle variations (Figure 5).
In general, these surface waters may be characterized either
as $Mg-SO_4$ waters (seeps), $Ca-SO_4$ waters (pits), or Mg-Cl
waters (spring and seeps). This diagram shows that these
waters can be differentiated based on variations in the
cation ratio (Ca versus Mg) and anion ratio (Cl versus
sulfate).

The RMD groundwaters range in composition
from $Ca-SO_4$ waters to $Ca-HCO_3$ waters. Only one RMD
groundwater sample, WCC-G2, is chloride-rich. All other
RMD groundwater samples are either strongly sulfate-
rich (e.g., R-A) or bicarbonate-rich (e.g., WCC-4M). The
strong influence of bicarbonate ion on groundwater
chemistry is due to interaction with carbonate minerals
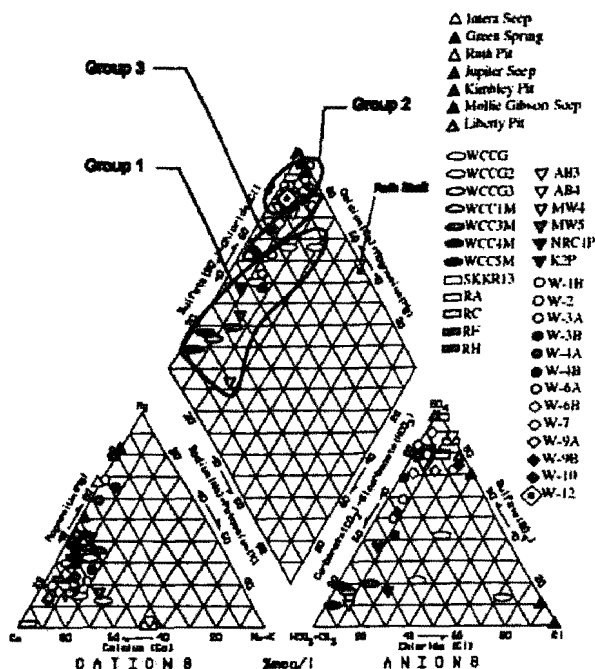(e.g., $CaCO_3$) in the regional limestone aquifers that have

57

Figure 5. Robinson Mining District, groundwater major
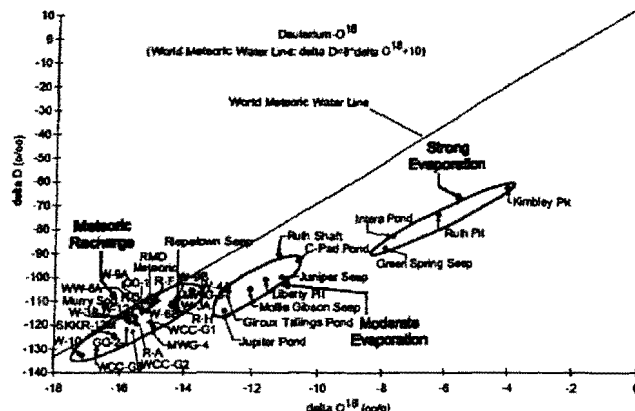elements cation and anion ratios.

Figure 6. Robinson Mining District, isotopic groupings
of water samples.

an important role in neutralizing historical releases of
anthropogenic sulfuric acid used to recover low grade
copper in select leach dumps. The presence of sulfate in
groundwater may also result from dissolution of naturally
occurring gypsum ($CaSO_4.2H_2O$) in sedimentary units
(observed in cuttings from well R-C), or in the mineralized
zone from oxidation of sulfide minerals (e.g., pyrite, FeS_2)
observed in W-12 cuttings.

The apparent clustering of groundwaters (Figure
5) suggests that individual groundwaters can be assigned
to one of three broad groups. Group 1 groundwater (which
includes Murry Springs) consists of groundwater in Giroux
Wash and Saxton Peak (located hydraulically upgradient
of the facility), that represent ambient non-mineralized
background water quality outside of geologically
mineralized zones. In contrast, Group 2 groundwater
consists of those wells that are located within, or adjacent
to, the mineralized block and are sulfate-rich, exhibiting
characteristics of mineralized groundwater (e.g., W-12,
located between the Star Pointer and Ruth Pits) or
anthropogenic effects. Group 3 groundwater consists of
those wells that exhibit water quality characteristics
intermediate between Group 1 and 2 groundwater, and
include groundwaters that may have been influenced by

historic mining activities. The extent to which Group 3
groundwater may or may not have been influenced by
anthropogenic activities is unclear given the insufficient
resolution provided by the trilinear diagrams.

Stable Isotopes (D and ^{18}O)

The groundwater and surface water δD versus
$\delta^{18}O$ data were plotted relative to the world meteoric water
line (MWL) that establishes the ratio of δD to $\delta^{18}O$ for
waters of meteoric origin (Craig 1961). Precipitation at
RMD (labeled RMD meteoric) plots directly on the MWL
(Figure 6).

Several obvious groupings of water can be
identified based on similar δD and $\delta^{18}O$ ratios, indicating
which water bodies are undergoing similar hydrologic
evolution. For example, water samples that plot close to
the RMD meteoric water point are derived from local
meteoric precipitation, and are grouped under the heading
"Meteoric Recharge." These include all groundwater
samples, and samples from Riepetown Seep, and Murry
Spring. The meteoric origin of these waters are confirmed
by generally low total dissolved solids content
characteristic of these locations, and indicate that
background or near-background water quality conditions
exist at these locations.

In contrast to the meteoric-derived δD-$\delta^{18}O$
relationships observed for background locations, waters
that may have been impacted by RMD mineralization and/
or anthropogenic activities are enriched in δD and $\delta^{18}O$ to
a degree that clearly separates them from other water
sources. These include all pit lake samples and waste
rock seeps. For example, Mollie Gibson Seep (see

58

"Moderate Evaporation" group) appears to represent water that is intermediate between the upgradient Ruth Pit water and meteoric recharge.

These data suggest that RMD waters, flow pathways and hydrogeochemical provinces may be distinguished based on geochemical criteria, but that this goal would require more sophisticated techniques than the typical Piper/Stiff diagram approach. Hence, the alkaline earth metals (e.g., Barium), alkali metals (e.g., Rubidium), the siderophile elements (e.g., Rhenium), and transition metals (e.g., Scandium) were analyzed to determine if these elements would provide better discrimination. Using these data, statistical techniques (i.e., cluster analyses) were employed to quantitatively identify elements that could be used to discriminate between background and mining impacted water in each hydrogeologic province.

Cluster Analyses

Data evaluation was performed to identify parameters and graphical techniques that could aid in identification and segregation of different groundwaters, as well as serve to define surface water/ groundwater relationships. Cluster analyses were performed to identify chemical parameters unique to particular surface waters and groundwaters, and to assist in segregating these waters into common groups.

The analytical data for Robinson district groundwater and surface water were standardized prior to the analysis by converting the concentrations for each parameter to units of standard deviation. This operation allowed equal weight to be placed on the low concentration trace elements as on the higher concentration metals, cations, and anions for organizing the sources.

A hierarchical tree diagram was constructed by calculating the squared differences in standardized parameter concentrations between sources, referred to as the distance between sources (sources = surface water or groundwater sample locations). The tree-like structure of the diagram allowed interpretation of the similarity or relatedness of the clusters such that the smaller the distance between any given source, the better the correlation between the sources.

In general, pit lakes, waste rock seeps and ponds, background wells and mineralized block wells clustered together in separate groups. Cluster analysis supported the major element and isotope data evaluation for grouping surface waters and groundwaters, and identified analytes within the various clusters (i.e., Ba, Sc, Re, and Rb) that yielded the maximum discriminatory power.

Tracer and Indicator Elements

Ideally, analytes used for source discrimination (tracers) must be above detection limits, and migrate conservatively in the subsurface. In contrast, indicator elements can be peculiar to a particular water type, but may not be useful tracers because of immobility in the subsurface downgradient from a source due to geochemical constraints on solubility. For example, evaluation of rare earth element (REEs) geochemistry determined that while the REEs are diagnostic indicators, they are of less use as tracers because of reactivity in the subsurface that reduces their solubility due to precipitation as REE–carbonate phases. However, such elements are useful indicators of background conditions if complexes formed by anthropogenic elements result in their disappearance from a groundwater. Although sulfate is a conservative tracer, its source at RMD is non-unique; hence viable tracer compounds were identified at RMD in reference to sulfate concentrations along the potential Intera Pond/ W-9b pathway.

Based on the results of the cluster analyses, three indicator elements were selected—Rhenium (Re), Scandium (Sc), and Rubidium (Rb)—that are both soluble and consistently elevated above method detection limits. These elements were compared with sulfate concentrations (a conservative but ubiquitous tracer at the RMD) downgradient from Intera Pond to assess their relative transport characteristics and use as indicator elements. A fourth element, Barium (Ba), was chosen because it is insoluble in the presence of sulfate (precipitating from solution as $BaSO_4$). Hence absence of Ba in groundwater is an excellent indicator of the presence of enough sulfate to precipitate barite in RMD groundwaters.

Data Analysis – Ternary and Quaternary Diagrams

Ternary diagrams were used to graphically evaluate the relationship between selected trace metals and REE in site surface waters and groundwaters. Ba, Sc, Re, and Rb were chosen based on statistical criteria, as elements useful to fingerprint the potential source relationships for site waters. Background wells are generally associated with high proportions of Ba, waste rock seeps and ponds with high proportions of Sc, and pit lakes with high Rb and Re proportions.

To better distinguish affiliations of waters in the center of the ternary diagram, a quaternary plot was constructed (Figure 7) with the Rb, Ba, Sc ternary as the base, and the Re molal percentage as the vertical axis. This three-dimensional representation allowed further discrimination of waters.
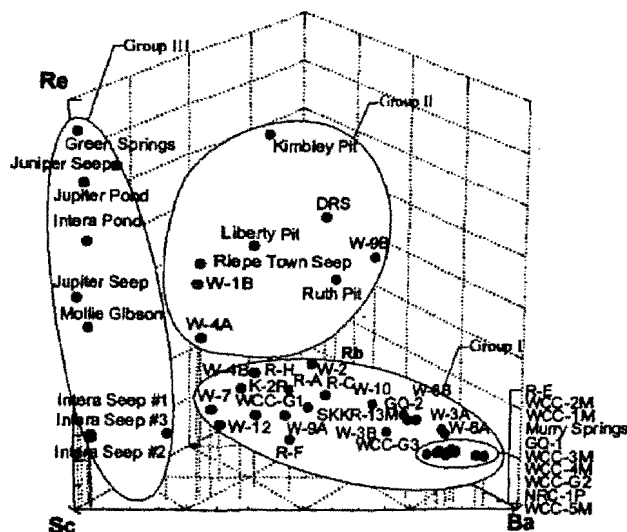
59

Figure 7. Robinson Mining District, quaternary diagram of water types using Re-Sc-Rb-Ba.

Discussion

Major elements and stable isotope data analyses were successful in 1) segregating different surface waters (e.g., pit lakes, seeps), and 2) providing coarse segregation of relatively poor versus good quality groundwaters. Further segregation of groundwaters required refined data analysis techniques using the trace elements Ba, Sc, Re, and Rb, which were identified through cluster analyses to each be strongly indicative of certain waters. The RMD surface and groundwaters can be partitioned into three general groups, 1) background (Group IA) and background/marginally impacted groundwaters

(Group IB), 2) pit lakes and marginally impacted waters (Group II); and 3) historic ponds and seeps related to waste rock (Group III).

Group IA Groundwater

Several wells and Murry Springs contain high proportions of barium that are clearly indicative of non-mineralized background water quality. These wells and Murry Springs are located outside the mineralized block, and away from the influence of either pit lakes or waste rock seeps.

Group IB Groundwater

The group IB wells contain variable proportions of Rb and Ba, and consistently low proportions of Re and

Sc. These wells are located throughout and beyond the RMD, intersecting a variety of lithologic units. This population encompasses ambient background water quality, as well as groundwater from wells which may have been affected by mineralization at the RMD.

Group II Pit Lakes

High proportions of both Re and Sc are indicative of Kimbley, Liberty and Ruth pit lakes (Figure 7). The ephemeral Riepe Town Seep, located southwest of the copper concentrator facility, and north of Liberty pit, is probably influenced by precipitation percolating through rocks comprising the northern area of Liberty pit, thus explaining its geochemical similarity to Liberty pit lake. The Ruth pit lake and Deep Ruth Shaft (DRS) groundwater both contain elevated proportions of Re and Sc (Figure 7) probably due to historical underground workings that connected the DRS to the Ruth pit.

Group III Waste Rock Seeps and Ponds

Waste rock seeps and ponds show high Sc and varying Re proportions. These waters are clearly segregated into a unique surface water group (Figure 7). Intera Pond/ Juniper Seep, Mollie Gibson Seep, Green Springs, Kimbley Pit, and Jupiter Seep/Pond comprise five distinct source areas that may have potentially impacted groundwater. The first four of these sources represent those that will be considered for incorporation into the subsequent fate and transport analysis. The potential Jupiter Seep/Pond source will be subject to further evaluation in the future. Pit lakes other than Kimbley Pit lake have been excluded at present because they will be imminently dewatered, and because they are hydrologically constrained to the mineralized block.

Conclusions

The Robinson district, Ely, Nevada is located in a complex, hydrogeological system consisting of 12 distinct provinces each with distinctive background chemistry. To help evaluate potential solute fate and transport along groundwater pathways resulting from historical mining practices, it was necessary to discriminate between background, mine-impacted, and historic source-impacted waters. Standard approaches such as Piper diagrams failed to provide sufficient discriminatory power. Therefore, a selected set of pit lakes, waste rock seeps, and surface water/groundwater samples were analyzed for a suite of major, minor and trace elements, rare earth elements (REEs), precious metals, and stable isotopes ($^{16}O/^{18}O$ and D/H) in an exploratory survey. The stable isotopes, $^{16}O/^{18}O$ and D/H distinguished between the three classes of water.

60

Background waters were found to contain barium above 10 μg/L, and less in mine-impacted waters due to precipitation of insoluble barium sulfate. Waste rock seeps contained high proportions of scandium, while pit lakes contained high proportions of rhenium and rubidium. Because these elements are conservative tracers in the groundwater environment, they proved useful in discriminating between sources. A quaternary based on barium, scandium, rhenium and rubidium proved effective at differentiating between background and potentially mine impacted waters, a conclusion supported by statistical analysis.

Literature Cited

BHP. 1996. Liberty Interim Waste Rock Management Plan. BHP-Nevada Mining Company, Robinson Operations.

Winters Company. 1992. Memorandum from Ken Edmiston to Harry C. Smith re: Copper Dump Leaching at Robinson, May 21, 1992.