Mine Water and the Environment (2001) 20: 81–97 © IMWA Springer-Verlag 2001

*Technical Article*

# Hydrogeochemistry of the Getchell Underground Mine--Part 1: Mine Water Chemistry

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**Abstract.** The Getchell underground operations in Northern Nevada intersect groundwater associated with marble and hornfel lithologies and a sulfide bearing ore hosted within a 30-km long shear zone system. The deposit is classified as Carlin-type gold mineralization. A distinct feature of the mineralization is the high proportion of arsenic sulfides present in the ore and associated altered wallrock. This results in an intense arsenic enrichment, with some zones containing as much as 30% arsenic, and 0.5-2% arsenic throughout the mineralized envelope.

Most of the groundwater in the area is well buffered by the calcareous host rocks and show a macrochemistry of Ca-Na-$HCO_3$. Along the shear zone and in zones within the hornfel host rock, the waters are less alkaline and more saline, and have a chemistry of Na-Mg-Ca-$SO_4$-$HCO_3$. This latter water type occurs in sulfide-bearing zones.

Arsenic speciation analysis and theoretical predictions demonstrate that higher arsenic concentrations are associated with reducing conditions, with higher Na/Ca ratios, and with low concentrations of Fe. In these waters, As occurs as arsenite, along with trace concentrations of mono-methyl arsonic acid and di-methyl arsinic acid. Natural attenuation of As appears to occur along groundwater flow paths due to co-precipitation and adsorption onto hydrous ferric oxide particles. However, elevated As is still a notable feature of groundwater quality throughout the Kelly Creek basin. This elevated As occurs in bedrock groundwater during underground mine development, rather than in near-surface alluvium groundwater. Due to this and the protracted history of mining, it is not possible to define a true background value for water quality in the area other than acknowledging that bedrock groundwater is mineralized and has little association with seasonal recharge and water quality in the alluvium cover.

**Key words:** Arsenic, Getchell Mine, groundwater, hydrogeochemistry, Nevada.

## Introduction

The Getchell underground mine, owned by the Getchell Gold Company, is located in northwestern Nevada along the eastern flank of the Osgood Mountains, approximately 70 km northeast of Winnemucca. Mining has occurred on the site during several intervals since 1934. The property has primarily produced gold and arsenic, though minor amounts of copper and tungsten were produced early in the mining history of the area. The geology and hydrogeology of the site is complex due to a myriad of faults that offset geological units on site and juxtapose permeable and impermeable units. As a consequence, distinct hydrogeological units can be identified based on both groundwater elevations and geochemistry.

Groundwater quality can vary considerably over relatively short distances, as has been demonstrated in a number of recent studies. In an assessment of hydrogeochemical exploration techniques in the local watershed (the Kelly Creek Basin), the concentrations of Mn, Fe, As, Sb, W, and Au were observed to be higher in the vicinity of known mineralization than in wells sampled from unmineralized bedrock (Grimes et al. 1995). Reducing conditions favoured the mobilization of some elements such as Mn, Fe, Co, As, and Sb. A study by Bennett and Tempel (2000) found that groundwater evolves from $CaSO_4$-type to Na-K-$HCO_3$ type and, due to natural attenuation, was inferred not to present a significant impact to water quality in the Kelly Creek basin. More recently, an enlarged database using historical mine data as well as that of Grimes et al. (1995) produced hydrogeochemical maps of the main water types in the Kelly Creek basin; again, noticeable compartmentalisation of groundwater was observed in both the alluvium and bedrock. The data indicates minimal interaction between the two zones and supports the assumption of Grimes et al. (1995) that groundwater flow is predominately controlled by the North-South Getchell fault.

In order to assess the groundwater chemistry, samples were taken during underground development. In this way, groundwater emanating from aquifers in which interaction had occurred with mineralized host rocks could be distinguished from those in which the water had flowed through unmineralized rocks. This type of characterization will allow future changes in groundwater quality to be understood, particularly in areas of naturally high levels of trace elements. As shown in a number of recent studies, background water quality may vary considerably from specified regulatory requirements, particularly with respect to As, making the regulatory limits difficult to apply in the context of naturally elevated As-rich groundwaters (Welch et al. 1988; 2000).

At Getchell, the concentration and valence of arsenic within the groundwater is a major concern. Arsenic is associated with respiratory, neurological, and cardiovascular disorders; chronic exposure has also been linked to skin, lung, and bladder cancer (Gorby 1994; Nriagu 1994). This paper reports the characterization of groundwater within the mine and focuses on the arsenic geochemistry. As no similar case studies have been published for other mines in northern Nevada, this study provides an important benchmark for future studies in this region and mine waters in general.

## Geology and mining history

Mining at Getchell has primarily focused on near-surface bulk heap leachable deposits that have been exploited via open pits. More recently, underground activities were initiated. The Getchell underground mine is the current source of production and is accessed via adits at the base of the Main Pit. The Turquoise Ridge (TR) deposit is currently being developed and will be accessed by a shaft. Annual production in 1998 was around 7080 kg Au (250,000 ounces) from the whole site. The mine is currently under care and maintenance while exploration outlines further reserves.

The geology of the Getchell property comprises Paleozoic volcano-sedimentary rocks (Figure 1), which have been extensively thrust faulted (Berentsen et al. 1996). These were intruded by a granodiorite stock and related hypabyssal intrusives and underwent further faulting. Mineralization at Getchell has been dated to 39 million years using the Rb-Sr method on galkhaite (Tretbar et al. 2000). Emplacement of the stock generated a 3km wide metamorphic aureole represented by a garnet-rich skarn at the margin flanked by a wollastonite calc-silicate skarn, biotite-cordierite hornfels, and andalusite hornfels. The lithologies occur in broadly east-west trending belts. The major focus of gold-bearing mineralization is associated with a N-S trending shear zone.

Broadly, the mineralization changes from sulfide skarn mineralization through a quartz-pyrite association in ductile-brittle deformation, to replacement style sediment-hosted micron gold mineralization. The later phases of mineralization are characterized by widespread occurrence of realgar and orpiment. After prolonged exposure to air and light on the mine site, the realgar is altered to the more stable polymorph, pararealgar. The final phase of mineralization contains As-Tl-Hg sulfosalts, porous pyrite grains and Au in a quartz-kaolinite-adularia matrix.

## Hydrogeology

It is believed that groundwater occurs in structurally compartmentalized aquifers in the vicinity of the Getchell fault, particularly within the mineralized blocks, based on the observed structural compartmentalization within the open pits and the underground workings. This hypothesis is supported by potentiometric surface mapping and aquifer pump testing conducted on site (Hydro-Search 1995; Hydrologic 1996; SRK 1996).

Unaltered basalts east of the Getchell Fault Zone (GFZ) (Figure 2) produce large amounts of water but in the underground workings, virtually all the high yielding flows are associated with sheared and fractured hornfels at the contact with marble (Figure 3). In general, the Comus and Preble metasediments do not act as principal water-bearing zones. Fluid flow is generally along N-S and NW-SE trending structures that crosscut these lithological units.

Altered zones produce less water than unaltered zones in the wallrock and act as aquitards due to the dominance of clay minerals (as hydrothermal alteration products of silicates), such as in the vicinity of the TR ore zone. Other important aquitards in the vicinity include the Osgood Mountain stock to the west and the argillic-altered basalts to the east. Relatively high water production is possible from deep ore zones, such as along the 4775N drive, which produced a flow rate in access of 20 L/s for over three months and 5 L/s thereafter for a similar period. Current mine water inflow ranges from 25-38 L/s from the Getchell Mine and 30-40 L/s from TR. Groundwater generally flows south to southeast, with local recharge directly from outcrops and from infiltration during seasonal runoff. Two types of flow mechanisms dominate the bedrock aquifer

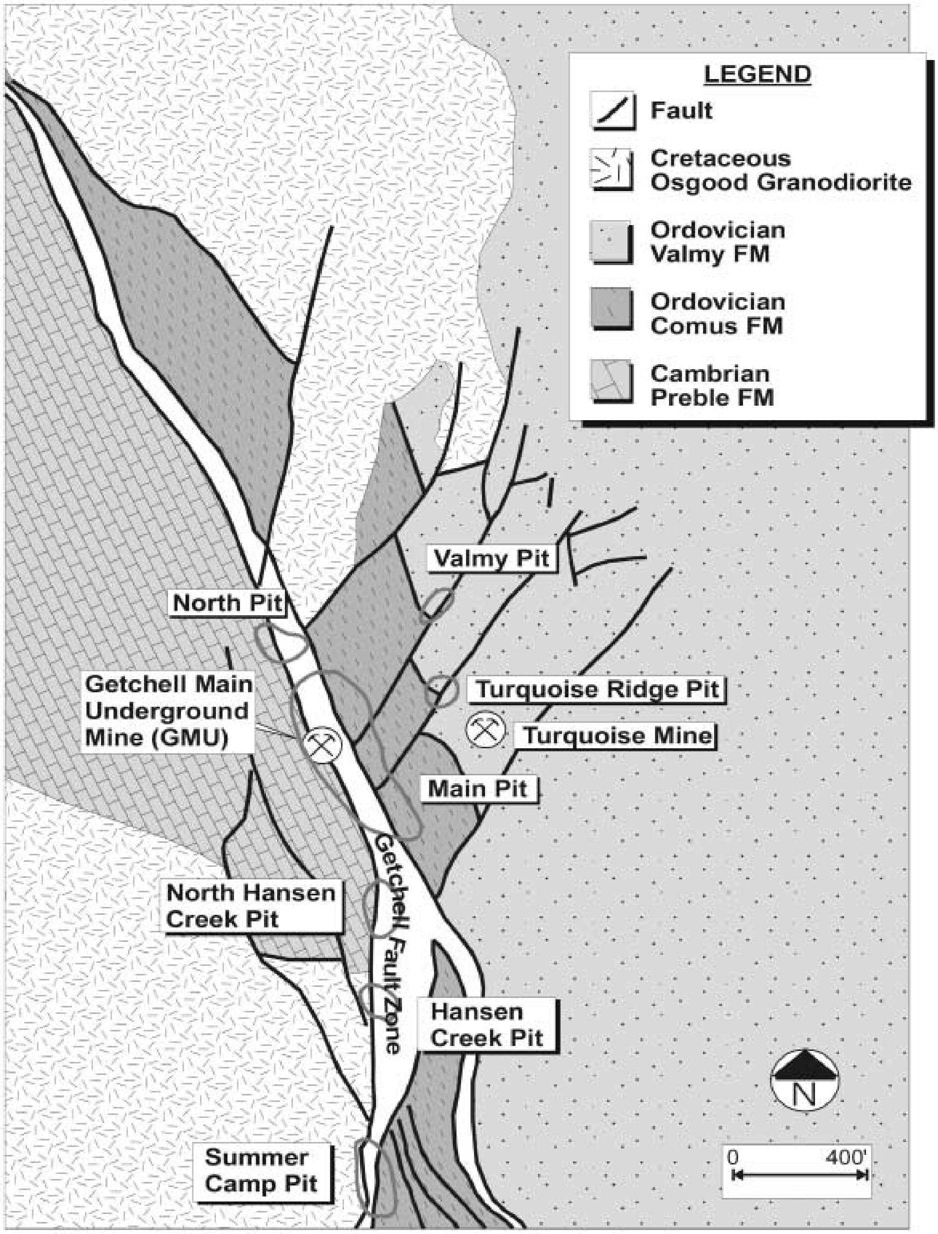

**Figure 1.** Simplified geology of the Getchell mine site

hydrogeology: compartmentalization (lateral flow retarded by clay-rich gouge) and fracture flow (somewhat unrestricted flow associated with minor fault deformation and fracture-induced permeability). The first appears to be controlled by faults that exhibit visible displacement along dip. The locations of the sampled levels are shown in Figures 3 and 4.

## Methodology

### Sampling

Water samples were collected from exploration boreholes underground, from natural fissures, and along fault zones. The water was collected in 1 L polyurethane bottles, which had been washed with 10% nitric acid and allowed to free drain prior to sampling. The water was filtered in the field at 0.45 µm; the filter was preserved in zip-lock bags for further analysis of the solid fraction. Bennett and Tempel (2000) observed the presence of hydrous ferric oxide (HFO), barite, and calcite on well screens of monitoring wells in the alluvium on the Getchell property, so we wished to assess if similar precipitates formed in the mine. The samples collected and target analytes are shown in Table 1.

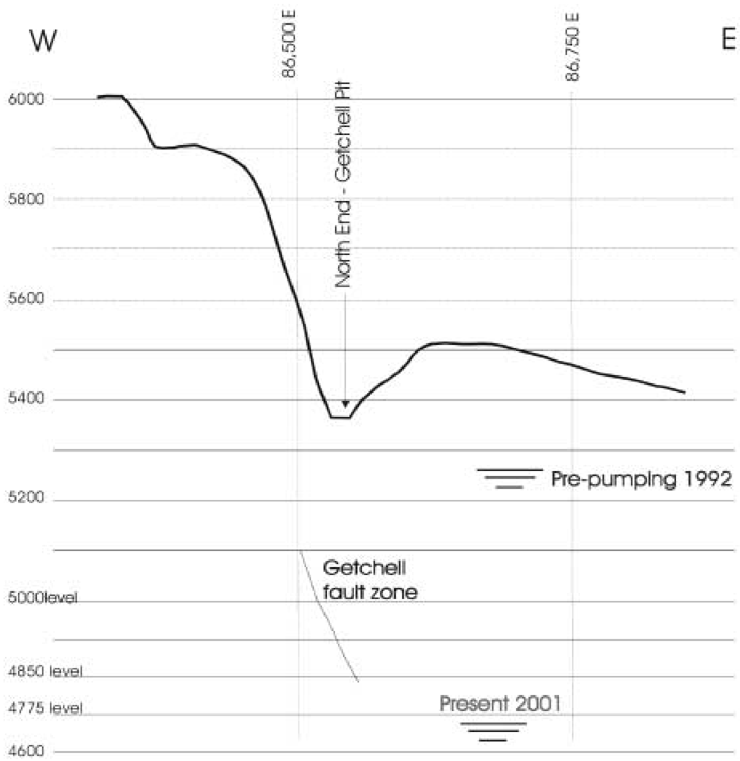

**Figure 2.** Hydrogeological cross-section of the Getchell underground mine (Hydrologic 1996)

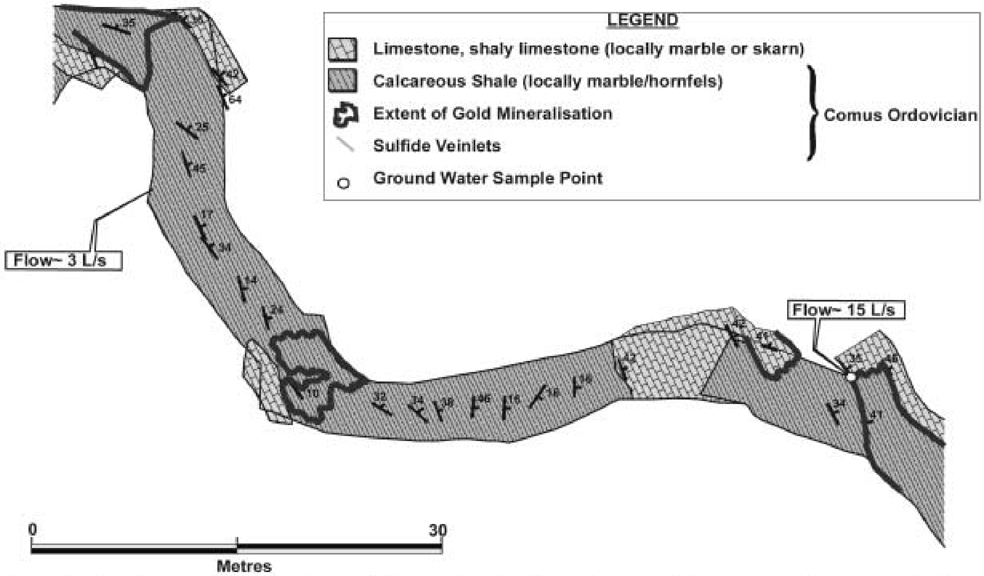

**Figure 3.** Geological cross-section showing location of high flow zones near major shear zones and low flow zones in fractured wallrock, Section 4850/182W, Getchell Mine (Hydrosearch, 1995)

## Analysis

Due to problems with sample preservation, sulfide analysis was carried out on site using a Hach field spectrophotometer. The pH, electrical conductivity, redox, temperature, and dissolved oxygen were also measured in the field. Water samples were analyzed by Sierra Environmental Monitoring of Sparks, Nevada using ion-chromatography, atomic absorption spectrometry, and inductively coupled plasma mass spectrometry (ICPMS). They also conducted the inorganic arsenic speciation analysis. Batelle NW Marine Science Laboratories of Seattle, Washington conducted the organic speciation analysis. The filter papers were analyzed at Cardiff University, Wales using X-Ray Diffraction and back scatter mode on an electron microscope fitted with an energy dispersive detector. Microanalysis of the filter solids was undertaken at Aberystwyth University using laser ablation ICPMS (Perkins et al. 1998).

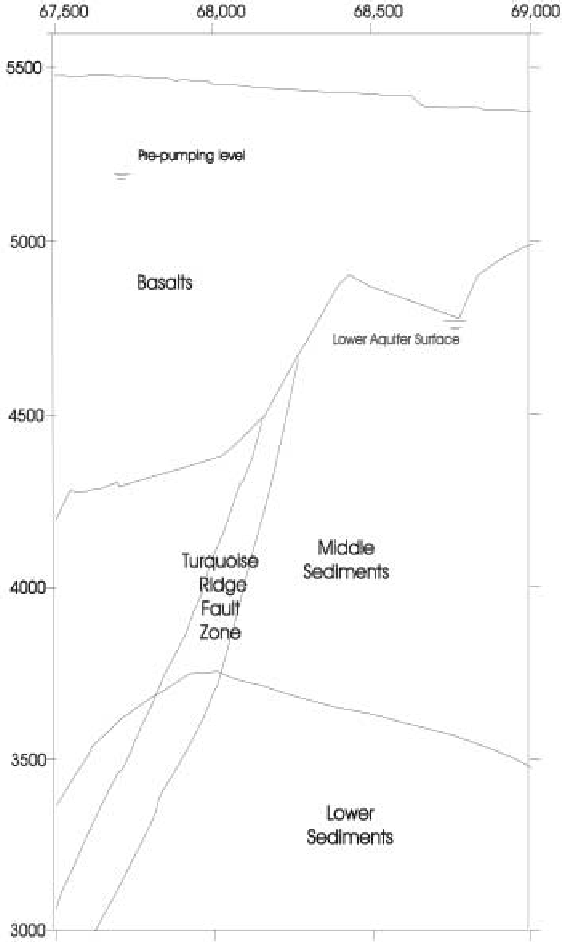

**Figure 4.** Hydrogeological cross section, Turquoise Ridge (Hydrologic 1996)

Geochemical speciation and saturation indices were calculated using the program MINTEQA2 (Allison et al. 1991), using a modified database that has additional As species thermodynamic data incorporated to account for complex As speciation.

## Results

Groundwater data for the Kelly Creek basin is very limited apart from water from alluvium wells or farm drinking wells. However, some chemistry data is available and is reported in Table 2. All of these waters are essentially Na-Ca-$HCO_3$ type or Na-Ca-Cl-$HCO_3$ type waters except that from wells in the vicinity of the old tailings, which plot as Ca-Na-Cl-$HCO_3$-$SO_4$ (or mixed) type waters. It can be observed that in the vicinity of the old tailings, evidence exists of anthropogenic input to alluvium groundwater, particularly with respect to As. Up-gradient of the mine, however, groundwater still contains As at levels higher than 0.05 mg/L and is similar to groundwater collected from the Getchell underground mine with respect to macrochemistry and trace elements. Indeed, this similarity to bedrock groundwater chemistry appears to indicate that Getchell mine water collected in-situ is consistent with so called "background" water quality. The old tailings site is some distance from the Getchell mine or TR and is down-gradient of both facilities (Table 1). The concentration range for representative groundwaters from Getchell and TR are shown in Table 3. The full database is reported in SRK (1999). Mine waters from the Getchell Mine can be classified (Figure 5) as follows:

Na-Ca-$HCO_3$ type: Water collected from boreholes in marble and away from sulfide mineralization.

Ca-Na-$HCO_3$-$SO_4$ type: Water collected from holes close to sulfide mineralization. Typically, a mixed marble-hornfels sequence or sulfide-mineralized bedrock will host such groundwater.

Ca-Na-$SO_4$ type: Observed in holes that are within mineralized rocks.

Only minor increases in chloride and total dissolved solids (TDS) occur with depth; host rock lithology is more important than depth in influencing the major solute chemistry. This effect can be localized, with water on the same elevation reflecting varied host rock chemistry and overall geochemical signature.

The waters collected from TR show only slightly different chemistries. A Ca-Na-$HCO_3$-$SO_4$ type macrochemistry is observed in boreholes that drain mineralized areas that are typically circumneutral and reducing. Water in marble host rocks show a Ca-Mg-$HCO_3$ type that appears to be the most common macrochemistry within unmineralized bedrock zones of the mine. These waters are typically oxidizing and circumneutral or mildly alkaline. The third TR water type is similar to the Getchell fault zone water and has a Ca-Mg-$HCO_3$-$SO_4$ chemistry. These waters have a higher TDS and sulfate content.

The trace element chemistry of the mine waters show distinct patterns that conform to the major element chemistry.

Ca-(Na-Mg)-$HCO_3$ type

These waters show comparatively low amounts of trace elements (Table 3). For example, hole 120 on level 4865 shows only trace levels of most metals, including 0.008 mg/L As, 0.56 mg/L Fe and 0.018 mg/L Mo. The water is neutral and highly reducing (Eh −135 mV). In these waters, the principal source of arsenic in the rocks, arsenic sulfides, will be insoluble, while the iron can be leached from many sources and would be stable in the carbonate waters

**Table 1.** Summary of analytes tested, method used and limits of detection and accuracy (all values in mg/l except where otherwise stated)

| *Analyte* | *Method* | *Detection limit* | *Accuracy, ± %* | *Sample type* |
|---|---|---|---|---|
| pH (su) | Field meter | 0-14 | ±0.2 su | In-situ |
| Eh (mV) | Field meter | ±500 | 30 | In-situ |
| Electrical Conductivity, µmhos | Field meter | 0-20000 | 15 | In-situ |
| Temperature, °C | Field meter | -10 - 80 | ±1-3°C | In-situ |
| Na | FAA | 0.01 | 10 | A/F |
| K | FAA | 0.01 | 10 | A/F |
| Be | ICPMS | 0.001 | 5 | B/C |
| Mg | ICPMS/FAA | 0.01 | 5 | A/F |
| Ca | ICPMS/FAA | 0.01 | 5 | A/F |
| Ba | ICPMS | 0.01 | 5 | A/F |
| Boron, B | ICPMS | 0.01 | 5 | B/C |
| Aluminium, Al | FAA | 0.05 | 10 | B/C |
| Thallium, Tl | ICPMS | 0.002 | 5 | B/C |
| Alkalinity | Titration | 0.1 | 15 | A/F |
| Lead, Pb | ICPMS | 0.003 | 5 | B/C |
| Ammonia, $NH_4$ | Ion-Chromatography | 0.1 | 10 | A/F |
| Nitrate, $NO_3$ | Ion-Chromatography | 0.3 | 15 | A/F |
| Nitrite, $NO_2$ | Ion-Chromatography | 0.02 | 10 | A/F |
| Total P | ICP | 0.02 | 20 | A/F |
| Arsenic, As III | Hydride generation | 0.005 | 5 | D/E |
| Arsenic, As V | Hydride generation | 0.005 | 5 | B/C |
| MMAA | Hydride generation | 0.01 | 5 | A/F |
| DMAA | Hydride generation | 0.01 | 5 | A/F |
| Arsenic, As | ICPMS | 0.001 | 5 | B/C |
| Antimony, Sb | ICPMS | 0.003 | 5 | B/C |
| Sulfide, $HS^-$ | Colorimetry | 0.02 | 10 | In-situ |
| Sulfate, $SO_4^{2-}$ | Ion-Chromatography | 0.1 | 10 | A/F |
| Selenium, Se | ICPMS | 0.001 | 10 | B/C |
| Fluoride, F | Ion-Chromatography | 0.1 | 10 | A/F |
| Chloride, Cl | Ion-Chromatography | 0.1 | 5 | A/F |
| Chromium, Cr | ICPMS | 0.002 | 5 | B/C |
| Molybdenum, Mo | ICPMS | 0.002 | 5 | B/C |
| Manganese, Mn | ICPMS | 0.01 | 5 | B/C |
| Iron, Fe | ICPMS/FAA | 0.01/0.05 | 5 | B/C |
| Iron, Fe II | ICPMS/FAA | 0.01/0.05 | 5 | D/E |
| Cobalt, Co | ICPMS | 0.001 | 5 | B/C |
| Nickel, Ni | ICPMS | 0.002 | 5 | B/C |
| Copper, Cu | ICPMS | 0.001 | 5 | B/C |
| Silver, Ag | ICPMS | 0.001 | 5 | B/C |
| Zinc, Zn | ICPMS | 0.01 | 5 | B/C |
| Cadmium, Cd | ICPMS | 0.001 | 5 | B/C |
| Mercury, Hg | ICPMS | 0.0002 | 5 | B/C |

Sample type (all 1 L sample bottles): A--unfiltered, unpreserved; B--filtered at 0.45 µm and acidified with 10 ml concentrated nitric acid; C--unfiltered and acidified with 10 ml concentrated nitric acid; D--filtered at 0.45 µm and acidified with 10 ml concentrated hydrochloric acid; E--unfiltered and acidified with 10 ml concentrated hydrochloric acid; F--filtered at 0.45 µm and unpreserved.

**Table 2.** Background water quality in the Kelly Creek Basin

| *Analyte* | *Kelly Creek Basin* | |
|---|---|---|
| | Range | Mean |
| pH (su) | 6.5-8.8 | 7.8 |
| Eh (mV) | -210-410 | 178 |
| Electrical conductivity (µmhos) | 320-10200 | 721 |
| Temperature, °C | 9.39-27.2 | 18.1 |
| Na | 18-190 | 44.4 |
| K | 2-3200 | 24.7 |
| Mg | 3-96 | 21.8 |
| Ca | 10-380 | 67.3 |
| Ba | 0.005-0.25 | 0.052 |
| Aluminium, Al | 0.05-2.1 | 0.031 |
| Thallium, Tl | <0.0002-0.004 | 0.0008 |
| Alkalinity | 72-800 | 188 |
| Lead, Pb | <0.0003-0.024 | 0.003 |
| Nitrate, NO$_3$ | 0.1-460 | 6.39 |
| Arsenic, As III | 0.001-6.3 | 0.054 |
| Arsenic, As V | 0.0009-20.0 | 0.031 |
| Arsenic, As | 0.0009-20.0 | 0.147 |
| Antimony, Sb | 0.0001-0.37 | 0.03 |
| Sulfate, SO$_4^{2-}$ | 3.51-640 | 123 |
| Selenium, Se | <0.002-0.04 | 0.008 |
| Fluoride, F | 0.08-5.1 | 0.88 |
| Chloride, Cl | 7.7-7200 | 73.7 |
| Chromium, Cr | <0.002-0.008 | 0.0009 |
| Manganese, Mn | 0.01-2.32 | 0.21 |
| Iron, Fe (total) | 0.01-48.0 | 0.37 |
| Nickel, Ni | 0.001-0.6 | 0.017 |
| Copper, Cu | 0.0005-0.07 | 0.004 |
| Silver, Ag | <0.0001-0.003 | 0.001 |
| Zinc, Zn | 0.0006-1.2 | 0.025 |
| Cadmium, Cd | <0.0001-0.084 | 0.002 |
| Mercury, Hg | <0.0001-0.001 | 0.0004 |

as a ferrous carbonate species. Similarly, from hole 82 on the 4775N drive, the oxidising, circumneutral waters have only slightly higher oxyanions levels for As (0.28 mg/L), Mo (0.37 mg/L), and Se (0.02 mg/L).

Water in borehole 30054 on the 1550 level of TR reflects geological source host rock geochemistry and/or flow path chemical environment. Arsenic is low compared to other borehole waters analyzed from the site (0.85 mg/L, of which all is present as arsenite). On a Flicklin diagram (Flicklin et al. 1992), these waters plot as low metal- alkaline waters similar to background groundwaters for the Kelly Creek basin (Figure 6). Due to the higher mobility of oxyanions, such as arsenic, in alkaline groundwaters, higher concentrations of oxyanions are observed, overlapping with the fields for waters inferred as originating from "mineralized" bedrock (Figure 7).

### Ca-Na-HCO$_3$-SO$_4$ type

These waters drain from known areas of mineralization or inferred mineralized blocks. The macrochemistry of the water varies in response to the lithology, from hornfels to marble. Transition metals are present, such as along the 4805 level where up to 0.023 mg/L Ni is observed. The main elevated metals are Mn, Co, and Ni; all three occur as trace elements in pyrite from Getchell (Bowell et al. 1999). Consequently, these waters occupy a large area on the Flicklin plot and overlap with the other two water compositions observed (Figure 6). Compared to transition metals, metalloids such as As and Sb are greatly elevated over background levels in most wells, with up to 7 mg/L combined Cr+As+Se+Sb oxyanions in the groundwater (Figure 7). Such water is typically reducing. Where ferric iron is observed, the concentration of all three oxyanions quickly decrease, presumably because the combination of the oxidised oxyanion and formation of HFO phases results in preferential adsorption and co-precipitation of these phases.

In one of the older boreholes in this type of groundwater, the steel pipe has corroded, yielding up to 68 mg/L total Fe in circumneutral, low salinity (TDS ~300 mg/l) groundwater. This was the only steel pipe that was observed to show this effect, which may also be related to the high sulfide content in this water (0.3 mg/L).

Trace element chemistry showed high arsenite content with traces of boron (0.13 mg/L) and sulfide (0.3 mg/L). Antimony was also detected at 0.012 mg/L but transition metals were generally low in this water with total Fe being 0.89 mg/L, of which 0.65 mg/L was Fe$^{2+}$. Manganese, Ni, and Zn were present at 0.022 mg/L, 0.015 mg/L, and 0.22 mg/L, respectively.

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### Ca-Na-SO$_4$ type

These waters are highly saline, as well as alkaline (up to pH 9.11) and reducing (Eh –60mV). Sulfide is stable in these waters with a maximum value of 6.5 mg/L. Arsenic and antimony (in reduced forms) were

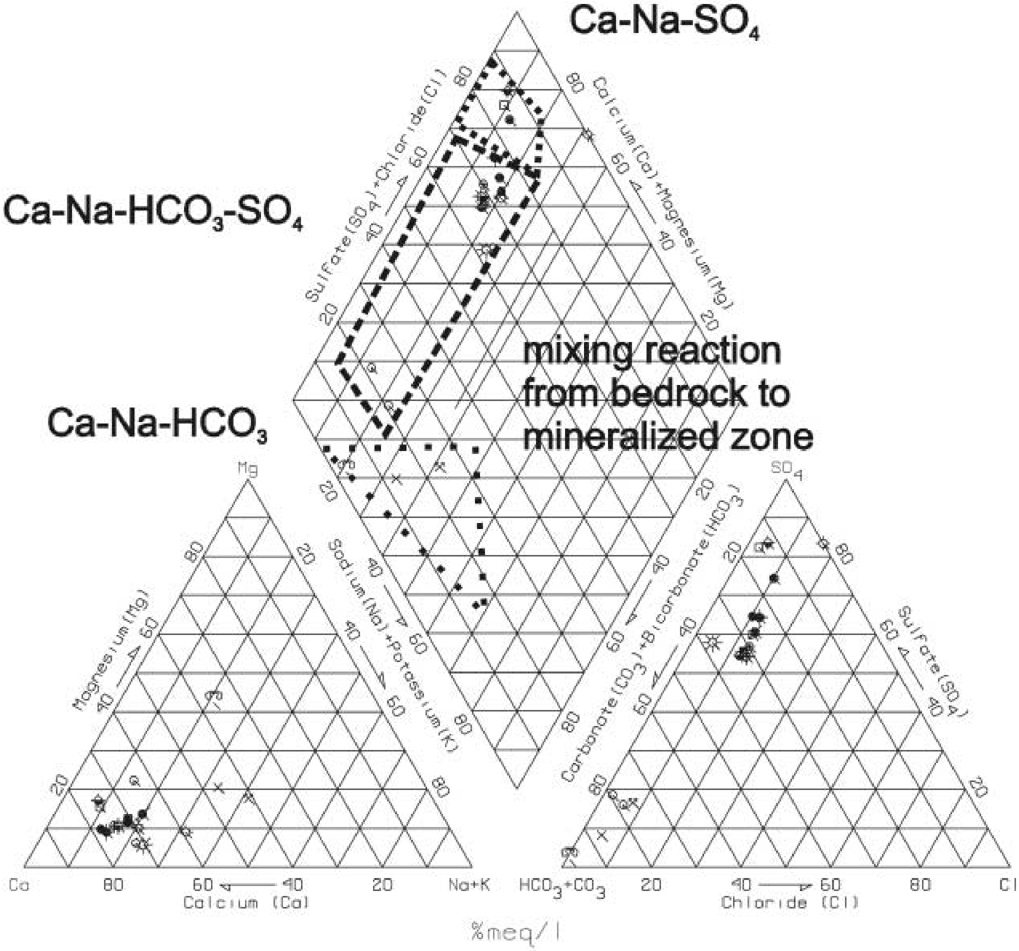

**Figure 5.** Piper diagram of groundwaters from Getchell Mine and Turquoise Ridge

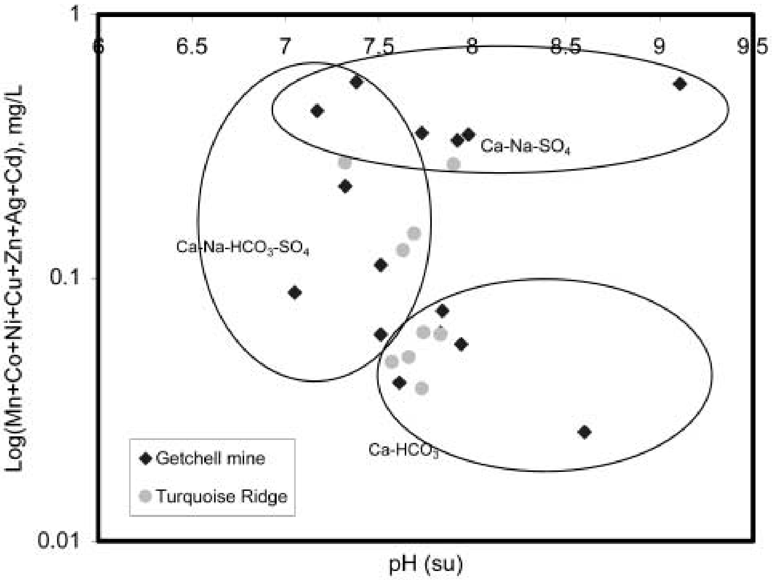

**Figure 6.** Flicklin diagram for the Getchell Mine and TR groundwaters (after Flicklin et al. 1992)

present at concentrations in excess of 1 mg/L. Transition metals were also present at unusually high concentration for alkaline water but are predicted to be stable as hydroxide and/or sulfide species, such as $Zn(HS)_2$ (aq). These include Fe (0.68 mg/L), Cd (0.008mg/L), Cu (0.006 mg/L), Mn (0.02 mg/L), Hg

**Table 3**. Range and mean of parameters analysed in groundwaters from the Getchell mine and Turquoise Ridge (in filtrates, 0.45 μm)

| *Analyte* | *Getchell Main Underground* | | *Turquoise Ridge Shaft* | |
|---|---|---|---|---|
| | Range | Mean | Range | Mean |
| pH (su) | 7.05-9.11 su | 7.76 | 5.32-7.9 | 7.07 |
| Eh (mV) | -185-291 | 22.5 | -124-366 | 179 |
| Electrical Conductivity, | 469-1661 | 363 | 508-1075 | 699 |
| Temperature, °C | 17.7-23.1 | 19.9 | 10.6-15.9 | 13.1 |
| Na | 16-44 | 24.7 | 14-47 | 31 |
| K | 2.2-3.9 | 2.93 | 2.1-6.1 | 3.62 |
| Be | <0.003 | nd | <0.001 | nd |
| Mg | 2.7-46 | 10.6 | 5.9-36 | 18.1 |
| Ca | 37-330 | 106 | 42-190 | 96.7 |
| Ba | 0.01-0.2 | 0.07 | 0.008-0.061 | 0.03 |
| Boron, B | 0.06-0.08 | 0.065 | 0.06-0.12 | 0.094 |
| Aluminium, Al | <0.05-0.01 | nd | <0.05-0.35 | 0.021 |
| Thallium, Tl | <0.002-0.068 | 0.005 | <0.002-0.002 | nd |
| Alkalinity | 22-202 | 103 | 61-146 | 99.9 |
| Lead, Pb | <0.003-0.004 | nd | <0.003 | nd |
| Ammonia, $NH_4$ | <0.1-7.1 | 0.4 | <0.1-2.3 | 0.71 |
| Nitrate, $NO_3$ | <0.1-2.21 | 0.47 | <0.1-0.4 | 0.31 |
| Nitrite, $NO_2$ | <0.1-0.2 | nd | Not analysed | |
| Total P | 0.02-0.91 | 0.19 | <0.02-0.81 | 0.407 |
| Arsenic, As III | 0.028-7.01 | 2.37 | 0.62-1.5 | 0.99 |
| Arsenic, As V | 0.005-0.13 | 0.043 | <0.005-1.1 | 0.39 |
| Arsenic, As | 0.08-7.09 | 1.37 | 0.025-6.61 | 2.16 |
| Antimony, Sb | <0.003-4.8 | 0.592 | <0.003-0.016 | 0.005 |
| Sulfide, $HS^-$ | <0.1-6.5 | 0.669 | 0.19-0.3 | 0.263 |
| Sulfate, $SO_4^{2-}$ | 26-810 | 407 | 95-520 | 231 |
| Selenium, Se | <0.001-0.003 | nd | <0.001-0.001 | nd |
| Fluoride, F | <0.1-1 | 0.3 | <0.1-1.1 | 0.22 |
| Chloride, Cl | 8.5-30 | 22.2 | 21-76 | 44.1 |
| Chromium, Cr | 0.001-0.026 | 0.010 | <0.001-0.009 | 0.005 |
| Molybdenum, Mo | 0.01-0.37 | 0.18 | Not analysed | |
| Manganese, Mn | 0.007-0.2 | 0.05 | 0.006-0.023 | 0.042 |
| Iron, Fe III | <0.05-0.3 | 0.17 | <0.05-0.08 | 0.03 |
| Iron, Fe II | 0.12-2.7 | 0.98 | <0.05-1.4 | 0.15 |
| Cobalt, Co | <0.001-0.002 | nd | Not analysed | |
| Nickel, Ni | 0.005-0.15 | 0.033 | 0.008-0.047 | 0.023 |
| Copper, Cu | <0.001-0.008 | 0.003 | <0.001-0.01 | nd |
| Silver, Ag | <0.001-0.002 | nd | <0.001-0.01 | nd |
| Zinc, Zn | <0.01-0.2 | nd | <0.01-0.22 | 0.14 |
| Cadmium, Cd | <0.001-0.001 | nd | <0.001-0.003 | nd |
| Mercury, Hg | <0.0005-0.061 | nd | <0.0005 | nd |

[1] total As/Fe not speciated; nd=not determined, insufficient analyses above detection to be meaningful

(0.061 mg/L), Ni (0.13 mg/L), and Zn (0.02 mg/L). While not particularly high, these concentrations are unusual at pH 9. Such high concentrations could be explained by the observed presence of colloidal fraction sulfide minerals and/or organic matter in the filter precipitates.

Water draining the partially oxidised main ore zone from TR showed a similar composition. The waters were more oxidised, with increased sulfate (over 400 mg/L) and lower sulfide (0.19 mg/L). The arsenic was 43% arsenite and 57% arsenate. Barium, Mn, and Ni concentrations were higher in this water (0.037, 0.047, and 0.044 mg/L, respectively). Iron speciation reveals the presence of ferric iron, although ferrous iron is still dominant (up to 94% of total iron). These observations suggest that even within bedrock, chemical zoning may exist. Samples collected using a depth sampler for one sub-vertical borehole reflect this zoning into oxidized and reduced zones. Higher Fe, As, and Sb is observed with depth into the reduced zone, reflecting the higher mobility of the reduced species for these elements, while the opposite is true for Mn, Ni, Zn, and sulfate (Figure 8).

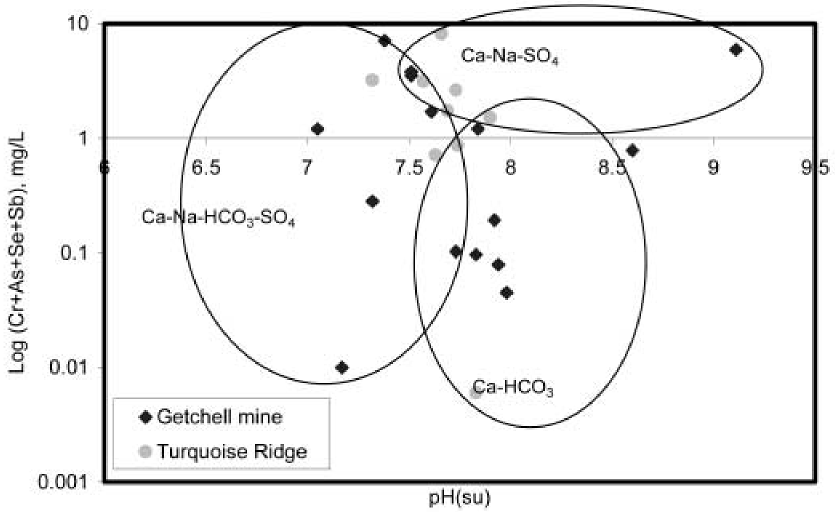

**Figure 7.** Oxyanions vs pH diagram for groundwaters from Getchell and TR. Note the separation of fields for the major water types.

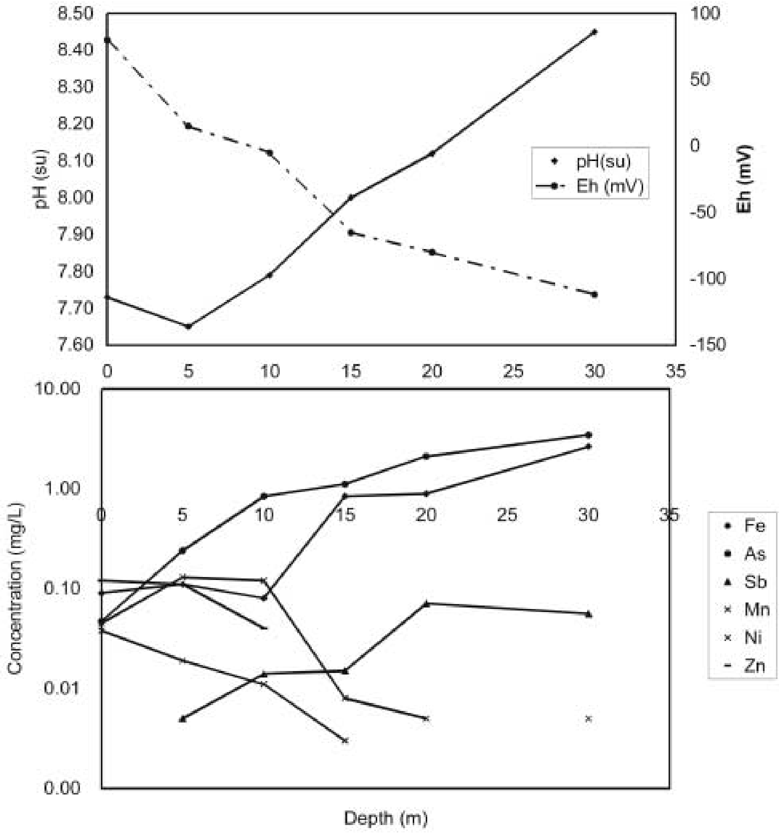

**Figure 8.** Downhole hydrogeochemistry, TR borehole 4775/198

## Arsenic Speciation

Arsenic speciation was measured directly in some groundwater samples, and in general shows the dominance of arsenite over arsenate, with the highest arsenic concentrations reflecting a dominance of arsenite (Table 3). An increase in arsenite concentration with pH is observed with TR data but the inverse was true at Getchell due to the influence of other parameters, such as source, mineral-wallrock interactions, and the concentration of other parameters such as Fe, Ca, Mn, and Mg. The

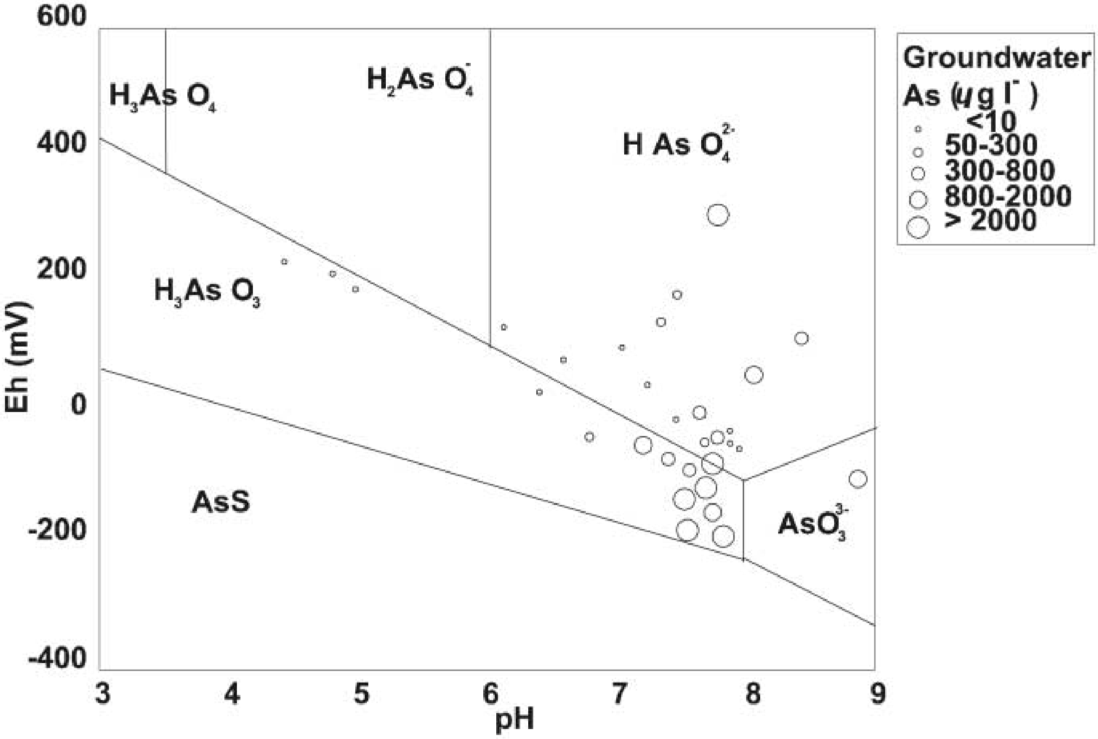

**Figure 9.** Getchell groundwater arsenic concentrations plotted on an Eh-pH diagram for the system As-S-O-H at 298K

exception is the one sample from TR where arsenate was ~ 0.87 mg/L and arsenite only 0.62 mg/L.

When plotted on an Eh-pH diagram (Figure 9), it can be observed that not only is total arsenic higher at lower Eh-higher pH conditions but it is predicted to be dominated by the arsenite species, $H_3AsO_3$. Additionally, the data is close to the stability field of AsS, which may explain the apparent stability of pararealgar (ambient temperature isomorph of AsS) in the mine, even though other sulfides are readily oxidised in the presence of the groundwater.

Predictions of mineral saturation using saturation indices (SI, Table 4) reflect the stability of sulfides in some groundwaters with positive SI (reflecting saturation with respect to water chemistry) for pyrite, pararealgar, and orpiment. Intriguingly, no secondary arsenic minerals showed a positive SI and all were undersaturated, and so would be predicted to dissolve.

Thermodynamic calculations by MINTEQA2 also predicted that over 55% of arsenic in all samples analysed from Getchell and over 60% of arsenic at TR would be in equilibrium as $H_3AsO_3$ or $H_2AsO_3^-$ with the arsenate species, $H_2AsO_4^-$ and $HAsO_4^{2-}$ also being important (Table 5). The presence of As (III) and As (V) species in the same water, aerobic or anaerobic, indicates that using As(III)/As(V) ratios as a measure of redox conditions (Cherry et al. 1979) is not valid, as redox equilibrium is not established. Alternatively, a form of dynamic equilibrium may exist in the mine waters in which more than one water may mix along the flow paths, possibly the regional Ca-Na-$HCO_3$ surface water recharged from the Osgood Mountains mixing with a water derived from sulfide-water interactions within the fault zone.

A small suite of samples was analysed for organoarsenic compounds. Traces of monomethyl arsonic acid (MMAA) (up to 170 µg/L) and of dimethyl arsinic acid (DMAA) (up to 20 µg/L) were identified (Table 3). These levels were subordinate to arsenite and arsenate but confirm the presence of methylating agents within the mine water capable of utilising arsenic. Some species of acidophillic bacteria have been shown to be tolerant of arsenite and derive energy for chemoautotrophic growth from arsenite oxidation (Wakao et al., 1988). Although these bacteria typically utilise acidic environments (pH 3-4), it is possible that within the micro-environment of pyrite or orpiment oxidation, such conditions are available through mechanisms such as:

$$FeS_2 + 3.5O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$$

or

$$As_2S_3 + 6H_2O + 7O_2 = 2H_2AsO_4^- + 3SO_4^{2-} + 8H^+$$

The occurrence of such reactions could be argued to be natural, though undoubtedly accelerated by the "anthropogenic" action of underground mine development, which allows a larger flux of oxygenated air into the mineralized bedrock than would otherwise occur. This influx may be the primary cause of the apparent "disequilibrium" observed in water quality data and predicted by geochemical modelling. As such, this modifies background water quality, complicating the determination of the mine's impact on groundwater.

## Hydrous Ferric Oxide Composition

A negative correlation exists in the data from Getchell for arsenate and, to a much lesser extent, arsenite, with ferric iron in the filtered fraction, while a positive correlation exists in the total fraction (Table 6). For the majority of filters, only calcite, hydrous ferric oxide and barite were present, but in some cases, pararealgar was also observed. Other sulfide phases observed included pyrite, orpiment,

**Table 4.** Range for theoretical speciation of arsenic and saturation indices (SI) of As-phases determined by MINTEQA2

| *Species* | *Getchell* | *Turquoise Ridge* |
|---|---|---|
| $H_2AsO_4^-$ | 1.2-19% | 1.2-31% |
| $HAsO_4^{2-}$ | 5.7-25% | 2.3-63% |
| $AsO_4^{3-}$ | 0-1% | 0-1% |
| $H_3AsO_3$ | 2-89% | 3.8-90% |
| $H_2AsO_3^-$ | 0-3.4% | 0-8.7% |
| $AsO_3^{3-}$ | 0-1.2% | 0-1.6% |
| $SI_{realgar}$ | -6.626 - 1.687 | -11.251- 5.669 |
| $SI_{orpiment}$ | -14.350 - 13.710 | -34.733 - 15.557 |
| $SI_{pyrite}$ | -12.763 - 11.236 | -7.094 – 13.334 |
| $SI_{FeAsO4.2H2O}$ (scorodite) | -6.090 - -5.125 | -10.247 - -4.991 |
| $SI_{arsenolite}$ | -14.335 - -2.731 | -30.983 - -1.983 |
| $SI_{Ca3AsO4.26H2O}$ | -36.333 - -3.796 | -10.411 - -4.333 |

**Table 5.** Arsenic geochemistry (All concentrations in mg/L unless otherwise stated)

| *Sample* | *4775N* | *4775/198a* | *4775/196* | *TRW001* | *TRW002* | *TRW003* |
|---|---|---|---|---|---|---|
| pH (su) | 7.38 | 7.73 | 7.98 | 7.9 | 7.74 | 7.69 |
| Eh (mV) | -185 | -65 | 186 | -124 | 80 | 311 |
| Fe, total | 2.9 | 0.15 | 0.16 | 0.89 | 0.10 | 0.53 |
| Fe 0.45µm[1] | 2.9 | <0.05 | <0.05 | <0.05 | <0.05 | 0.19 |
| Fe(II), total | 2.7 | 0.12 | 0.13 | 0.65 | 0.10 | 0.50 |
| Fe(II) 0.45µm | 2.7 | <0.05 | <0.05 | 0.07 | <0.05 | 0.08 |
| As total | 7.09 | 0.088 | 0.033 | 1.50 | 0.85 | 2.6 |
| As 0.45µm | 6.73 | 0.047 | 0.027 | 1.40 | 0.83 | 1.72 |
| As (III) total | 7 | 0.071 | 0.028 | 1.48 | 0.65 | 1.5 |
| As(III) 0.45µm | 6.53 | 0.034 | 0.022 | 1.29 | 0.61 | 0.62 |
| As (V) total | 0.09 | 0.017 | 0.005 | 0.010 | 0.20 | 1.1 |
| As (V) 0.45µm | 0.013 | 0.003 | 0.005 | 0.010 | <0.005 | 1.1 |
| MMAA 0.45µm | 0.170 | 0.010 | <0.010 | 0.088 | <0.010 | <0.010 |
| DMAA 0.45µm | 0.020 | <0.010 | <0.010 | 0.015 | <0.010 | <0.010 |
| As (III)/As(V)[2] | 502 | 11.3 | 4.4 | 129 | ND[3] | 0.56 |

1. 0.45µm denotes the sample concentration after filtering at 0.45µm filter size; 2. Ratio refers to 0.45µm filtered sample; 3. ND signifies not determined due to As(V) concentration being below detection

**Table 6: Correlation coefficients for As-species with pH and iron**

|  | *pH* | *Fe (total)* | *Fe (filter)* | *AsIII (filter)* | *AsV (filter)* |
|---|---|---|---|---|---|
| PH | 1.000 |  |  |  |  |
| Fe (total) | 0.428 | 1.000 |  |  |  |
| Fe (filter) | -0.678 | 0.998 | 1.000 |  |  |
| AsIII filter | 0.496 | 0.478 | -0.756 | 1.000 |  |
| AsV filter | 0.433 | 0.562 | -0.877 | 0.565 | 1.000 |

R(95%)=0.450; r(99%)=0.500; r(99.9%)=0.780

sphalerite, and stibnite. No secondary arsenic minerals were observed but this may only indicate that concentrations were too low to be identified by XRD or that the minerals were not sufficiently crystalline to yield a recognisable pattern.

The trace element composition of hydrous ferric oxide (HFO) phases is shown in Table 7. The HFO phases show a high concentration of heavier elements and these are proportionally concentrated in the HFO particles over average water composition. The presence of some metals, such as Al, Cr, Mn, Co, and Ni, is probably due to co-precipitation or absorption of the metal with Fe into the structure of the hydrous ferric oxide. In the case of arsenic and antimony, it is far more likely that their presence is due to surface adsorption of oxyanions such as $HAsO_4^{2-}$ (Bowell 1994). The HFO collected from the oxidised zone show a considerably higher As content than HFO phases from within the mine (Table 6), even though hydrogeochemical As concentrations are close to the average (1.49 mg/L). This reflects the higher arsenate to arsenite content of this water and the greater adsorption potential of arsenate over arsenite species (Bowell 1994).

## Discussion

### Geological Controls on Hydrogeochemistry

Getchell is typical of the class of gold deposits defined as "disseminated gold in metasediments" or Carlin-type deposits, which produced in excess of 200 t (7 million ounces) worldwide in 1999 (Mining Journal 2000). These deposits are typically large-tonnage, low-grade epigenetic deposits hosted predominantly in carbonate rock formations. They are formed through the focusing of hydrothermal fluids along zones of weakness such as deep fault zones and mixing of deep crustal waters with meteoric recharge (Berger and Bagby 1991; Bertensen et al. 1996; Kuehn and Rose 1995; Teal and Jackson 1997). Host rocks are often carbonaceous and contain abundant calcite and dolomite. Sulfide levels in the mineralization can range from <1% to 20-30% and are dominated by abundant marcasite and pyrite that show morphologies from idiomorphic crystals to porous, microcrystalline grains (Bowell et al. 1999; Simon et al. 1999). Possible accessory minerals include realgar and orpiment (noticeably at Getchell where ores can grade up to 30% As), stibnite, Hg-Tl-As sulfosalts, and rarely arsenopyrite, sphalerite, and galena (Bagby and Berger 1985).

Sulfide chemistry is an important control on hydrogeochemistry at Getchell. The major arsenic hosts, realgar and orpiment, are not particularly reactive at circumneutral pH although their solubility increases

**Table 7.** Composition of Hydrous Ferric Oxide Compounds from Getchell mine

| *Location* | *4775N* | *4775/198a* | *4850/182* | *TRW001* | *TRW003* | *SCP wall* |
|---|---|---|---|---|---|---|
| Drainage pH (su) | 7.38 | 7.73 | 9.11 | 7.9 | 7.69 | 6.6 |
| Filtrate mineralogy[1] | Ba,Cc,HFO, Ka, Py | Ba,Cc,HFO | Ba,Cc, HFO, Pr, Py | Ba,Cc,Ka Pr,Py,Orp, St | Ba,Cc,HFOSc | Ba, Cc, Caas,HFO, Sc, Pr |
| Elements | All analyses by LAICPMS[2] and are expressed as mg/Kg | | | | | |
| Co | 9.11 | 2.98 | 59.9 | 61.3 | 50.2 | 66.4 |
| Ni | 13.2 | 5.87 | 522 | 719 | 81.2 | 58.8 |
| Cu | 6.79 | 20.0 | 28.2 | 102 | 65.0 | 76.1 |
| Zn | 29.4 | 14.1 | 79.8 | 81.4 | 131 | 149 |
| As | 1930 | 850 | 788 | 2560 | 6120 | 9670 |
| Se | 11.8 | 2.78 | 12.5 | 56.4 | 141 | 355 |
| Ag | 1.22 | 1.43 | 3.76 | 44.3 | 11.3 | 87.3 |
| Cd | 3.18 | 1.20 | 8.92 | 6.1 | 7.9 | 11.9 |
| Sb | <1 | 4.02 | 4.55 | 310 | 382 | 492 |
| Hg | <1 | <1 | <1 | 12.2 | 1.9 | 459 |
| Pb | <1 | <1 | 5.09 | 7.91 | 563 | 3780 |
| U | 1.92 | 4.26 | <1 | <1 | 5.12 | 3.5 |

[1] Mineralogy by XRD: Ba= Barite; Caas- Calcium arsenates; HFO= Hydrous Ferric Oxide includes goethite; Ka= Kaolin; Pr-Pararealgar; Op=orpiment; Pyr=Pyrite; Sc=Scorodite; St=Stibnite; [2]All analyses performed using Laser Ablation Inductively Coupled Mass Spectrometry. All samples prepared as probe blocks. Instrument used, VG Instruments PQH+ICP and VG LaserLab run in fixed Q-mode (Bowell et al., 1999).

considerably at higher pH (pH > 9). Consequently, the mobilized arsenic must have an alternative source. Arsenopyrite is present at Getchell but in fairly limited amounts; however, arsenian pyrite is widely dispersed and is the main gold host in the mineralization (Bowell et al. 1999). The arsenian pyrite typically has > 1wt% As in rims and can be as much as 5wt%. This pyrite is typically porous or poorly crystalline and fine-grained, and so is probably highly reactive (Bowell et al. 1999; Simon et al. 1999). Additionally, the presence of arsenic in the pyrite lattice induces semi-conductor properties that can make the pyrite more reactive (Thornber, 1992). Consequently, it is plausible that the main source of hydromorphic or mobile arsenic at Getchell is not the abundant realgar-orpiment minerals but rather arsenian pyrite. A caveat that should be added, however, is that under ambient conditions, realgar reorganises to produce a finer grained polymorph, pararealgar. This phase was common in many of the filter papers and where total arsenic is considerably higher than filtered arsenic, this is the probable cause of the difference.

The abundant carbonate content of the host rocks is reflected in the circumneutral pH of the groundwater. The low content of base metal sulfides is also reflected in the low concentration of first row transition metals.

## Arsenic Hydrogeochemistry

The hydrogeochemistry of arsenic is dominated in aerobic groundwaters (defined here where dissolved oxygen > 1mg/L) by arsenate species of the type $H_nAsO_4^{n-3}$ (Figure 10). In anaerobic groundwaters (dissolved oxygen < 1 mg/L), the reduced form, arsenite, $H_nAsO_3^{n-3}$, dominates (Figure 10). Where methylating agents are present, the organoarsenic acids, MMAA and DMAA, can be formed. As at Getchell, these are generally present in trace amounts in anaerobic groundwaters (Table 4). In strongly sulfidic environments, arsenic sulfide species may be present, and in this study, AsS has been demonstrated in ther- modynamic predictions to form a portion of the speciation of As in the anaerobic groundwaters at Getchell (Table 5). Other sulfidic complexes may be formed at ambient temperatures and have a general chemistry of $H_nAs_3S_6^{n-3}$ (Webster 1990; Helz et al. 1995). Where high arsenic concentrations have been observed in the GUM waters, it is possible that oligomeric forms, such as $As_4O_6$ or $As_3O_3(OH)_3$, may exist (Tossell 1997).

The presence of both arsenite and arsenate forms in the groundwaters may not only reflect a lack of redox equilibrium but also active oxidation-reduction reactions as a result of mineral-water interactions (Stumm and Morgan 1996). Arsenate reduction may occur due to reaction with a reductant such as Fe(II) or a mixed Fe(II)-Fe(III) species, as has been observed for Se (VI) reduction to Se (IV) (Myneni et al. 1997). Oxidation of arsenite could occur in response to increased dissolved oxygen or reaction with an oxidant such as Mn (IV), as observed in laboratory experiments (Driehaus et al. 1995; Scott and Morgan 1995).

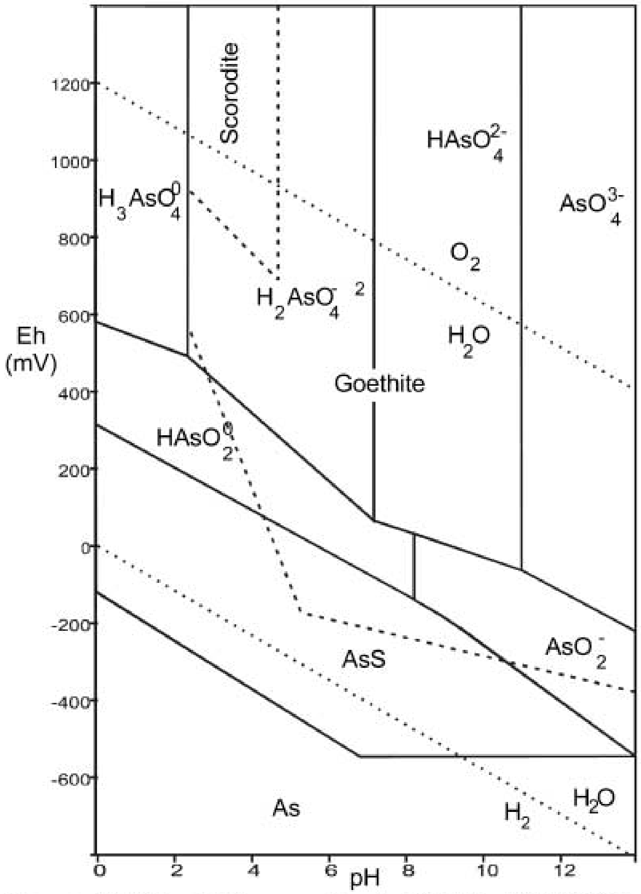

**Figure 10.** Eh-pH diagram for As-S-O-H at 298K (S= $10^{-3}$M; As= $10^{-6}$M)

A positive correlation occurs in the total fraction between arsenate and total Fe. A possible explanation for this is the strong adsorption of arsenate and to a lesser extent arsenite onto amorphous or poorly crystalline hydrous ferric oxide (HFO) (Sigg and Stumm 1980; Waychunas et al. 1993; Bowell 1994; Jain et al. 1999). The ability of HFO phases to adsorb arsenic species is influenced by the mineral speciation and crystallinity of the iron mineral or phase, groundwater pH, presence of competing oxyanions such as organic acids and phosphate and by the presence of other adsorbent surfaces. The sorption decreases in the order As(V)>DMAA=MMAA> As(III) below pH 7 and As(V)>As(III)> MMAA=DMAA above pH 7. Sorption decreases in the order amorphous HFO> ferrihydrite> goethite> lepidocrocite> hematite (Bowell 1994). Increased concentration of oxyanions that compete for adsoprtion sites would reduce arsenic sorption on iron minerals. Greater sorption occurs in the pH range 4-7.5; above this, the $pH_{pzc}$ (point of zero charge) occurs and the potential for adsorption quickly diminishes (Deng and Stumm 1990; Stumm and Morgan 1992). Therefore, both a drop in pH and an increase in competing anions would increase arsenic leaching. Although arsenite adsorption is limited by comparison to arsenate, the rate of adsorption is faster (Raven et al. 1998). The rate of adsorption is initially rapid but then slows for a longer period, during which adsorption is controlled by diffusion of the oxyanion into the iron mineral particles (Fuller et al. 1993). As crystallization of a HFO, such as ferrihydrite occurs, arsenic is released (Waychunas et al. 1993).

Remobilization of arsenic will occur if the physico-chemical nature of the environment in which the HFO resides changes. This may include dissolution of the HFO or scavenging of adsorbed species or an increase in pH or a decrease in redox potential. Increase in the concentration of competing oxyanions will also result in an increase in groundwater arsenic. This may explain the highly variable anomalies for As in groundwater previously reported throughout the Kelly Creek basin (Bennett and Tempel 2000; Grimes et al. 1995).

### Implications for establishing baseline conditions

There is considerable variation in groundwater chemistry along the Getchell fault due to differences in bedrock structure, geology, mineralization, and alteration. This chemistry is further complicated by the disequilibrium produced by accelerated oxidation of sulfides in bedrock as a result of oxygenated air penetrating into the underground workings.

The discrimination of groundwater in the mine into one of the identified sub-types allows interpretation and prediction of geological conditions along the flowpath. Of particular importance, water along the Getchell Fault Zone is naturally mineralized and has elevated As levels. Although up gradient wells show elevated As concentrations it is clear that along the fault zone, groundwater does not form an equilibrium with the mineralized host rocks as mineral-water reactions actively occur.

Although these are natural processes, it makes defining a baseline value difficult. Similarly, there are difficulties in applying a set value to water in the area since the processes that buffer water quality are dynamic; water quality is continually evolving. These processes have been active for geological time, though accelerated by mining. The Getchell site illustrates that in a historic mining area, pre-mining background water quality is difficult to assess and regulatory guidance should be based more on defining a range of trigger concentrations for response rather than stipulating a single value standard. The term trigger concentration is defined here as a concentration range that if the upper value is exceeded, action is required to determine the source of the elevated value and then determine if the concentration increase is related to mining or natural processes.

A further important issue is that bedrock groundwater is markedly different from alluvium groundwater, not described in this paper. These differences are important and result in a marked difference in chemistry between the two sets of groundwater (Grimes et al., 1995; Bowell et al., in prep). As these two forms of groundwater (bedrock and alluvium) are separated by a head difference of ~130m, regulatory guidance for water quality should show different ranges of trigger values for each type rather than defining one set of values to cover all groundwater.

## Conclusions

Groundwater from the Getchell Mine can be classified into three different types based on their water quality and on their proximity to mineralized zones:

Type 1: waters from areas away from the sulfide mineralization or from formations containing significant marbles that are $Ca\text{-}HCO_3$-dominated.

Type 2: waters from sulfide mineralized zones that are $Ca\text{-}Na\text{-}HCO_3\text{-}SO_4$-dominated.

Type 3: waters from sulfide mineralized zones that are $Ca\text{-}Na\text{-}SO_4$ dominated.

All of these water types are typically alkaline, with Type 1 having a higher pH range than the others. Type 1 waters typically contain a range of the constituents Al, As, Fe and Mn in excess of drinking water standards. Type 2 and 3 waters typically contain a range of the constituents including TDS, sulfate, Al, As, Fe, Mn and Zn in excess of drinking water standards. Type 2 and 3 waters contain As and Fe in a reduced oxidation state as well dissolved sulfide with other minor elements. Constituents of concern are most likely leached from the hornfels and from oxidation of the sulfides.

Type 2 waters dominate groundwater flowing into the Getchell Main and TR underground mines. They appear to be a blend of waters buffered by the host marble/limestone unit with a contribution from hornfels-groundwater reactions. The mine waters reflect the compartmentalized nature of bedrock groundwater in the Kelly Creek basin. The hydrochemistry demonstrates constituent concentrations above maximum discharge limits (MDL) typically set for such waters. The significant differences that occur throughout the mine in bedrock groundwater and in alluvium groundwater (Bowell et al., in prep) suggest that the application of a set of single value standards is unreasonable to cover the whole property. Rather, values should be defined based on hydrogeological blocks or compartments and major water types. In this way, background variations, historic and natural "anthropogenic" sources and future impacts can be better understood and managed accordingly.

## Acknowledgements

This study has been published with the approval and support of Getchell Gold Corp, a member of the Placer Dome group. The views expressed are entirely those of the author. I am grateful to John Barta for approval, review and discussion. Dr Bill Perkins of Aberystwyth Univ is thanked for assistance with LAICPMS work. The study has greatly benefited from a thought-provoking review by Adrian Brown.

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