

Chapter D

ENVIRONMENTAL BEHAVIOR OF TWO MOLYBDENUM PORPHYRY SYSTEMS

Michele L.W. Tuttle, Richard B. Wanty, and Byron R. Berger

INTRODUCTION

This paper compiles geological, hydrological, and geochemical data required to understand the environmental behavior of metals associated with two molybdenum (Mo) porphyry systems. The two systems represent a high fluorine, granite Mo system (Climax-type) and a low fluorine granodiorite system (deposit types described in Cox and Singer, 1985; Soregaroli and Sutherland Brown, 1976). The low-fluorine deposit (Buckingham Stockwork Mo deposit) is located on Battle Mountain in Nevada and the Climax type deposit (Mount Emmons/Redwell deposit) is beneath Red Lady and Redwell Basins, Colorado (fig. 1). The water quality of streams, natural springs, mine discharge, and ground water from drill holes are assessed in the region of these two deposits. In addition, the geology and controls on the hydrology are used to establish a framework for the water quality data.

The goals of this work are:

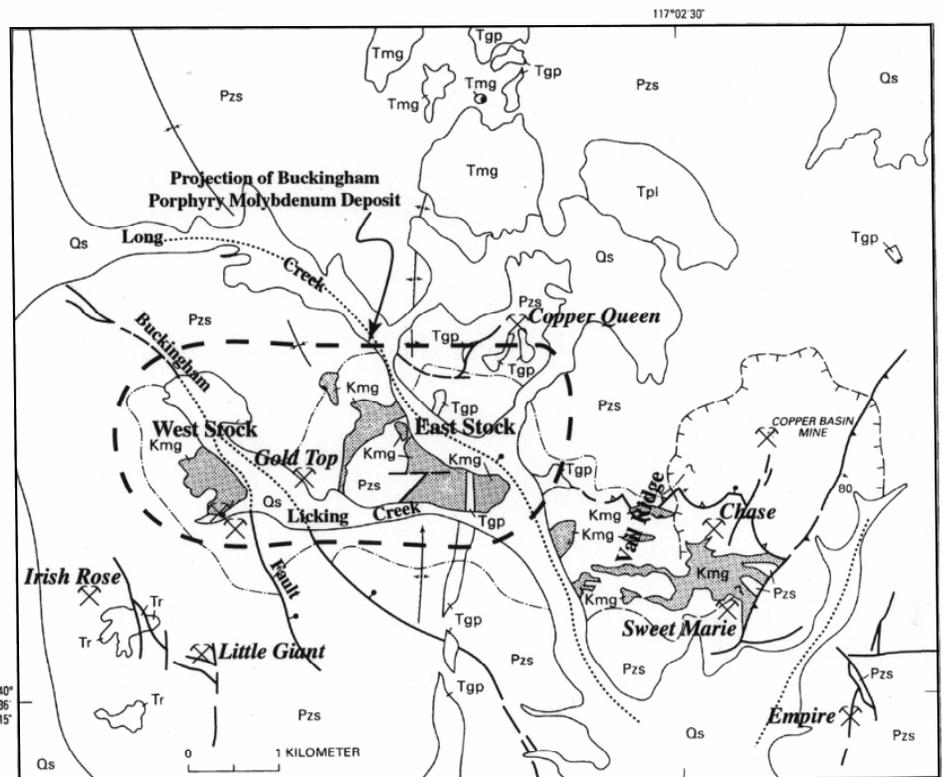
1. Establish background concentrations of metals in streams flowing through undisturbed mineralized Mo porphyry deposits,
2. Describe geochemical characteristics of waters associated with both high- and low-fluorine Mo porphyry deposits in undisturbed and mined drainages,
3. Recognize the important geochemical processes that control these characteristics (e.g. metal adsorption and precipitation),
4. Determine the appropriate sampling density needed to recognize diagnostic geochemical characteristics to assess water quality near and downstream from the deposits,
5. Understand how climate affects water composition, and
6. Integrate geochemical data with the geology and hydrology within the drainage basins.

BACKGROUND

Battle Mountain, Nevada

Long Canyon and Licking Creek cross the Buckingham Stockwork Mo deposit (also referred to as the Buckingham porphyry Mo deposit). There are very few mines in the Long Canyon drainage. The lower portion of the canyon represents an undisturbed mineralized area with its upper reaches well outside the mineralized area (fig. 1). Samples from the upper reaches of the stream provide valuable data to assess the water quality attributed to the unmineralized host-rock lithology in the area. A small spring (perhaps an uncompleted drill hole; sample site 1) just outside the Mo deposit produces waters that may be in contact with the Mo mineralized stockworks at depth. We have interpreted this spring water to be a natural “deposit drainage” into Long Canyon.

All samples collected along Licking Creek were within the boundary of the Buckingham Stockwork Mo deposit (fig. 1). As mines and their dumps are common throughout the drainage, we have characterized Licking Creek as a disturbed mineralized area. Buckingham Camp Creek, a tributary to Licking Creek, was a site of the Buckingham Camp where ore was processed. Water from the Buckingham Camp Creek, a small tributary into Licking Creek, represents drainage from the mines and processing dumps. Along the Buckingham fault at the confluence of Buckingham Camp Creek and Licking Creek, a spring discharges high contents of trace metals. We interpret this spring water as “deposit drainage” and, although natural, is geochemically similar to water in Buckingham Camp Creek.



EXPLANATION

- Tr Rhyolite (Tertiary) Surficial
- Qs Superficial deposits (Quaternary)
- Tgp Granodiorite porphyry (Tertiary)
- Tmg Monzogranite (Tertiary)
- Tpl Porphyritic leucogranite (Tertiary)
- Kmg Monzogranite porphyry (Cretaceous)
- Pzs Sedimentary rocks (Paleozoic)
- Contact
- Faults—Dashed where approximate; dotted where concealed. Bar and ball on downdropped side. May show dip
- ⊥ Normal
- ⊥ Low-angle gravity glide—Sawteeth on upper plate
- ⊥ Thrust—Sawteeth on upper plate
- ⊥ Anticline—May show direction of plunge
- ⊥ Syncline
- - - Boundary of Buckingham quartz stockwork—Queried where location uncertain
- ⊥ Boundary of Copper Basin open-pit mine

Figure 1. Generalized geologic map of the Late Cretaceous Buckingham porphyry molybdenum deposit, Battle Mountain, Nevada (Theodore and others, 1992). A projection of the outer boundary of the molybdenum deposit is indicated by the dashed line. Some of the major Late Cretaceous and Early Tertiary polymetallic vein and skarn deposits are indicated in italics.

Redwell Basin, Colorado

Redwell Basin was mined for base metals (zinc, lead, and copper) that occur in the breccia pipe above the two Redwell deposits (fig. 2). Ground-water discharges into the Redwell Basin from these old mine workings. Above most of these seeps, an old drill hole produces water that flows into a small tributary of Redwell stream. The ground water flowing from the drill hole likely is from various levels within the porphyry/breccia pipe complex, making it impossible to isolate the geochemical characteristics of the Mo porphyry from that of the accompanying epithermal base-metal mineralization. This complexity affects most drainages associated with Mo porphyry systems due to the proximal position of base metals, or, as is the case at Battle Mountain, later mineralization events that overprint the porphyry system. The ground water being discharged at the drill hole, although derived from a composite of deposit types, provides the best approximation of the geochemistry of water draining from the high fluorine Mo porphyry system in this relatively undisturbed drainage basin.

Climate

The climate is distinctly different between the Nevada and Colorado study sites, and, because climate is thought to be an important control on the environmental behavior of metals, these differences were integral variables in this study. The surface elevation at the Buckingham deposit is 1,646 m (5,400 ft) to 2,011 m (6,600 ft). The town of Battle Mountain (elevation 1,383 m) some 10 km to the north of the deposit receives 19 cm precipitation per year and has a mean annual temperature of 9.5°C. Average annual evapotranspiration as calculated by Shevenell (1996) is between 60 and 120 cm and depends strongly on elevation. The Mount Emmons/Redwell deposit sits beneath high alpine valleys. The Redwell basin is at 2,865 m (9,400 ft) to 3,658 m (12,000 ft) elevation. The town of Crested Butte (elevation 2,700 m) receives 60 cm precipitation per year and has a mean annual temperature of 1.1°C.

GEOLOGY

Buckingham Porphyry Molybdenum Deposit, Battle Mountain, Nevada

The study site is the location of an unmined, largely buried porphyry molybdenum deposit and associated veins (fig. 1). The deposit is related to a ~86 Ma composite, porphyritic intrusive into feldspathic sandstone, quartz arenite, and shale of the Upper Cambrian Harmony Formation (Theodore and others, 1992).

1. Lithology. The Cambrian(?) Harmony Formation in the Battle Mountain range consists of interbedded quartz arenite, subarkose, arkose, pebbly quartz arenite, shale, and minor limestone (Roberts, 1964). In the Buckingham area, the Harmony consists predominantly of graded sandstone including quartz arenite, arkose, subarkose, and litharenite with minor amounts of shale, calcareous shale, and greenstone (Theodore and others, 1992). According to Roberts (1964), the mineralogy of the sandstones is quite variable, but generally consists of quartz (60-80%), feldspar ($\geq 20\%$), mica (2-5%), and matrix cement. The feldspars are a mix of orthoclase, microcline, and sodic plagioclase in proportions that regionally average $\approx 65\%$ potassium feldspar and $\approx 35\%$ oligoclase to sodic andesine. The matrix cements variably consist of clays, calcite, and quartz. Compaction, diagenetic clay growth, and hydrothermal metasomatism have reduced porosity in the Harmony Formation to $< 1\%$ (Theodore and others, 1992). Ranges of whole-rock chemical analyses of the Harmony Formation from Theodore and others (1994) are given in Table 1.

Intrusive igneous rocks in the Buckingham area range from Late Cretaceous monzogranite to Eocene monzogranite to Early Oligocene(?) rhyolite, porphyritic leucogranite, and granodiorite porphyry (fig. 1). The porphyry molybdenum deposit is genetically related to ≈ 86 Ma monzogranites that occur in a generally east-west zone that may be divided into three groups— West stock, East stock, and Vail Ridge dikes and plugs (cf. Theodore and others, 1992). There are four main compositional groups of monzogranitic rocks: 1) monzogranite porphyry, 2) megacrystic monzogranite porphyry, 3) aplite, and 4) a late-stage breccia pipe.

The Cretaceous intrusive phases show variable degrees of hydrothermal alteration. In the West stock, there are quartz, less abundant K-feldspar and clay- or white mica-altered plagioclase, and white mica- or chlorite-altered biotite phenocrysts. The groundmass consists predominantly of fine-grained white mica and disseminated pyrite. Locally, the white mica is intergrown with molybdenite. Stockwork quartz or quartz-

Figure 2. Geologic map of the Redwell Basin study area (from Gaskill and others, 1967). Stratigraphic units include Km: Mancos Shale, Kmv: Mesa Verde Formation, Toc: Ohio Creek Formation, Tw: Wasatch Formation, gp: granodiorite porphyry, f: Redwell Basin breccia pipe.

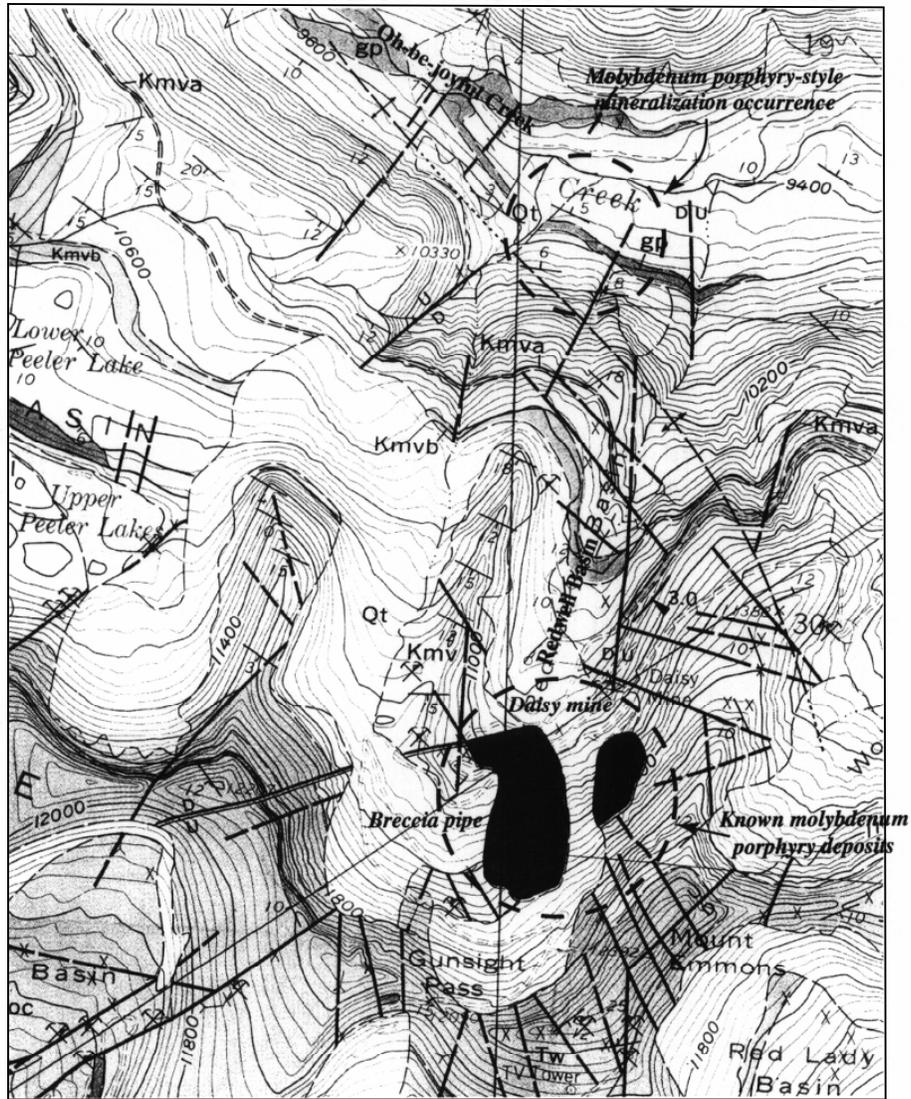


Table 1. Ranges of analytical data in weight-percent on the Upper Cambrian Harmony Formation in the Buckingham Camp region, Nevada (from Theodore and others, 1992).

SiO ₂	57.8 - 88.3
Al ₂ O ₃	5.48 - 19.6
Fe ₂ O ₃	0.76 - 2.55
FeO	0.12 - 5.5
MgO	0.45 - 3.03
CaO	0.16 - 8.26
Na ₂ O	0.53 - 2.05
K ₂ O	1.17 - 5.83
TiO ₂	0.38 - 1.03
P ₂ O ₅	<0.05 - 0.11
MnO	<0.02 - 0.08
CO ₂	0.01 - 6.3
F	0.02 - 0.05

sericite veins characterize the West stock and can be up to 40-50 volume percent of the rocks locally (Theodore and others, 1992). Pyrite occurs in the veins as well as molybdenite. The East stock is similar to the West stock, but there is an early-stage potassic alteration stage and pervasive clay alteration of plagioclase is more common. The Vail Ridge intrusions consist of narrow dikes and small equant masses and are located east of the porphyry molybdenum deposit. Nevertheless, phyllic to argillic hydrothermal alteration is intensive and there is disseminated molybdenite. Megacrystic monzogranite is most abundant in the East stock and it is inferred to intrude the porphyritic monzogranite. Aplite is a minor component of the intrusive system. The breccia pipe is located in the East stock and is interpreted to be part of the latest stage of porphyry molybdenum deposit formation.

Between about 39 and 37 Ma, numerous dikes and plutons were emplaced in the Buckingham area (Theodore and others, 1992). The main loci are north of the Buckingham porphyry molybdenum deposit just north of the Copper Queen mine (fig. 1) and south of Buckingham in the vicinity of the Little Giant mine (fig. 1). These rocks include a diverse variety of compositions such as biotite-hornblende monzogranite, porphyritic leucogranite, rhyolite, granodiorite, and minor diorite. Ranges of analytical data for some of these rock types are given in Table 2.

2. Structural geology. The Battle Mountain range is bounded on the north and south by regional, northwest-southeast striking right-lateral strike-slip faults (T. Hildenbrand, USGS, unpublished data, 2000). The faults within the range form a system of faults linking these two strike-slip fault zones. This duplex of faults provided the permeability and structural control for Cretaceous to Pliocene igneous intrusions and related hydrothermal activity.

Veins within and adjacent to the Buckingham Cretaceous monzogranites parallel the east-west trend of the intrusions, although the most strongly developed vein sets strike from east-west to N60°W (Theodore and others, 1992). In the molybdenum orebodies in the East and West stocks, post-mineralization N25°W faults cross-cut the orebodies and are interpreted to be normal-oblique faults by T. Loucks and C. Johnson (in Theodore and others, 1992). These faults consist of significant gouge and breccia zones, but the amount of rotation along these faults is unknown. One of them, the Buckingham fault, is estimated by Loucks and Johnson (in Theodore and others, 1992) to be 100-225 m thick and have had 520 m of dip slip and 175 m of right-lateral slip.

3. Mineral Deposits. The Late Cretaceous Buckingham porphyry molybdenum deposit is a composite of seven mineralizing events (cf. Loucks and Johnson in Theodore and others, 1992). The molybdenum deposit encompasses five events related to two phases of intrusion in the West stock and three in the East stock. Some events form conical zones of veins localized at the apices of monzogranitic intrusions. The highest grades are developed where the mineralization events overlap. Accompanying stockwork and disseminated pyrite-molybdenite mineralization are chalcopyrite, scheelite and tetrahedrite. Some chalcopyrite occurs in the quartz-pyrite-molybdenite veinlets. However, copper concentrations tend to be highest in the peripheral parts of the molybdenum orebodies, occurring in chalcopyrite and freibergite.

Low-grade, disseminated chalcopyrite, pyrrhotite, tetrahedrite, and pyrite are found in late-stage dikes that crosscut the molybdenum mineralization (cf. Loucks and Johnson in Theodore and others, 1992).

Table 2. Ranges (in wt %) of analyses on Late Eocene to Early Oligocene intrusive rocks in the Buckingham Camp region. Column 2 are data from biotite-hornblende monzogranite, column 3 from porphyritic leucogranite, and column 3 from rhyolite (from Theodore and others, 1992).

	<u>Monzogranite</u>	<u>Leucogranite</u>	<u>Rhyolite</u>
SiO ₂	66.0 - 70.25	61.52 - 69.3	72.82 - 76.9
Al ₂ O ₃	13.46-15.73	14.1 - 16.48	12.7 - 13.27
Fe ₂ O ₃	0.62 - 4.29	0.05 - 1.83	0.03 - 1.48
FeO	1.8 - 2.73	0.58 - 3.82	0.12 - 1.11
MgO	1.14 - 2.84	1.9 - 2.8	<0.01 -0.39
CaO	2.32 - 5.38	4.41 - 7.64	0.55 - 1.14
Na ₂ O	2.02 - 3.75	2.55 - 3.9	2.3 - 3.55
K ₂ O	2.73 - 4.88	0.47 - 3.77	4.3 - 5.73
TiO ₂	0.33 - 0.54	0.37 - 0.73	0.08 - 0.28
P ₂ O ₅	0.12 - 0.19	0.11 - 0.25	0.02 - 0.07
MnO	0.02 - 0.08	<0.02 - 0.08	0.01 - 0.06
CO ₂	0.03 - 0.13	0.04 - 0.64	0.03 - 0.08
F	0.09	0.02 - 0.08	0.01 - 0.02
Cl	--	--	0.0012-.0055

High-grade, Late Eocene to Early Oligocene polymetallic veins crosscut the Buckingham porphyry orebodies and also crosscut Early Tertiary intrusive rocks (Theodore and others, 1992). Examples include the Little Giant and Irish Rose mines (fig. 1). Veins in the Little Giant mine occur along faults that strike N20°W to N65°W in the Harmony Formation (Roberts and Arnold, 1965). Oxide ores consisted of iron oxides, jarosite, cerussite, anglesite, and pyrrhotite with some remnant argentite and polybasite. The primary ore minerals include pyrite, arsenopyrite, galena, sphalerite, and minor tetrahedrite. The Irish Rose mine ores were mined from veins that strike N20°W to N10°E in the Harmony Formation. The primary ores consist of arsenopyrite, pyrite, sphalerite, galena, chalcopyrite, and minor stibnite in a gangue of quartz and calcite (Roberts and Arnold, 1965).

Redwell Basin Porphyry Molybdenum Deposit, Redwell Basin, Colorado

The study site is the location of an unmined buried porphyry molybdenum deposit and associated veins (fig. 2). The deposit is related to a 17-16 Ma porphyritic granitic intrusive into the Cretaceous Mancos Shale and Mesa Verde Formations and the Tertiary Ohio Creek and Wasatch Formations (Gaskill and others, 1967).

1. Lithology. In the study area, the Cretaceous Mancos Shale consists of silty marine shale with interbeds of silty sandstone, sandy limestone, and carbonaceous shale. Shale intertongues with and is transitional into the overlying Cretaceous Mesa Verde Formation. The basal unit of the Mesa Verde, exposed in the lower reaches of Redwell Basin, consists of thick bedded and massive fine- to very fine-grained sandstone. A marine shale separates this lower sandstone from an overlying thick-bedded to massive medium-grained sandstone. Most of Redwell Basin drains across interbedded sandstone, shale, coal, and carbonaceous shale. The sedimentary rocks are altered in the vicinity of Miocene intrusions to pyrite-pyrrhotite-bearing hornfels (Thomas and Galey, 1982).

The Early Tertiary Ohio Creek Formation consists of massive feldspathic sandstone with pebbly lenses, interbedded sandstone, siltstone, shale, and carbonaceous shale, and feldspathic conglomeratic sandstone. The overlying Wasatch Formation consists of well-indurated conglomerates, sandstone, siltstone, and conglomeratic feldspathic sandstone (Gaskill and others, 1967). Near intrusive rocks, these formations are metamorphosed to quartzite, argillite, and argillaceous hornfels.

An igneous breccia pipe complex (fig. 2) crops out in the wall and floor of upper Redwell Basin (Gaskill and others, 1967). The pipes are composite, consisting at the surface of rhyolite and rhyolitic

breccia (Sharp, 1978). The rock is very fine grained and intensely altered. Partial chemical analysis of the altered rocks at the surface are given in Table 3.

Table 3. Ranges (in wt. %) of partial chemical analyses of altered Miocene granitic rocks in the Redwell and adjacent Red Lady basins (after Thomas and Galey, 1982).

SiO ₂	70.5 - 78.5
K ₂ O	3.1 - 4.6
Na ₂ O	0.04 - 2.08
CaO	0.49 - .80
F	0.15 - .80

2. Structural Geology. The Redwell Basin molybdenum deposit is localized in a zone of predominantly N50°E-striking faults (fig. 2) referred to as the Elk Basin fault zone by Sharp (1978). The deposit is located where a N30°W fault system intersects the northeastern zone. Northerly-striking faults bound the Redwell Basin, one of which (Redwell Basin fault) controls the strike of the lower reaches of the drainage.

3. Mineral Deposits. Two vertically-stacked stockwork molybdenum deposits were discovered during the 1970s beneath Redwell Basin (Thomas and Galey, 1982). The uppermost deposit is at a depth of ≈2400 feet. This deposit is just beneath the base of the breccia pipes exposed in the upper reaches of Redwell Basin (fig. 2). The breccia pipes show a distinct geochemical zoning from higher concentrations of molybdenum and tungsten at the base of the pipe to higher concentrations of lead and zinc in the upper part of the pipe and copper throughout the pipe (Sharp, 1978). The lead occurs in galena and argentiferous galena, the zinc in iron-rich sphalerite, and the copper in chalcopyrite and minor bornite. There are some vein zones in the breccia pipe where the total sulfide content exceeds 50%. Surrounding the breccia pipe, the sedimentary rocks contain secondary epidote, chlorite, and iron sulfide.

Exploration drilling in an area of hornfels and quartz veining found granitic intrusions and some molybdenite in stockwork veins at depth indicating porphyry-style mineralization at depth beneath an area just west of where the Redwell Basin drains into Oh-be-joyful Creek (Ludington and Ellis, 1983).

HYDROLOGY AND MAJOR-ELEMENT GEOCHEMISTRY

Battle Mountain, Nevada

Hydrology of the Battle Mountain area is characterized by mostly ephemeral surface runoff, superimposed on a fracture-controlled ground-water system. Streams flow during the spring and early summer months during snowmelt and periods of thunderstorms. Low annual precipitation results in overall sparse vegetation, with lush growth only within a few meters of perennial streams or in seep areas. Our samples were collected in May 1998, following a wetter than average winter and spring, at the locations shown in Figure 3. Estimated stream discharges ranged from 1 L/min to approximately 2000 L/min, based on measurements and visual estimates. Surface-water runoff is confined to deeply incised canyons in this high-relief region. Typical stream gradients are in the range of 6% to greater than 11%. During peak spring flows, the filled channels are typically less than a few meters wide, and tens of centimeters deep.

No completed wells were available for sampling on Battle Mountain at the time of our sampling trip. However, several “ground-water” samples were collected from mouths of springs distributed around Battle Mountain at a variety of elevations. Sample site 1, a spring near Long Creek (fig. 3), may actually be an uncompleted exploration well drilled into the Buckingham stock. Other springs sampled in the area include seeps such as at sample site 8. Because the aquifers on Battle Mountain are characterized by fracture flow, it is reasonable to assume a geologic-structural control on the location of springs and gaining stream reaches.

Interactions between ground water and surface water are exhibited throughout the Battle Mountain area, as springs, seeps, and gaining and losing stream reaches. As documented by Winter and others (1998), connections between ground and surface water are too numerous to be ignored. In Long and Licking creeks, numerous gaining and losing stream reaches were observed. These hydraulic data are supported by chemical measurements of major and trace elements, providing a consistent evaluation of the local hydrology around fracture systems. For example, sites 3 and 4 combine near the headwaters of Long Creek; site 2 is below the confluence. Based on the major-element chemistry of those samples, the water at

site 2 must also include at least one other water source. The cation composition of these samples, as shown in a piper diagram (fig. 4) shows sites 3 and 4, with site 2 shifted slightly towards the composition of site 1. The rare-earth element (REE) compositions (fig. 5) suggest an input of a water like sample 1 to the stream at site 2, consistent with the major cation compositions. Flow at site 2 was greater than the sum of sites 3 and 4, and a large positive vertical hydraulic gradient was observed at site 1, supporting the possibility of ground-water discharge in the vicinity of site 2. Sites 1 and 2 are located along Long Canyon just below the intersection of north to northwest faults with the Long Canyon fault (Theodore and others, 1992). Site 12 is approximately 2 km downstream from site 2 and its major and REE compositions are close to those for site 2, suggesting no further ground-water discharge, but not precluding the possibility of ground-water recharge.

In the Licking Creek drainage, the chemistry of the surface-water also implies some areas of ground-water discharge. For example, sites 5, 6, and 10 occur along a continuous reach of stream with no other surface-water tributaries. The major anion and cation compositions for sites 5 and 6 are indistinguishable, but sample 10 has higher concentrations of many major and trace elements, but lower concentrations of others. This observation suggests an additional input of ground-water discharge between sites 6 and 10 (approximately 1 km stream reach). Similarly, sites 7 (stream) and 8 (spring) are adjacent to each other, and appear similar from the Piper diagram (fig. 6). The concentrations of many trace elements and rare earth elements (REE) are significantly higher in sample 8 than in 7, but the concentration ratios of most of those elements for the two samples lie within a very narrow range (2.5 to 3.0, fig. 7). A likely scenario that would explain this narrow range of variation would be discharge of a ground water with a chemical composition similar to that of site 8 into a slightly more dilute, metal-poor stream to produce the observed chemistry of site 7. In support of this hypothesis, site 8 is a typical acidic, metal-rich drainage (pH 4.0; conductivity >1,100 $\mu\text{S}/\text{cm}$; $\text{SO}_4 > 600$ ppm; and Al, Mn, and Zn at ppm levels), whereas the other end member would have major elements similar in concentration to site 7, but with low metals and REE concentrations. A ground-water discharge scenario also makes sense based on the observations that sites 7 and 8 are within a few meters of each other, and the fact that the hydraulic head of ground water is sufficiently high to create the seeps at site 8.

Farther downstream on Licking Creek there is some evidence for ground-water discharge, but most of the changes are attributable to normal water-rock interactions. The primary change in water chemistry between sites 9 and 11 (approx. 2 km) is an increase in pH from approximately 7 to 8. This unit increase in pH appears to drive the adsorption or precipitation of metals such as Zn, Cu, Mn, Ni, Co, Cd, and REE's, and the desorption of oxyanion species such as As, Mo, V, and Sb. Aluminum concentrations increased slightly, consistent with a slightly increased solubility of gibbsite from pH 7 to 8. No appreciable change was observed in the major cation and anion concentrations.

Redwell Basin, Colorado

Surface water in the Redwell Basin originates from a variety of sources: springs and seeps, gaining stream reaches, mine drainages, and an uncapped drill hole with artesian flow. The average gradient of Redwell Creek is 28%, in a tightly confined drainage that is approximately 1 km wide and 2.5 km long. Discharge measurements made during the sampling trip ranged from 20 L/min to approximately 2000 L/min. Our sampling trip in August 1997 occurred during a typical pattern of clear mornings followed by intermittent afternoon thunderstorms. Sample sites are shown on Figure 3.

From the top of Mount Emmons to the bottom of the Redwell Basin, the land surface follows a series of slopes and ledges formed by outcrops of resistant sedimentary layers. These sedimentary boundaries, as well as the numerous steeply dipping fractures that crosscut the sediments and intrusive rocks, may be hydraulic conduits for ground water. The possibility of intergranular flow within these sediments is limited, as most of the rocks appear to be well cemented, especially in the vicinity of the intrusive rock body in the

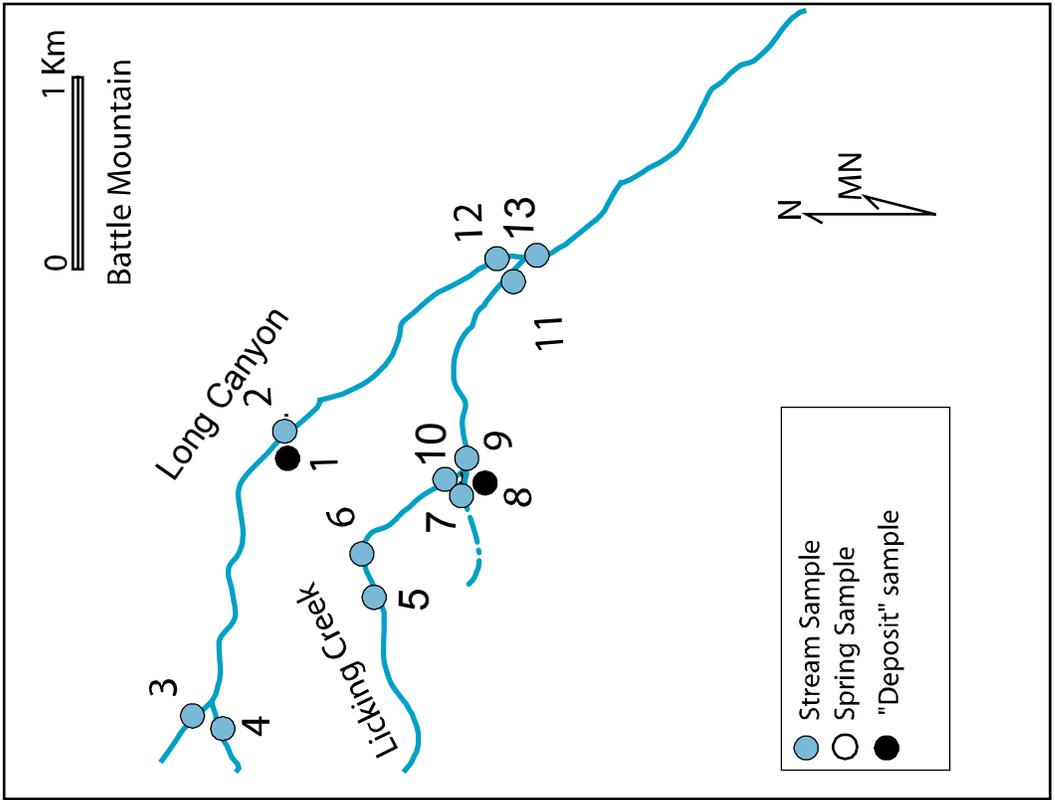
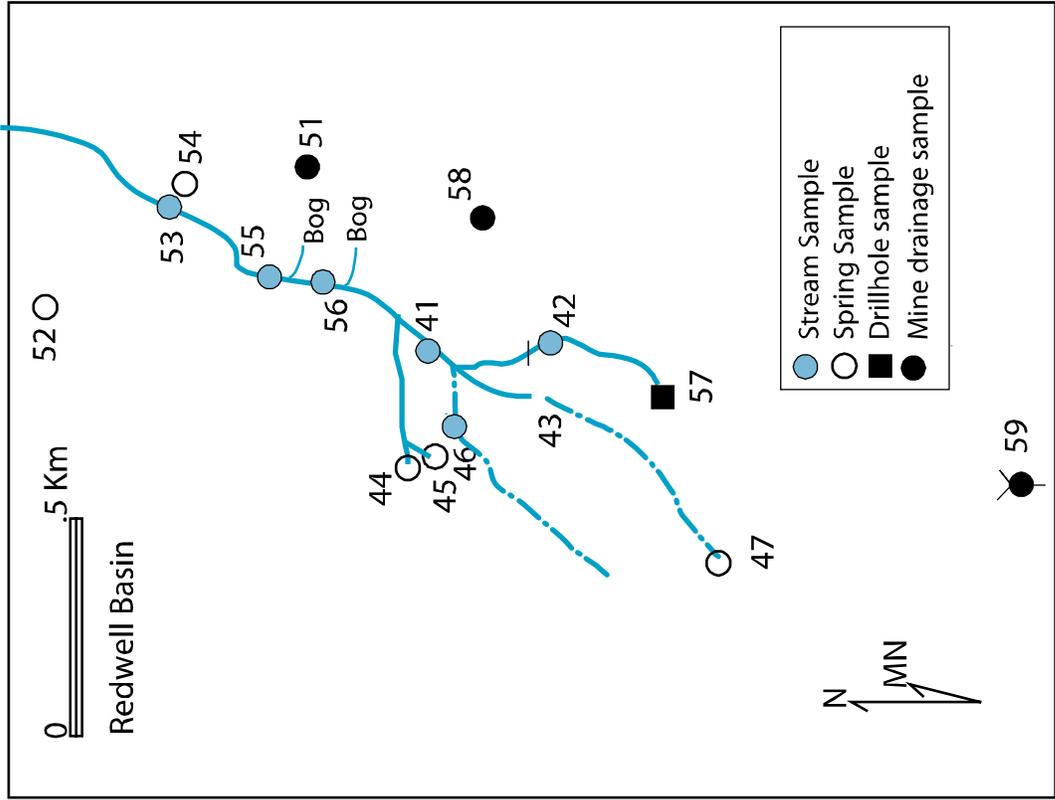


Figure 3. Map showing sample locations.

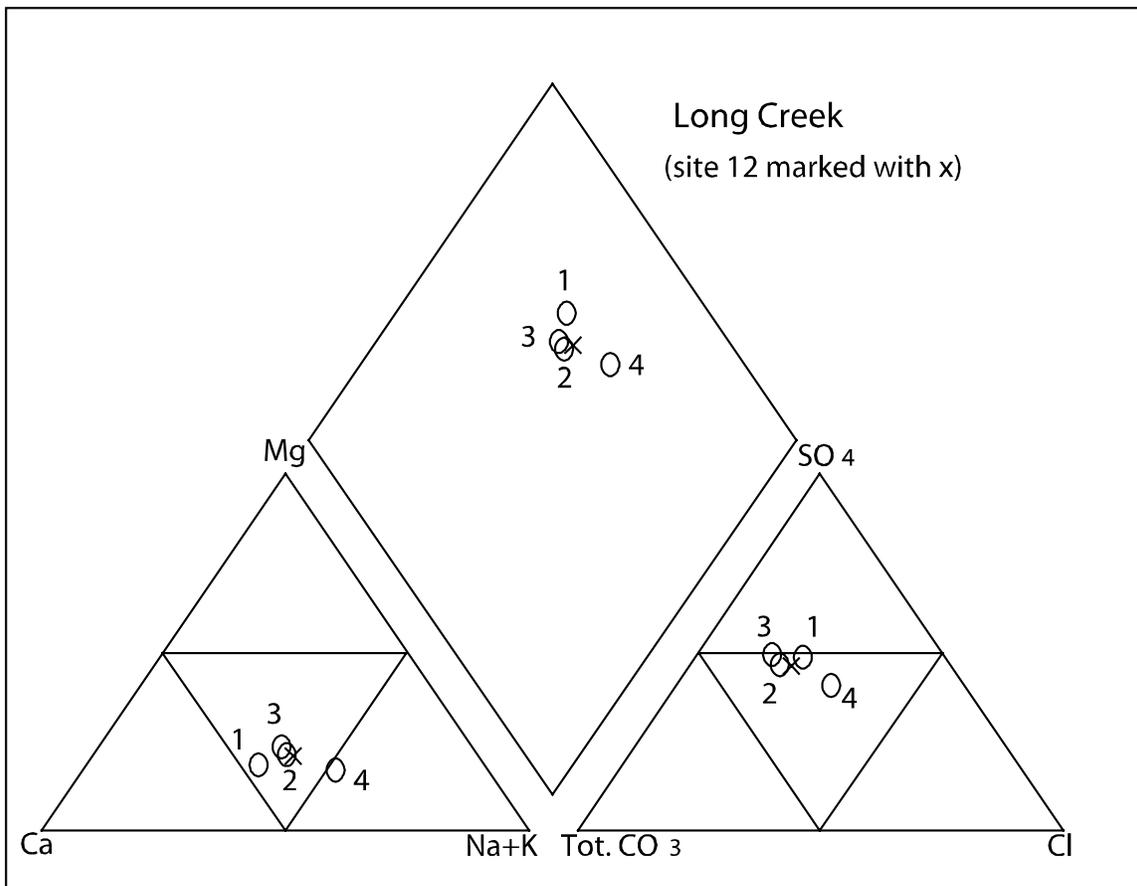


Figure 4. Piper diagram fro samples collected from Long Canyon, Battle Mountain, Nevada.

upper part of the basin. Further, distinct differences in water chemistries are observed over very short distances, suggesting a fracture-dominated flow system.

A remarkable feature of the ground-water chemistry in the Redwell Basin is the compartmentalization and isolation of chemically distinct packages of water within short distances. For example, site 44 (the "Red Well," a natural spring) has a pH of 3.6, is actively precipitating ferricrete, and has a conductivity of 200 $\mu\text{S}/\text{cm}$, but a few meters away, site 45 has a pH of 7 and a conductivity of 40 $\mu\text{S}/\text{cm}$. Similarly, sites 47 and 59, a few hundred meters apart, have pH values of 7.2 and 3.9, and conductivities of 40 and 130 $\mu\text{S}/\text{cm}$, respectively (fig. 8). The Piper diagram (fig. 9) also demonstrates compartmentalization in the form of "outlier" groups of points in both the cation and anion triangular fields. Other examples of dramatic chemical differences in close proximity exist in the Redwell Basin, and demonstrate the effective "trapping" of chemically distinct waters in non-connected (or minimally connected) fracture sets. As mapped by Gaskill and others (1967; see fig. 2), the Redwell Basin is extensively fractured, and, as discussed previously, the various fracture networks represent several structural elements. Interactions between ground water and surface water were observed mostly in the form of discharge areas, including springs, seeps, and artesian wells. Because of the extremely high relief of the Redwell Basin and the highly variable slopes, numerous springs and seeps occur in the basin, which, together with the relatively high rainfall, document the proximity of the water table to the ground surface.

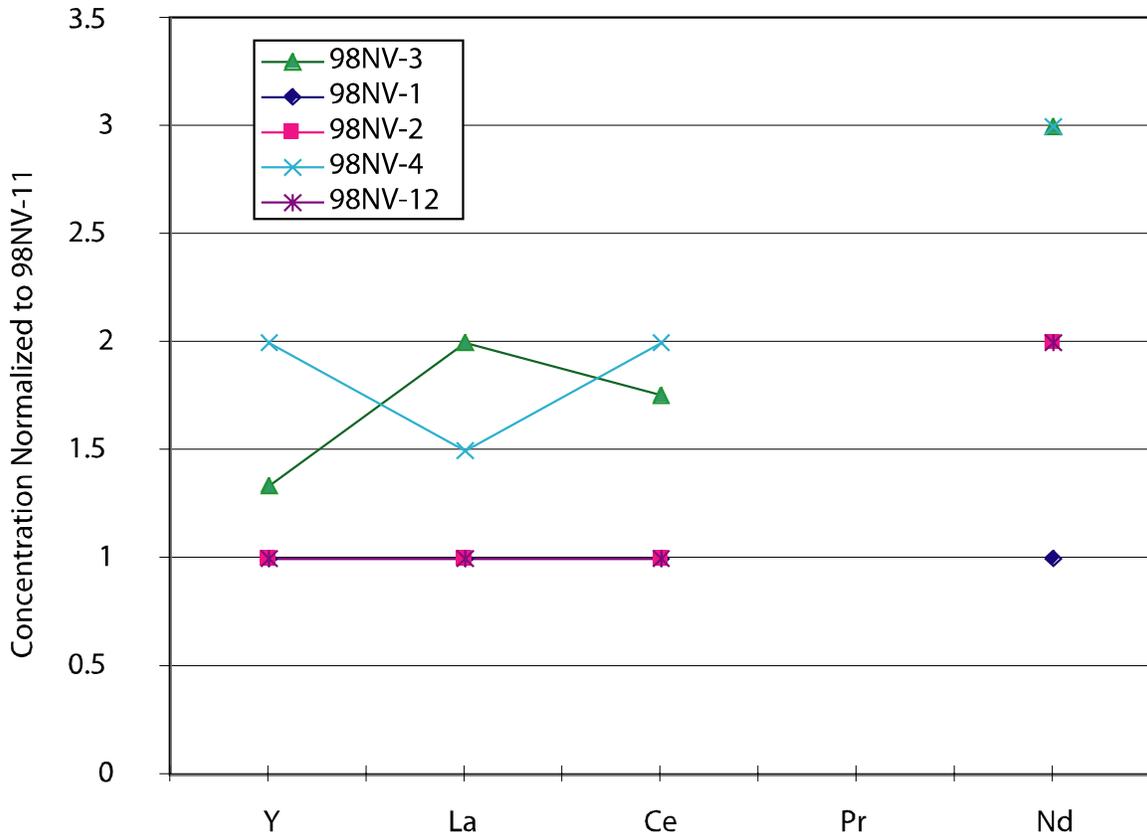


Figure 5. Rare earth element distribution in samples from Long Canyon.

Complexity introduced by epithermal systems overprinting on porphyry systems

Although our interest in the Redwell Basin stems from the occurrence of the porphyry-molybdenum deposits, there also are genetically related epithermal vein systems nearer to the surface. The latter have historically been mined and now contribute acidic, metal-rich drainage to the Redwell Basin. Resolving the discrete contributions of these chemically distinct waters is difficult, but may be possible using some geochemical tools. For example, sulfur isotope compositions will be discussed in a later section. Other parameters, such as certain element ratios or concentrations, might also be useful. For example, the ratios of F^- to Cl^- concentrations in the waters are distinctly high, owing to the presence of F-bearing minerals (fluorite, topaz, etc.) in the porphyry deposits and associated alteration. As shown in Figure 10, F^-/Cl^- molar ratios generally are greater than 2 and as high as 9.5. Such high F^-/Cl^- molar ratios can only be attributed to the leaching of F^- from minerals such as those mentioned. The rather large range of F^-/Cl^- molar ratios in the Redwell Basin (0.5 to 9.5) is a further indication of the compartmentalization of flow within the basin. Unfortunately, owing to analytical difficulties, the F^-/Cl^- molar ratios for samples 51 and 58 (drainages from epithermal-vein mines) could not be determined. As discussed below, sulfur isotopes suggest that the contribution of the “porphyry water” to site 57 (the artesian drill hole) is approximately 70%. The use of sulfur isotopes for this purpose makes the most sense, because the richest zone of sulfides coincides more closely with the ore zones. Other alteration haloes may extend spatially outward from the mineralized centers, and affect the water chemistry at a broader spatial scale. For instance, the “Red Well” (site 44) has the highest F^-/Cl^- molar ratio of all our samples, plus the concentrations of many major and trace cations in the artesian well lie between those of the Red Well and the mine drainages. There are, however, a number of exceptions to this mixing model indicating that the source of constituents in the Red Well remain inconclusive. Even though the spatial density of samples in the Redwell Basin is quite large, the relative contributions of epithermal vs. porphyry drainage chemistries are difficult to resolve.

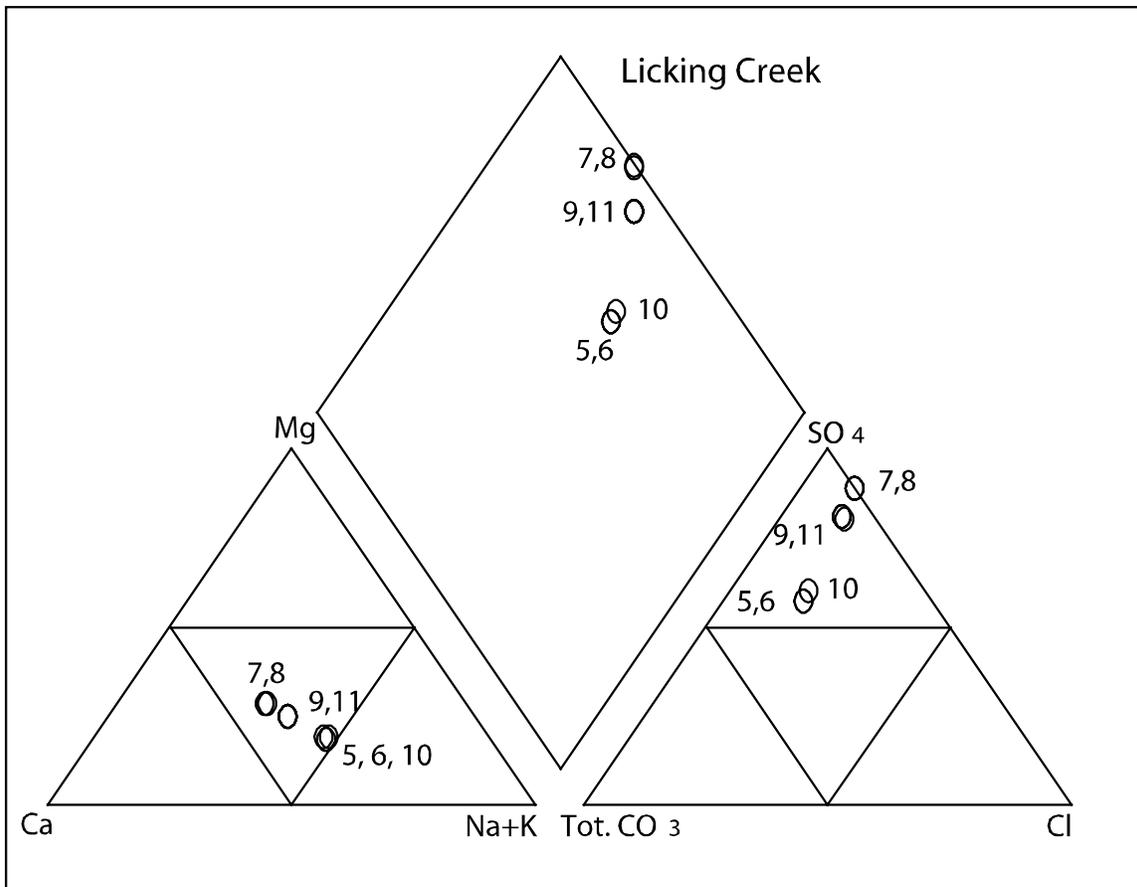


Figure 6. Piper diagram for samples collected from Licking Creek, Battle Mountain, Nevada.

METAL GEOCHEMISTRY

Chemistry and sulfur isotope geochemistry of deposit drainage

At each of the drainage basins sampled, waters draining the Mo deposits were collected (compositions are in Table 3). As discussed earlier, these waters may also include a component of waters draining the associated base-metal mineralization. At Battle Mountain, two such water samples were collected. The Buckingham “deposit” sample was collected from the seep flowing from the Buckingham Fault zone within the boundary of the Buckingham Stock Mo Deposit (site 8). This water has a pH of 4.0 and contains relatively little iron, although iron oxyhydroxides are found around the seep. Zinc accounts for almost 90% of the metal load.¹ The sulfur isotopic composition of the sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) in the water is +5.1‰; the value of the sulfur in molybdenite (MoS_2) in the deposit is +4.3 to +5.2‰ (T.G. Theodore as cited in Theodore and others, 1992).

The Long Canyon “deposit” sample was collected from a seep near the deposit boundary on the inferred Long Canyon Fault (site 1 on fig. 3). The water has a pH of 7.4 and was weakly effervescent, the likely gas is carbon dioxide. The dominant metal in this water is iron, however, nickel accounts for almost 50% and Mo for almost 30% of the metal load as defined previously. The sulfur isotopic composition of the sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) in the water is +5.2‰. Both the Long Canyon and Buckingham waters have very low fluoride to chloride molar ratios (F:Cl ratio, 0.02 and 0.04 respectively), consistent with the Buckingham stock hosting a low-fluorine type Mo deposit.

The Redwell “deposit” sample was collected from the drill hole known to penetrate the Redwell deposit (site 57 on fig. 3). The water has a pH of 2.9, a high iron concentration, and a high F:Cl molar ratio of 6.6. Zinc accounts for almost 80% of the metal load with copper and lead each accounting for

¹ Metal load is defined in this paper as the sum of metals excluding iron on a molal basis.

about 10%. The sulfur isotopic composition of the sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) in the water is +2.7‰; the value of the sulfur in molybdenite (MoS_2) in the deposit is +3.7 to +4.6‰ (Stein and Hannah, 1985). Sulfate associated with base-metal mine drainage ranges from +1.0 to -0.5‰ (see below). The higher $\delta^{34}\text{S}_{\text{SO}_4}$ value in the drill hole sample supports the hypothesis that discharging water contacted the Mo porphyry deposits as well as the base metal (mass balance calculations using sulfur isotopes suggests that 70% of the sulfate sulfur is from the porphyry system and 30% from the base-metal deposits).

Dissolved concentrations of metal in the stream drainages

Figures 11 through 13 graphically show how the log of the elemental concentrations in stream water spatially changes relative to concentrations in the “deposit samples.”² In Long Canyon (fig. 11), the mineralized, undisturbed site, only pH and Mo are consistently higher than in the deposit sample. Stream pH values are between 7.6 and 8.4; these alkaline values represent weathering of the volcanoclastic country rocks (see composition in Geology section), with possible contributions from removal of CO_2 by algal growth. High pH enhances the mobility of Mo by inhibiting adsorption on to iron oxides. The dissolved iron concentrations remain nearly constant throughout the stream and are very similar to those in the “deposit” sample, suggesting that precipitation of a mineral phase (goethite or amorphous $\text{Fe}(\text{OH})_3$) controls its concentration. Concentrations of most other metals in stream water are less than 1% of the concentration in the “deposit” sample and do not significantly change concentrations until Licking Creek enters the drainage (fig. 11).

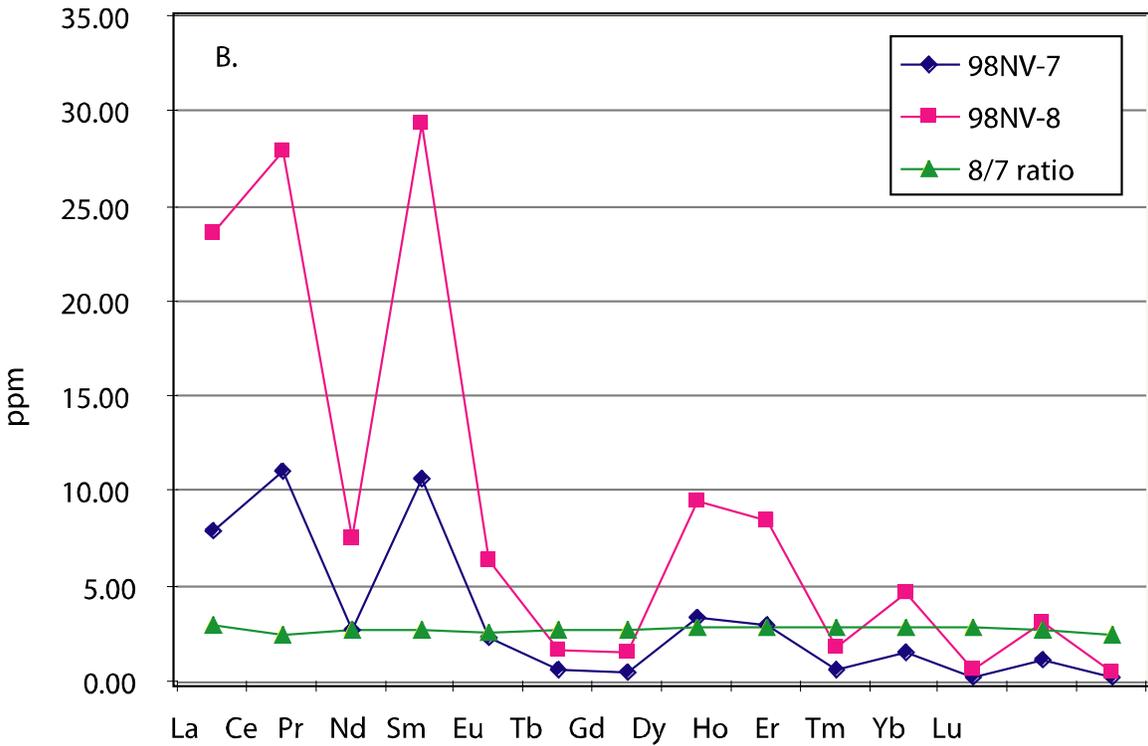


Figure 7. Rare earth element distribution in selected samples from Licking Creek.

² $\text{Log}(\text{variable in stream sample} / \text{variable in “deposit” sample})$. Samples that plot on the zero line have the same value as that of the “deposit” sample in the drainage. Samples with negative values have lower values and those with positive values have higher values than the “deposit” sample.

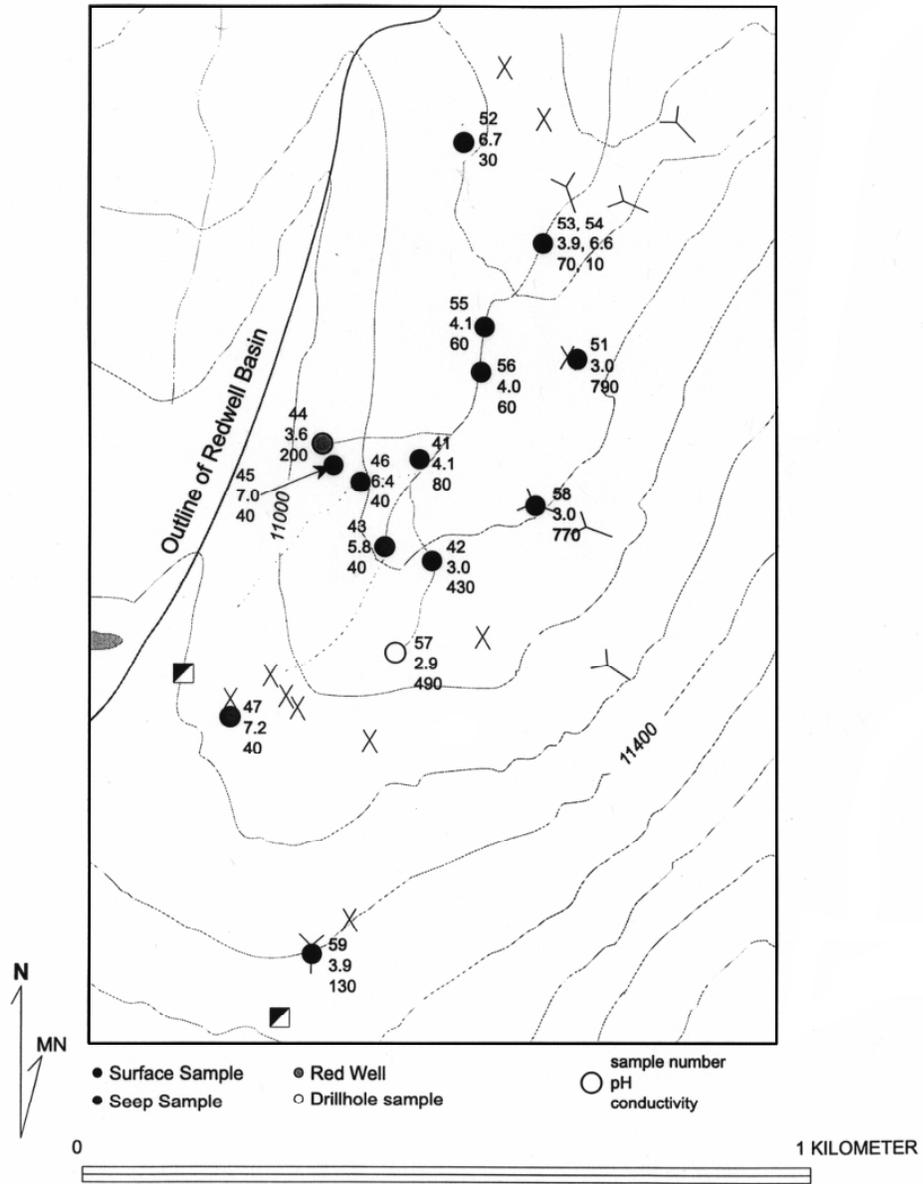


Figure 8. Map showing the distribution of pH and conductivity of samples from Redwell basin, Colorado.

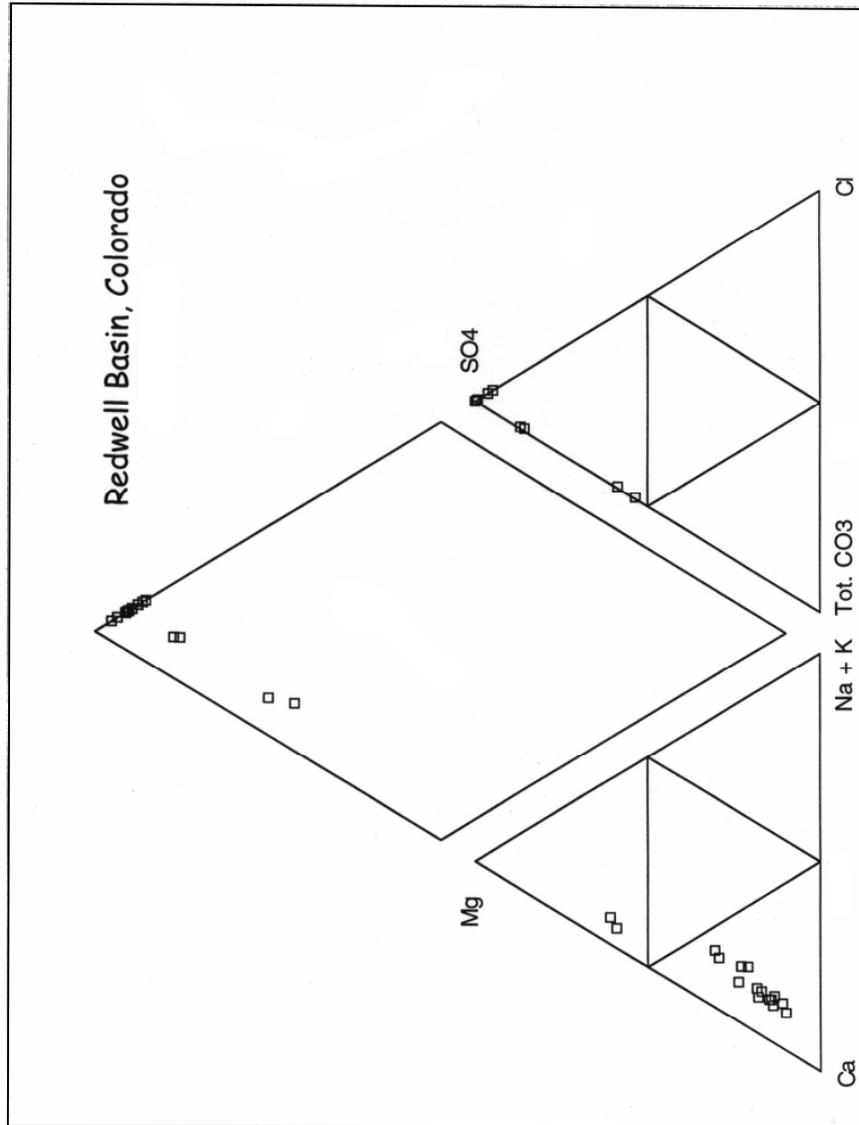


Figure 9. Piper diagram for samples collected from Redwell Creek.

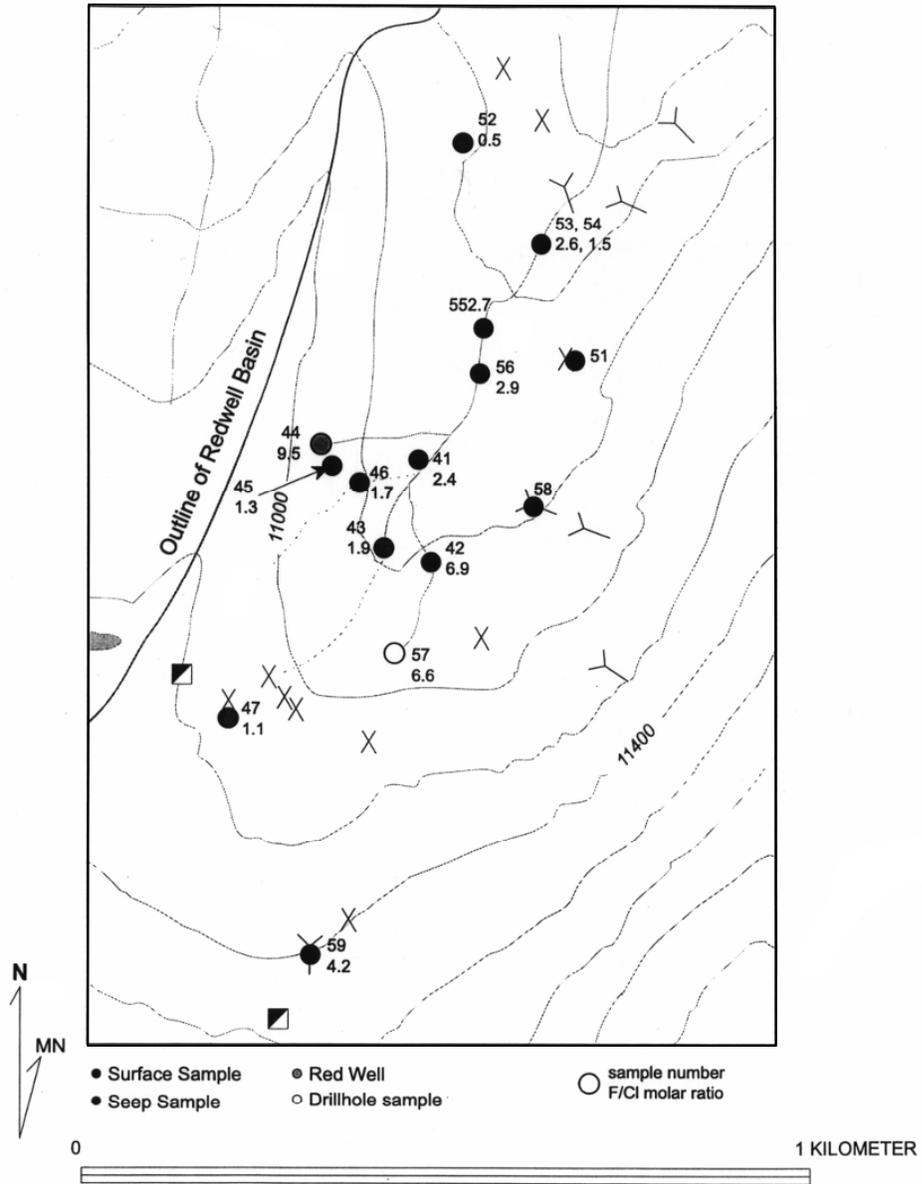


Figure 10. Map showing the distribution of F/Cl molar ratios of samples from Redwell basin, Colorado.

In comparison to Long Canyon, the base-metal load in Licking Creek (mineralized, disturbed site), increases substantially after the “deposit” sample enters the stream (fig. 12). Iron is similar in concentration to that in the deposit sample due precipitation of oxyhydroxides. Molybdenum and arsenic are higher in the stream water than in the deposit sample, consistent with the higher pH in the stream limiting adsorption onto freshly precipitated iron oxyhydroxides. Most metal concentrations decrease slightly when Licking Creek mixes with the more dilute Long Canyon, however, the relative metal concentrations are consistent with values ascribed to the “deposit” sample.

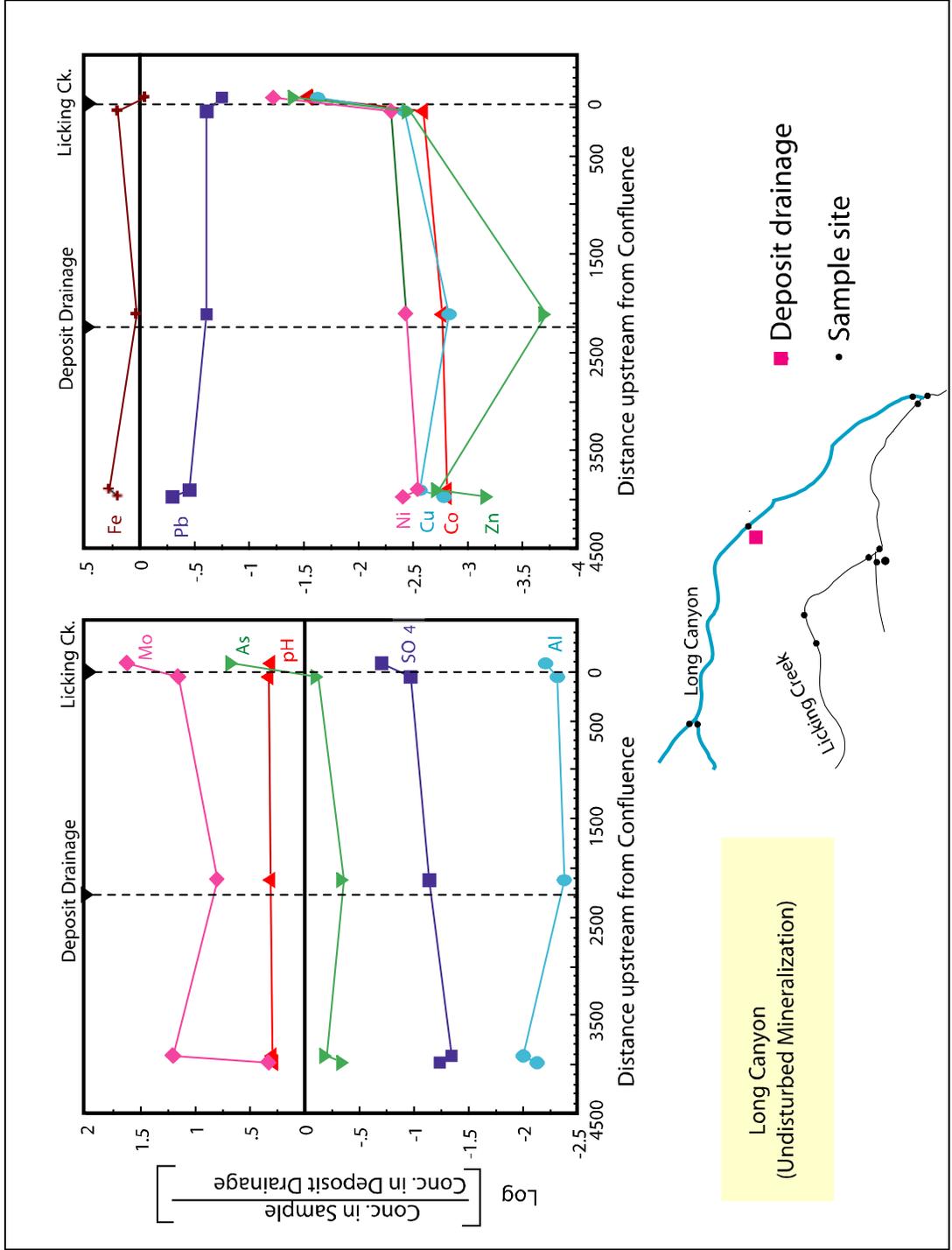


Figure 11. Log of the ratio of variables in Long Canyon samples to those in the "deposit" sample plotted against the distance upstream from the confluence of Long Canyon and Licking Creek.

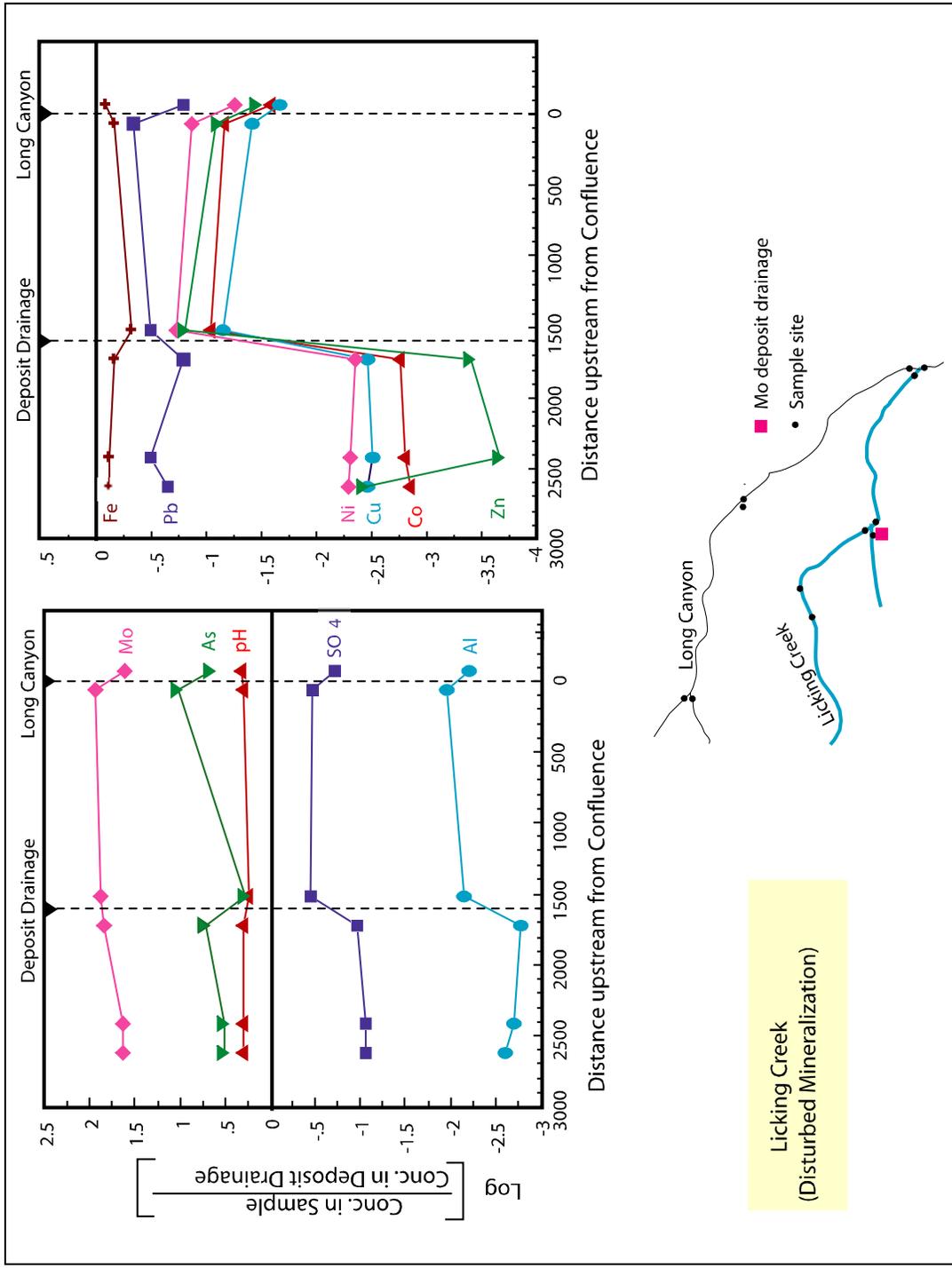


Figure 12. Log of the ratio of variables in Licking Creek samples to those in the "deposit sample plotted against the distance upstream from the confluence of Long Canyon and Licking Creek.

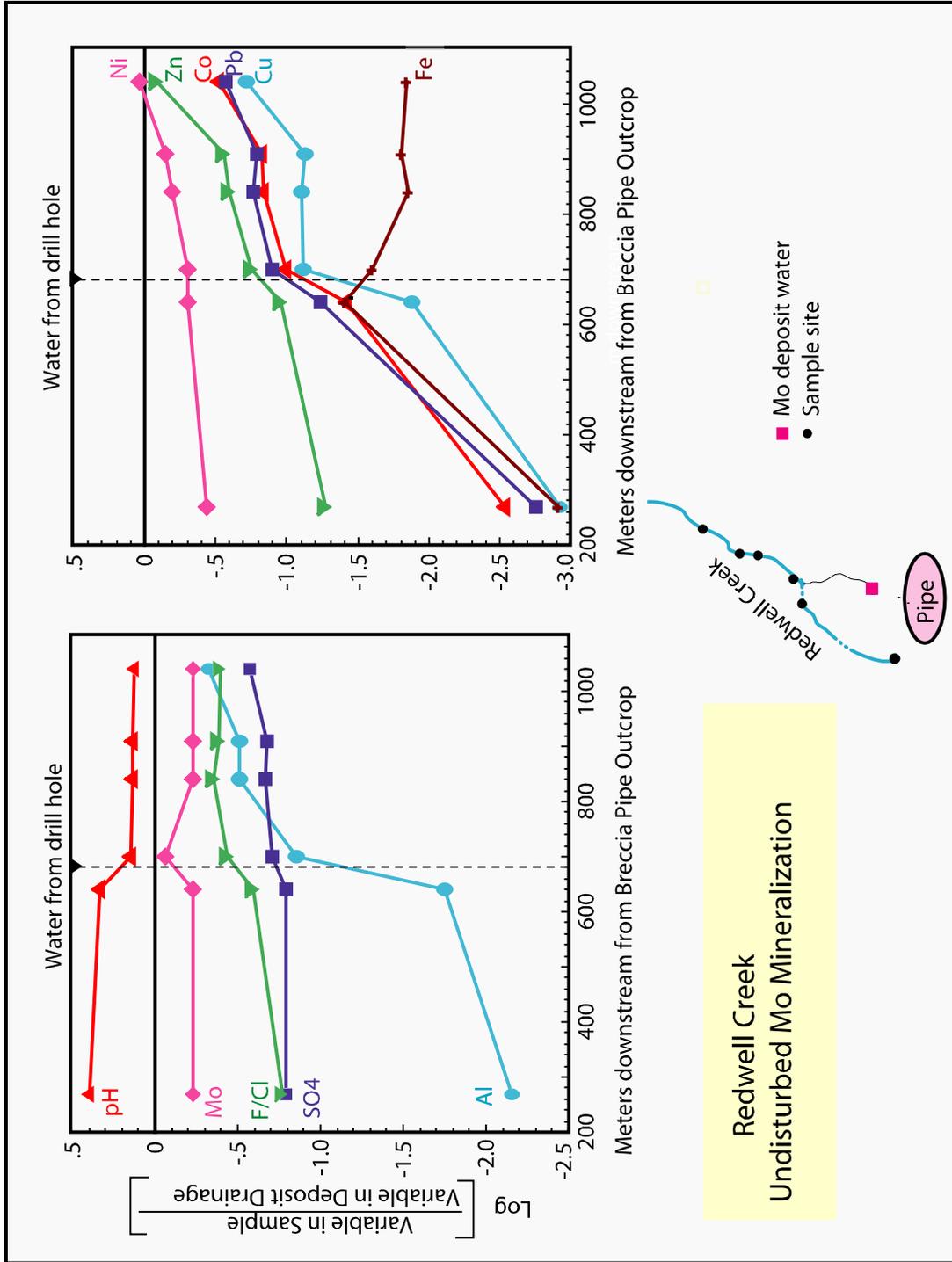


Figure 13. Log of the ratio of variables in Redwell Creek samples to those in the "deposit" sample plotted against the distance downstream from the breccia pipe outcrop.

Redwell Creek is compositionally distinct from background ground water (most upstream sample). Water in the stream mixes with inflow from the drill hole, and water with a high content of metals downstream of the drill hole (fig. 13). With the exception of Fe, most constituents plotted increase downstream from the drillhole. In contrast to concentrations at Battle Mountain, iron increases upon mixing with deposit drainage and then decreases as iron precipitates to form oxyhydroxides. Metal

adsorption is not apparent based on water composition. The pH of Redwell stream decreases upon input of the water from the drill hole and remains acidic downstream (3.9-4.1).

Figures 11, 12, and 13 show that the composition of the “deposit” sample is preserved downstream in the both Licking Creek and Redwell basin. Metal loads in Redwell basin are derived from base-metal mineralization with some contribution from the molybdenum porphyry system. In contrast, the composition of stream water in Long Canyon is not changed by the mineralization that occurs lower in the drainage.

Trends in sulfur isotopic composition of stream sulfate

To better understand the extent that the Mo porphyry and associated base-metal systems affect the water quality in Long Canyon and Redwell Stream, sulfur isotopes were investigated. Figure 14 shows the sulfur isotopic composition ($\delta^{34}\text{S}_{\text{SO}_4}$, ‰) of sulfate in the stream water, acid mine drainage (base-metal mineralization), and Mo porphyry “deposit” samples for all three streams.

The $\delta^{34}\text{S}_{\text{SO}_4}$ values in Long Canyon decrease from near 6.8‰ outside the mineralized zone to 6.4‰ after mixing with the deposit drainage to 5.7‰ just before mixing with Licking Creek. The decrease from 6.4 to 5.7‰ suggests that some water associated with the Mo porphyry deposit besides the seep sampled is entering Long Canyon. Values in Licking Creek, although decreasing downstream, are never above 5.4‰ (just above the value for sulfur in the molybdenites). This general decrease is likely reflecting a continuous input of sulfur from mineralization to the stream as it flows across the Mo porphyry system.

In Redwell Basin, the relative input of sulfur associated with base-metal mine drainage and the Mo porphyry can be estimated. Sulfate in base-metal mine drainage is always isotopically depleted in ^{34}S relative to the sulfate in the drill hole by over 2.5‰—this difference increases downstream. The effect of drill-hole water is apparent in Figure 14. The continual input of ^{34}S -depleted sulfate can be seen in the decrease of $\delta^{34}\text{S}_{\text{SO}_4}$ values in the stream. Values approach those of sulfate in the water draining base-metal deposits that enter Redwell Creek downstream through ground-water seepage. The decrease in $\delta^{34}\text{S}_{\text{SO}_4}$ values of base-metal drainage as a function of distance from the breccia pipe is consistent with the incorporation of sedimentary sulfur depleted in ^{34}S in the more distal base-metal deposits formed during emplacement of the Mo porphyry system (see Stein and Hannah, 1985).

CONCLUSIONS

The conclusions from our study are:

1. The F:Cl molar ratio in stream samples appears to be a reliable variable for distinguishing low- and high-fluorine Mo porphyry systems
2. Because the isotope composition of sulfur in the two Mo deposits is different from associated base metal mineralization, the relative contribution of each deposit type to sulfate in the streams can be estimated.
3. Geochemical processes such as metal adsorption and precipitation occur in all drainages, but in a disturbed area, the processes do not attenuate all the trace metals from deposit weathering.
4. The sulfur isotope data are more sensitive than chemical concentration data for tracking the influence of mineralization on water quality, especially in drainages that have not been disturbed by mining.
5. Fracture flow dominates ground-water flow in both study areas and is controlled by the local hydraulic head and regional stresses.
6. Climate, especially precipitation rates, plays an important role in ground-water discharge to and recharge from the streams.
7. Integration of chemistry, hydrology and regional geology provides a comprehensive understanding of the environmental behavior of both types of Mo porphyry systems.

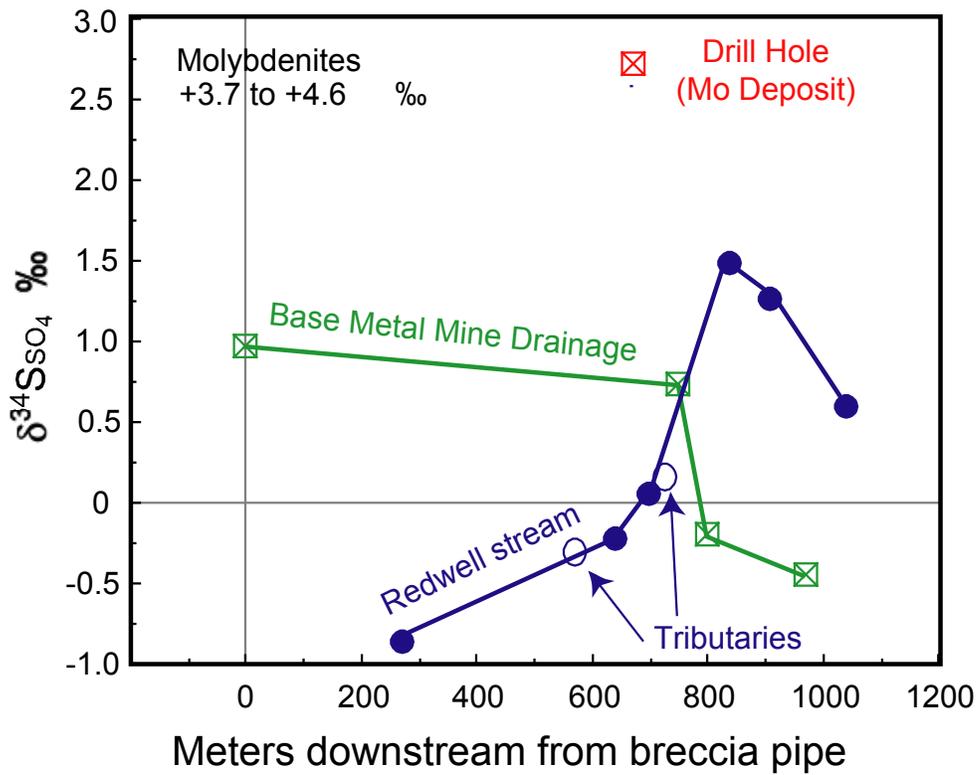
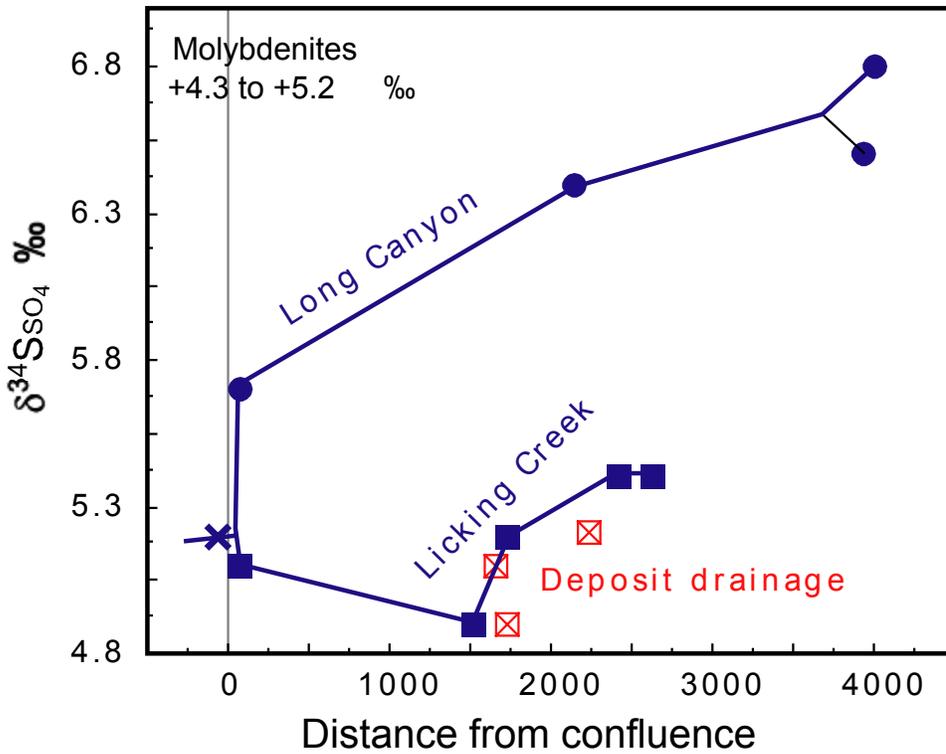


Figure 14. Distribution of $\delta^{34}\text{S}$ values in sulfate for Licking Creek and Long Canyon (upper graph) Redwell basin (lower graph).

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