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CALCULATIONS OF PRE-MINING GEOCHEMICAL BASELINES AT THREE STREAM JUNCTIONS IN THE VICINITY OF SUMMITVILLE, COLORADO

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ABSTRACT

Probable pre-mining geochemical baselines of stream waters in the vicinity of Summitville are calculated by combining chemical modelling of dominant in-stream reactions with mass-balance calculations. This technique emphasizes the importance of using a process-orientated, water-shed approach to the calculations of pre-mining baselines. The input of background surface-water chemistry for the mass-balance calculation from the developed mine site in the Wightman Fork and Cropsy Creek drainage basins is estimated using chemical data of stream waters collected from similarly mineralized but undisturbed areas in similar physically and geologically equivalent environments to Summitville. The stream-water metal loads from the unmineralized areas are determined directly by analyzing stream waters collected from unmineralized and undisturbed areas within the Wightman Fork drainage basin.

Geochemical baselines for pH, Fe, Al, Mn, SO_4, Cu, and Zn, prior to mining, were calculated for stream waters at: 1) Cropsy Creek at the junction with Wightman Fork; 2) Wightman Fork above the junction with Cropsy Creek; and 3) Wightman Fork at the junction with the Alamosa River. The conservative scenario (higher baseline geochemistry) is determined by assuming the chemistry of streams draining the Summitville area prior to mining was equivalent to a modern composite of chemistry of Alum and Bitter Creeks, which drain advanced argillic altered areas south of Summitville. The concentrations of copper and zinc in surface waters are assumed to have been originally greater at Summitville. The most likely scenario is determined by using water chemistry of a composite of streams draining several equivalent mineralized areas in Colorado.

The calculated pre-mining geochemical baselines at Summitville are much higher than baseline geochemistry measured in stream waters draining the undeveloped Calico Peak mineral system near Rico, Colorado, which is geologically and physically similar to Summitville. More reactive rocks in the Calico Peak area, particularly calcite, probably account for the lower geochemical baselines.

INTRODUCTION

Remediation of environmental problems associated with the Summitville mine (Fig. 1) has raised the question of what the pre-mining geochemical baselines of stream waters may have been in the vicinity of and downstream from the Summitville site. The mine site lies within the upper Wightman Fork and Cropsy Creek drainage basins. The presence of fossil iron bogs, particularly along the northeast base of South Mountain, indicates that prior to mining, natural acid drainage was generated by the oxidation of sulfides at Summitville. Thus, geochemical baselines of Wightman Fork and Cropsy Creek prior to mining were likely lower in pH and probably contained greater concentrations of metals such as iron, aluminum, copper, and zinc than streams draining unaltered areas within the Wightman Fork drainage basin.

The purpose of this study was to calculate the most likely pre-mining geochemical baselines of stream waters at three stream junctions. Geochemical baselines of stream waters are calculated by combining mass-balance calculations with chemical modelling of water-rock interactions in the stream channels, assuming likely buffering reactions and observed solids precipitating within the stream beds.

Geochemical baselines prior to mining are calculated for three points: 1) Wightman Fork above the junction with Cropsy Creek; 2) Cropsy Creek above the junction with Wightman Fork; and 3) Wightman Fork above the junction with the Alamosa River (Fig. 2). These three junctions were chosen because each contains waters draining the mine site.

WIGHTMAN FORK DRAINAGE BASIN

Elevation in the Wightman Fork basin ranges from 12,754 feet for North Mountain to 9400 feet at the junction of Wightman Fork with the Alamosa River. The climate is cool-humid with precipitation ranging from greater than 50 inches per year at the higher elevations to less than 30 inches in the southeastern portion of the drainage basin (Colorado Climate Center, 1984). Thunderstorms are common in summer, particularly July and August. Spring runoff usually occurs in May and June.

The study area lies within the eastern portion of the San Juan volcanic field. This volcanic sequence consists of Oligocene and younger volcanic rocks beginning with an initial eruption of intermediate composition lavas and breccia, followed by more silicic ash-flow tuffs, and ending with bimodal association of basalt and rhyolite (Lipman and others, 1970).

Two main events of alteration and mineralization occurred in association with the Platoro complex. The first event occurred during late-stage emplacement of monzonitic stocks around 29.1 to 27 m.y. ago (Lipman, 1975). The argillic altered area in the southeastern part of the drainage basin (referred to as the SE altered area) may have occurred during this event, but dating has not been done. This altered area was investigated only briefly and appears to be mostly argillic alteration, although advanced argillic alteration may be present.

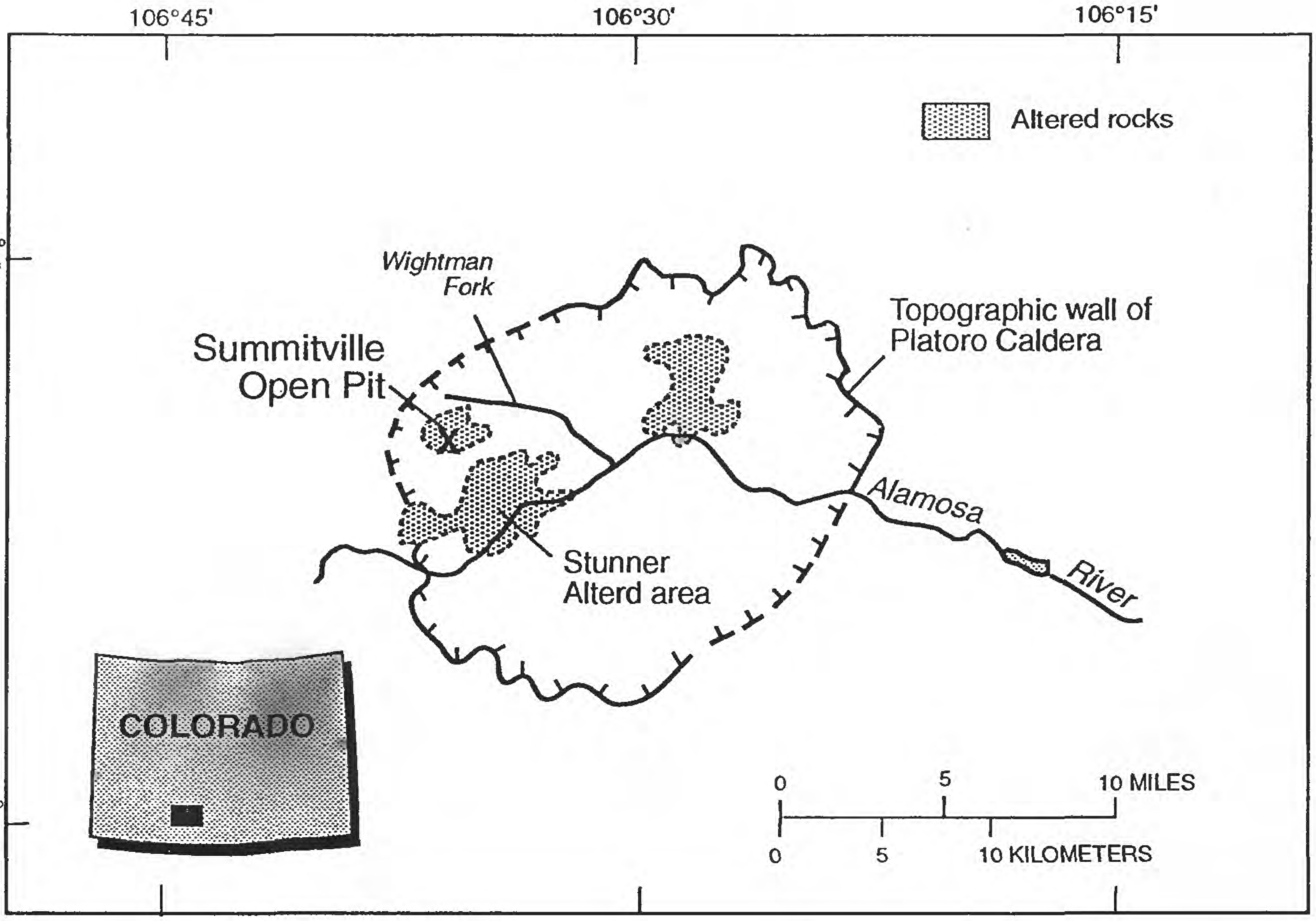

Figure 1.--Map showing Summitville and location of altered rocks in the upper Alamosa River basin.

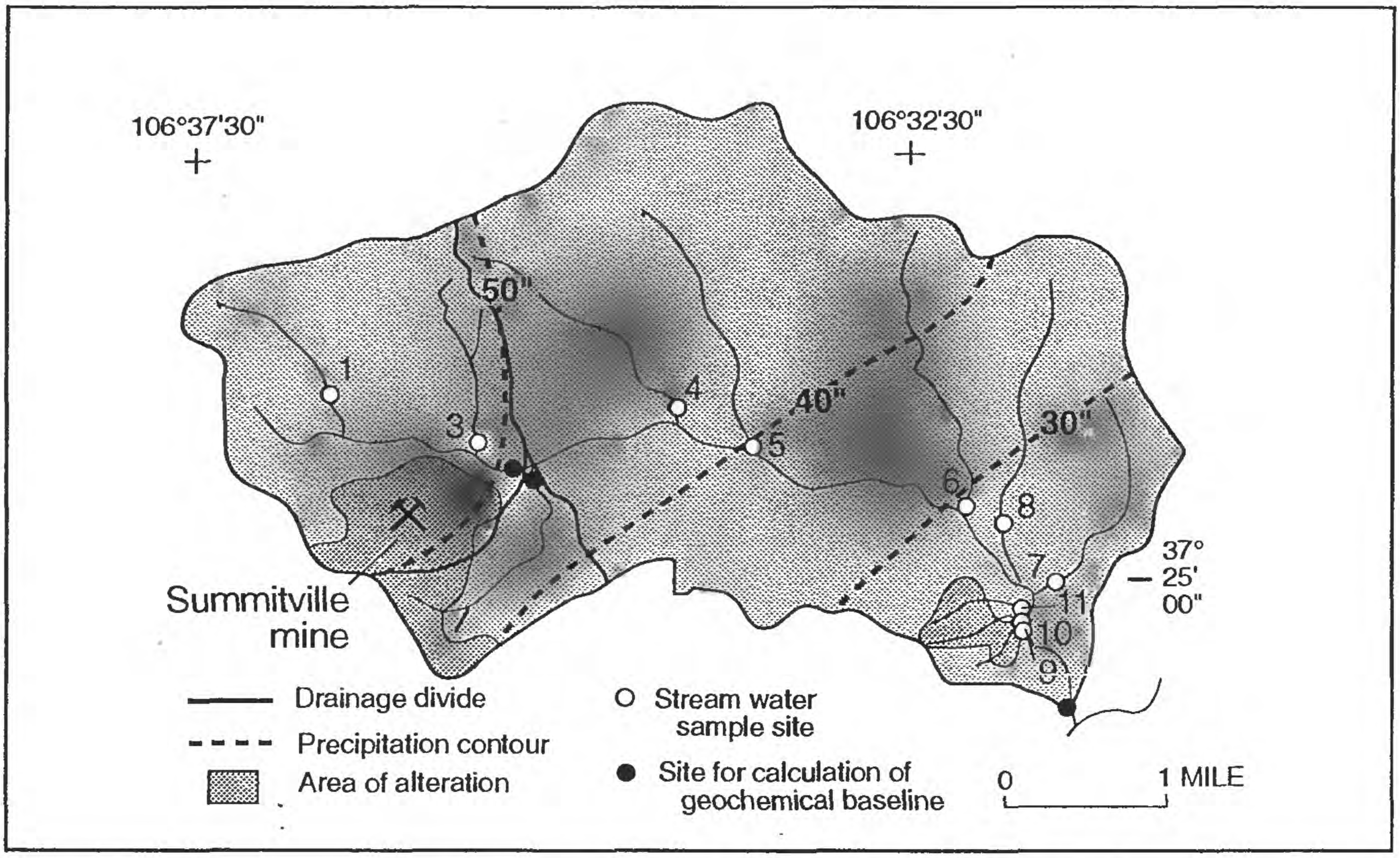

Figure 2.--Map showing drainage basins, altered rocks, precipitation, and stream-water sample sites in the Wightman Fork basin.

The second event was the emplacement of an underlying monzonitic stock at Summitville at 22.5 m.y. ago (Mehnert and others, 1973), which deposited gold, silver, and copper ore in a shallow volcanic environment. Alteration consists of zones emanating outward from a center of highly leached rocks in which only vuggy silica and ore minerals remain, to an advanced argillic zone with alunite, to an argillic zone, and finally to propylitized rock (Steven and Ratte, 1960).

Much of the present topography in the study area has been influenced by Pinedale glaciation (late Pleistocene), which was at its maximum approximately 18,000 years ago (Richmond, 1965). The glaciers were in retreat approximately 12,000 years ago, and only minor modification of the topography has taken place since then. Natural acid drainage and the formation of secondary iron oxide deposits began during melting of the glaciers and has continued since then. Both fossil and actively precipitating iron oxide deposits are present below pyritically altered rocks, particularly along the northeast base of South Mountain. These deposits consist mainly of masses of geothite and limonite and iron oxide-cemented gravel, conglomerates, and talus. Many of these deposits are presently or were associated with seeps that occur at changes in slope, particularly along the valley floor. In addition, hydrous iron oxide deposits are precipitating within stream beds of tributaries of Wightman Fork that are draining the SE altered area.

METHODS

Samples of water were collected from streams and seeps in the Wightman Fork basin, Calico Peak area, and the Redcloud Peak area during summer, 1994. Water samples were collected and analyzed according to methods discussed in Miller and McHugh (1994). Temperature and pH were measured at each site. Major and trace elements were determined either by graphite furnace or flame atomic absorption spectrophotometry or inductively coupled plasma-mass spectrometry. Anions were measured by ion chromatography, except for alkalinity, which was determined by titration with sulfuric acid.

For the mass-balance calculations, areas of precipitation, alteration, and drainage basins were determined digitally using GSMAP (Selner and Taylor, 1992).

WATER CHEMISTRY OF THE WIGHTMAN FORK BASIN

Samples of stream waters were collected in the undeveloped areas of the Wightman Fork basin. The chemistry of these waters was used to determine the input of dissolved species from the undeveloped areas for the calculation of the pre-mining geochemical baselines. Water samples were collected August 15, 1994. Stream-flow records of a gauging station approximately 10 miles SW of Summitville indicate a monthly mean flow for August of 53.5 cfs, and an average annual mean of 89.3 cfs for water years 1957-1992 (U.S. Geological Survey, 1993). Therefore the water samples, which were collected in August, probably have slightly higher metal concentrations than the mean annual sample.

Water samples were collected from 10 streams, all draining undisturbed areas (Fig. 2). The water chemistry ranges from low-ionic strength waters to natural acid drainage waters with high acidity, sulfate, and metals (Table 1).

UNDEVELOPED EQUIVALENT DEPOSITS TO SUMMITVILLE

Studies of background geochemistry of undeveloped mineral systems equivalent to Summitville were carried out to estimate background geochemistry of Summitville prior to mining. None of the mineral systems studied is an exact match to Summitville, but ranges of stream-water geochemistry can be determined and with assumptions, estimates can be made.

Upper Alamosa River and upper Cropsy Creek drainage

A study of stream waters draining undeveloped altered and mineralized areas within and adjacent to the upper Alamosa River basin was carried out in July 1993, by Miller and McHugh (1994). The upper Alamosa River drainage includes tributaries draining altered areas along the southern flanks of South Mountain, Cropsy Mountain, and Lookout Mountain. Advanced argillic alteration is present, particularly in the Alum, Bitter, and Iron Creek drainage basins (referred to as the Stunner altered area). Steep slopes form in these areas of soft ground with sparse to no vegetation. The rate of mechanical erosion for these areas is high. Fresh sulfides, particularly pyrite, are continuously exposed and oxidized, and streams draining these areas are chemically degraded. The range in concentrations of species for the most anomalous stream waters from these areas is shown in Table 2.

An undeveloped area with alteration associated with the Summitville deposit is the upper Cropsy Creek drainage. The range in geochemistry of the most anomalous stream waters from this area is also shown in Table 2. Prior to mining, the area of acid-sulfate alteration, which includes the Summitville mine site, probably generated natural acid drainage greater than that presently being generated in upper Cropsy Creek basin above the mine site. Probably more pyrite and sulfide minerals were originally present at the mine site than are present in upper Cropsy Creek basin above the mine site. In addition, the host rocks at the mine site have less buffering capacity to neutralize the acidity of the waters in contact with the oxidizing pyrite than rocks in upper Cropsy Creek above the mine site. Therefore, the background acidity generated at the mine site was probably greater than what is presently observed in upper Cropsy Creek basin above the mine site.

In contrast, the original terrain at the mine site was less severe than upper Cropsy, Alum, or Bitter Creek drainages, which produce large amounts of natural acid drainage. Steep relief allows mechanical erosion to keep ahead of chemical weathering, continuing to expose pyrite to the atmosphere and subsequent oxidation. In alpine areas with less relief, bogs and wetlands often form, which tend to reduce the exposure of oxygen to sulfides in the underlying rocks, decreasing oxidation and the

Table 1. Chemical analyses of stream waters from undisturbed areas of the Wightman Fork
[Conductivity in µS/cm, remaining species in mg/L except for Mn, Cu, and Zn in µg/L]

Site no.	pH	Conductivity	$SO_4^{=}$	Alkalinity	Fe	Al	Mn	Cu	Zn
				Unmineralized areas					
WW01	7.47	38	2.8	<1	0.14	<0.1	16	<1	1
WW03	7.25	51	5.4	27	.15	<.1	5.6	<1	1
WW04	7.55	72	7.0	37	.16	<.1	5.9	<1	1
WW05	8.16	120	10	66	.10	<.1	1	1	3
WW06	7.99	90	7.7	48	.05	<.1	<.9	<1	3
WW07	8.23	154	20	62	.02	<.1	<.9	<1	<1
WW08	8.32	172	24	70	<.01	<.1	<.9	<1	<1
				Mineralized areas					
WW09	6.94	459	220	4	<.01	.1	51	1	13
WW10	7.15	814	440	29	.04	<.1	38	<1	10
WW11	3.49	1,070	485	<1	27	12	780	3	110

Table 2. Chemical analyses of stream waters from undisturbed areas (after Miller and others, 1994)
[Conductivity in µS/cm; species in mg/L except for Cu and Zn in µg/L]

Site no.	Latitude	Longitude	pH	Conductivity	Sulfate	Alkalinity	Fe	Al	Mn	Cu	Zn
Upper Cropsy Creek											
SW28	37°24'56"	106°35'41"	4.40	150	49	<1	0.07	2.9	1.7	10	1,800
SW30	37°24'55"	106°35'39"	4.76	230	70	<1	.03	1.7	.82	10	130
SW31	37°24'52"	106°35'39"	6.70	460	220	<1	.22	17	5.9	46	1,200
SW32	37°24'49"	106°35'43"	4.69	140	39	<1	.01	2.1	.48	6	86
SW34	37°25'23"	106°37'16"	7.12	80	15	<1	.09	.1	.01	<1	34
SW35	37°25'27"	106°37'13"	7.33	70	7.2	1	.02	<.1	.01	<1	34
Background areas, Alamosa River Drainage Basin											
SW06	37°23'33"	106°23'04"	8.11	130	1.5	38	.03	.1	<.01	<1	4
SW07	37°23'50"	106°25'46"	8.13	150	7.2	50	.01	<.1	<.01	<1	4
SW33	37°26'06"	106°36'31"	7.25	40	.8	<1	.04	<.1	<.01	1	4
Mineralized areas, Alamosa River Drainage Basin											
Alum Ck	37°23'05"	106°33'59"	2.64	1,350	800	<1	141	55	2.7	250	710
Bitter Ck	37°23'42"	106°33'07"	3.44	340	95	<1	5.1	3.7	.58	7	68
Iron Ck	37°22'53"	106°36'09"	3.91	190	56	<1	1.6	3.0	.22	12	35

generation of natural acid drainage. Mechanical erosion is less than or in steady state with respect to chemical weathering. The northeastern slope of South Mountain is partially forested with conifers, suggesting stable slopes unlike the soft ground with steep slopes and sparse vegetation present on the south side of the Summitville district in the upper drainages of Alum, Bitter, and Iron Creeks. The presence of trees suggests slope stability and lack of strongly acidic soils. Miller and McHugh (1994) concluded that, except for copper which was assumed to be originally higher in concentration at the mine site, the geochemical background of stream waters draining the Summitville mine site prior to mining (Cropsy Creek above the junction with Wightman Fork) would probably fall between the geochemistry of stream waters presently draining upper Cropsy Creek above the mine site (a minimum) and Alum Creek at its confluence with the Alamosa River (a maximum).

Calico Peak area

A study was carried out of an undeveloped mineral system equivalent to Summitville in the Calico Peak area northwest of Rico, Colorado. The system resembles Summitville and occurs in a similar geologic and physical setting. The physical setting includes attributes such as climate, rainfall, elevation, topography, vegetation, and erosion. The area around Calico Peak has undergone minimal mining, and no significant mines occur in the study area. The study area is underlain by altered porphyritic biotite-hornblende latite of the Calico Peak Porphyry (Pratt and others, 1969), which includes a stock centered at Calico Peak and several dikes. Pervasive alteration includes significant alunite and sericite (Naeser and others, 1979). Pyrite occurs as disseminations and along fractures in the altered area. Fossil iron bogs and ferricrete were observed within and below the altered areas, particularly along the northeastern slope of Calico Peak.

Water samples were collected from 20 streams draining the study area from July 19-20, 1994 (Fig. 3). The geochemical analyses of stream waters are shown in Table 3. Waters with $pH<5$ are from first-order drainages with low-flow volume at or near their headwaters in the altered area. These waters represent natural acid drainage from the altered and mineralized zone of a mineralized system similar to Summitville. The Calico Peak area has not been drilled, so the occurrence and amounts of sulfides other than pyrite are unknown. One sample of rock from a prospect pit contained 1.3 percent copper. The range in pH, iron, manganese, aluminum, and sulfate at this time of year may be similar to waters draining Summitville prior to mining.

In the headwaters draining the altered area, the waters have low pH and high sulfate and metals concentrations. As the waters mix downstream with tributaries from unmineralized areas, the pH and sulfate concentrations increase and copper, zinc, iron, and aluminum concentrations generally decrease. At site 23, which approximates the junction of Wightman Fork above Cropsy Creek in terms of total area and percent of mineralized and unmineralized rocks above the junction, $pH = 8.1$ and copper, zinc, iron and

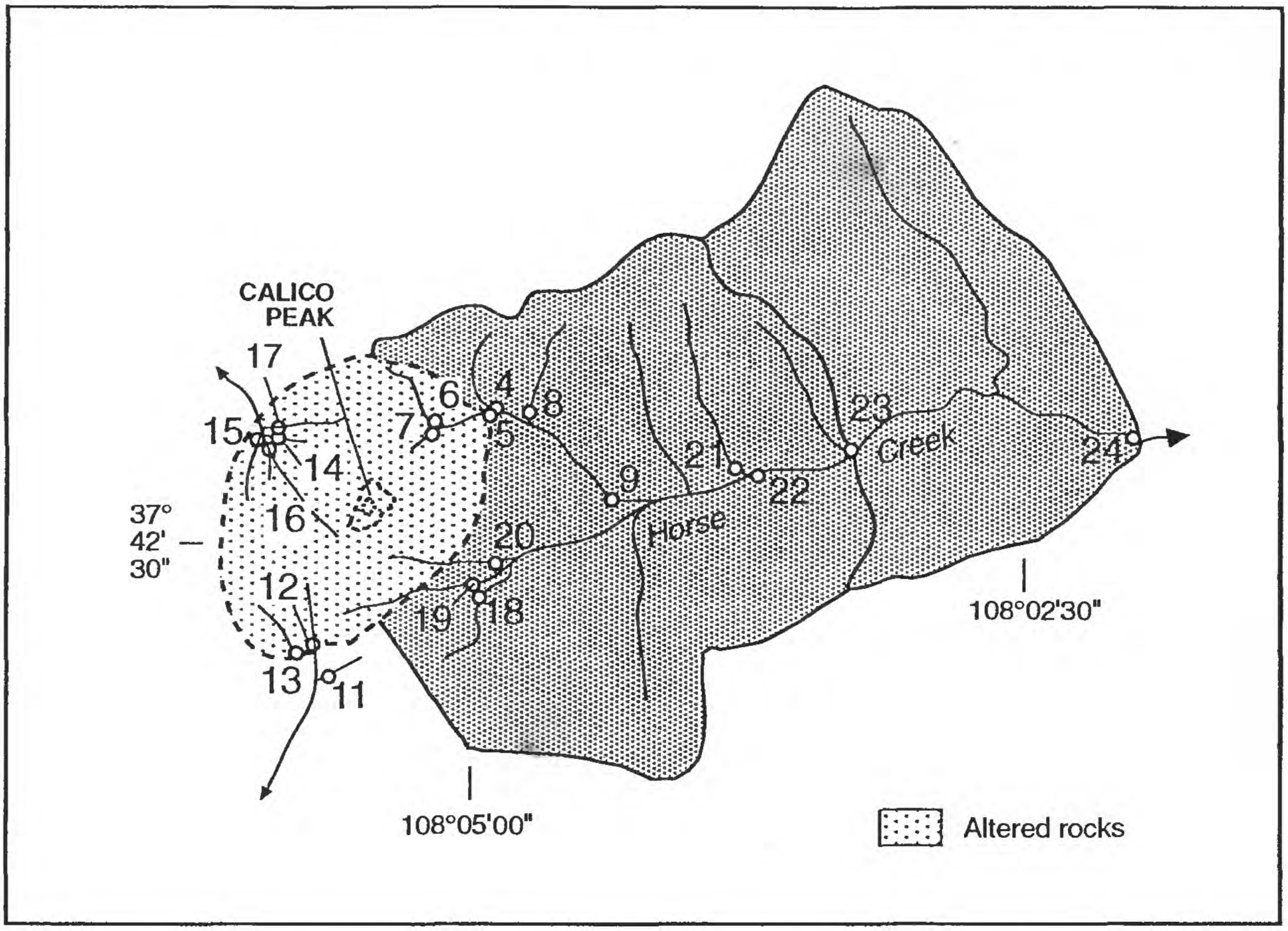

Figure 3.--Map showing location of streams, altered rocks, and stream-water sample sites in the vicinity of Calico Peak.

Table 3. Chemical analyses of stream waters from Calico Peak area, Colorado
[Conductivity in µS/cm; species in mg/L except for Cu and Zn in µg/L]

Site no.	Latitude	Longitude	pH	Conductivity	Sulfate	Alkalinity	Fe	Al	Mn	Cu	Zn
CW4	37°42'56"	108°04'49"	6.62	66	17	2	0.02	<0.1	<0.01	<0.6	<5
CW5	37°42'55"	108°04'51"	4.63	83	18	<1	.06	.5	.11	65	82
CW6	37°42'53"	108°05'07"	3.33	263	63	<1	.89	2.0	.45	350	320
CW7	37°42'51"	108°05'06"	4.15	168	50	<1	1.48	2.4	.22	12	65
CW8	37°42'54"	108°04'42"	7.11	156	25	60	.01	<.1	<.01	<.6	<5
CW9	37°42'35"	108°04'22"	7.79	119	25	27	.15	.1	.03	5.8	10
CW11	37°42'02"	108°05'37"	6.19	88	26	7	.01	.1	<.01	<.6	<5
CW12	37°42'08"	108°05'39"	4.22	88	27	<1	.05	.9	.26	2.0	45
CW13	37°42'07"	108°05'42"	5.77	36	7.1	<1	.01	<.1	<.01	1	6
CW14	37°42'52"	108°05'48"	5.60	82	26	6	.42	.4	.11	.6	20
CW15	37°42'53"	108°05'52"	3.84	155	48	<1	.46	2.5	.11	3.8	47
CW16	37°42'51"	108°05'50"	3.60	122	29	<1	.65	2.0	.04	2.9	34
CW17	37°42'53"	108°05'50"	3.98	130	42	<1	.20	1.1	.08	140	38
CW18	37°42'19"	108°04'54"	7.10	195	44	40	.02	<.1	<.01	<.6	5
CW19	37°42'20"	108°04'55"	7.21	82	15	27	.01	.1	<.01	.9	<5
CW20	37°42'24"	108°04'52"	5.79	75	24	<1	.05	.3	.07	6.0	28
CW21	37°42'42"	108°03'46"	7.45	170	20	59	.01	<.1	<.01	<.6	<5
CW22	37°42'42"	108°03'43"	7.05	141	42	20	.38	<.1	.62	9.1	66
CW23	37°42'46"	108°03'18"	8.10	316	50	132	.03	<.1	<.01	<.6	<5
CW24	37°42'47"	108°02'04"	7.94	223	40	78	.02	<.1	.05	.7	6

aluminum have decreased to low, nearly background values. Except for sulfate, stream water chemistry for Horse Creek returned to nearly background values in a stream distance of 3.5 km. One difference between Calico Peak and Summitville mineral systems may be that copper and zinc concentrations in rocks were probably greater in the surface and near surface at Summitville prior to mining than at Calico Peak.

Redcloud Peak area

The Redcloud Peak area, several miles west and southwest of Lake City, Colorado, was selected for study because no significant mining or acid mine drainage is associated with the study area. The study area was determined to have high potential for base and precious metals in vein and breccia-pipe epithermal deposits and moderate potential for molybdenum and copper porphyry deposits (Sanford and others, 1987). The study area lies mostly within the Lake City caldera, and exposed rocks are mainly a caldera-fill sequence of high silica to quartz trachytic ash-flow tuffs and caldera collapse breccia. Resurgent doming and faulting resulted in emplacement of quartz syenite and quartz monzonite intrusions into the collapse sequence. Alteration consists of bleached and iron-stained rocks and small silicified and brecciated masses. The area's physical setting and climate is similar to Summitville.

Water samples were collected from 33 streams. The results of geochemical analyses of stream waters with $pH<5$ is shown on Table 4.

Published literature

The closest undeveloped deposit found in the literature that is most nearly equivalent and in a similar physical setting to the Summitville deposit is the Mount McIntosh-Pemberton Hills area in northern Vancouver Island, British Columbia (Koyanagi and Panteleyev, 1993). The deposit is an advanced-argillic, acid-sulfate copper-gold system hosted in volcanic rocks in a temperate-humid climate. Hydrothermally altered and leached silica caps form prominent bluffs along linear alteration zones with base and precious metal deposition. Sulfide mineralization consists of abundant disseminated and massive stratabound iron sulfides, mainly pyrite, with associated enargite and copper sulfides. A study was carried out by Koyanagi and Panteleyev (1993) to investigate natural acid-drainage of streams draining this deposit. Samples were collected from 34 streams and standing swamps. Geochemical analyses of selected species of the four stream waters with the highest copper concentrations are shown in Table 5. The maximum copper concentration is 320 $\mu g/L$ in the small headwater streams. At short distances downstream, these streams return to nearly background levels of copper. The climate in the study area is wetter than at Summitville. Therefore stream waters draining the Mount McIntosh/Pemberton Hills area are probably slightly more dilute than at Summitville prior to mining.

CALCULATION OF GEOCHEMICAL BASELINES PRIOR TO MINING

Table 4. Chemical analyses of stream waters with pH ≤ 5, from Redcloud Peak area, Colorado
[Conductivity in µS/cm; species in mg/L except for Cu and Zn in µg/L]

Site no.	Latitude	Longitude	pH	Conductivity	Sulfate	Alkalinity	Fe	Al	Mn	Cu	Zn
RW12	37°56'54"	107°26'19"	4.92	127	49	<1	<0.01	1.6	0.45	4.3	110
RW14	37°56'56"	107°26'25"	3.58	320	106	<1	.45	2.6	1.6	3.2	280
RW16	37°56'28"	107°27'13"	4.17	148	53	<1	.07	1.7	1.0	2.5	83
RW30	37°58'22"	107°26'33"	4.42	140	52	<1	.07	2.1	.62	2.2	130
RW32	37°57'53"	107°27'04"	3.90	194	74	<1	6	4.4	.47	5.9	93

Table 5. Chemical analyses of the four most anomalous stream waters in metals from Mount McIntosh-Pemberton Hills area, Vancouver Island, B.C. (from Koyanagi and Panteleyev, 1993)
[Conductivity in µS/cm; species in mg/L except for Cu and Zn in µg/L]

Site	pH	Conductivity	Sulfate	Fe	Al	Cu	Zn
Hushamu Creek Tributary	3.7	54	228	0.55	16.5	320	40
Hushamu Creek	3.9	163	31	.01	1.89	120	10
Hepler Creek Tributary	4.1	100	18	.01	.82	70	10
Hepler Creek Tributary	3.9	152	51	.35	3.47	30	10

Geochemical baselines prior to mining are calculated for three points: 1) Wightman Fork above the junction with Cropsy Creek; 2) Cropsy Creek above the junction with Wightman Fork; and 3) Wightman Fork above the junction with the Alamosa River (Fig. 2). Species used for the calculations are pH, sulfate, iron, aluminum, manganese, copper, and zinc. These were chosen because they have the greatest potential for exceeding water-quality standards for streams draining the Summitville mine.

Mass-balance calculations

Wightman Fork and Cropsy Creek drainages receive waters draining both mineralized and unmineralized rocks. The waters from the unmineralized areas dilute concentrations of metals and raise pH values of waters derived from the mineralized areas. The amount of a chemical species contributed by a given drainage above the point for calculation of baselines depends on the percent of mineralized and unmineralized rocks and the amount of water flowing through the drainage basin. The amount of water that flows through a particular basin in a season can be estimated by the drainage area and the amount of annual precipitation received. Some precipitation is lost by evaporation, but it is assumed that evaporation is approximately the same throughout the drainage basins.

Estimates of the chemical composition of stream waters for the unmineralized drainage basins are made directly by chemical analyses of stream waters from tributaries of the Wightman Fork draining unmineralized rocks (Table 1). For unmineralized drainage basins, in which water chemistry was not determined, an estimate of the water chemistry using an equivalent basin is used for the calculations. Estimates for drainage that are developed (containing mines with significant acid mine drainage) are made by using data collected from streams draining mineral systems comparable to Summitville in similar climatic and physical settings. By multiplying the amount of mineralized and unmineralized areas of the drainage basin by average annual precipitation and then multiplying by the concentration of the stream water chemistry determined or estimated for the unmineralized and mineralized portion of the basin, the mass of each constituent contributed by the individual basin is determined. The Wightman Fork drainage basins showing altered areas, precipitation, and locations of stream water samples collected from undeveloped drainages are shown in Fig. 2. Areas and percent of mineralized and unmineralized rocks and precipitation in the three basins are shown in Table 6.

Chemical modelling

Sulfate is probably the only element shown in the tables that behaves conservatively. The concentrations of other species are controlled by processes, other than dilution, that take place in the stream channel. As an example, dissolved iron, which is derived from waters draining the altered areas, is composed of species such as Fe^{2+} and Fe^{3+}. These species will react with oxygen in the stream bed during mixing, lowering pH according to:

$Fe^{2+} + .25\ O_2 \rightarrow Fe(OH)_3 + 2H^+$ and $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$.

Table 6. Areas and weighted percent (area x precipitation) of mineralized and unmineralized areas of three drainage basins in the vicinity of Summitville, Colorado

Drainage basin	Area (km^2) Unmineralized areas	Area (km^2) Mineralized areas	Total	Weighted percent Unmineralized areas	Weighted percent Mineralized areas
Cropsy Creek above Wightman Fork	1.67	0.63	2.30	72.2%	27.8%
Wightman Fork above Cropsy Creek	7.46	1.59	9.05	82.5%	17.5%
Wightman Fork above Alamosa River	36.83	3.88	40.71	90.7%	9.3%

Dissolved aluminum will precipitate as pH trends toward neutral. One possible reaction is:

$$Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 3H^+.$$

The above reactions may be reversible and consume acid, possibly seasonally, in transitional reaches of streams. Copper and zinc may adsorb or coprecipitate onto freshly precipitated hydrous metal oxides. Therefore these metals are not conservative. Although the pH values will be lowered by precipitation of hydrous metal oxides, they will tend to rise by the neutralizing effect of mixing with tributaries containing carbonate and bicarbonate ions:

$$CO^{3}_{2-} + H^+ \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons H_2CO_3.$$

The reaction will stop when all the carbonate and bicarbonate ions are used up. The effect of these processes, except for adsorption of copper and zinc on to hydrous metal oxides, on the concentration of species of the stream waters is estimated by using the chemical modelling program PHREEQE (Parkhurst and others, 1980). In addition, the effects of mixing various percentages of water from mineralized and unmineralized portions of a basin are calculated using PHREEQE. For the chemical modelling, 50 percent of the total dissolved iron and aluminum in stream waters, draining the mineralized areas, is assumed to react with O_2 and/or H_2O. Hydrous metal oxides are precipitated, and pH values decrease. In contrast, as the acid-waters mix with the bicarbonate waters draining the unmineralized areas, pH values will increase. Phreeqe was used to mix the proportions of waters draining the mineralized and unmineralized shown in Table 6.

Conservative scenario

For the conservative scenario, the geochemical baselines are determined by assuming the chemistry of stream waters draining the altered areas is equivalent to the chemistry of streams waters draining the Stunner altered area south of Summitville. Concentrations of species used for the conservative scenario (Table 7) are estimated by using the composite stream water chemistry of Alum and Bitter Creeks (Table 2). Concentrations of species from the unaltered areas in the Wightman Fork basin were determined directly or estimated using equivalent drainages in the Wightman Fork basin (Table 1). The assumption is made that 50 percent of the iron and aluminum in solution from waters draining the mineralized areas precipitates as hydrous oxides, lowering the pH from 3.5 to 2.53. In addition, the amount of mineralized area is increased by 10 percent above what was calculated. Using this data, the pre-mining geochemical baselines are calculated at the three junctions (Table 8).

Most likely scenario

The chemistry of stream waters draining the advanced argillic altered area such as Alum Creek is probably more degraded chemically than streams draining the Summitville site prior to mining. The pH, sulfate, iron, manganese, and aluminum concentrations of stream waters used for the most likely scenario (Table 7) is a composite of the chemistry of stream waters

Table 7. Stream water chemistry used for calculation of pre-mining geochemical baselines of three junctions in the vicinity of Summitville, Colorado
[Species in mg/L except Cu and Zn in µg/L]

	pH	Sulfate	Alkalinity	Fe	Al	Mn	Cu	Zn
Conservative scenario								
Unmineralized areas	8.0	10	50	0.05	0.1	0.01	1	4
Mineralized areas	3.5	200	0	100	15	.6	1,500	1,000
Most likely scenario								
Unmineralized areas	8.0	7	50	.01	.1	.01	1	4
Mineralized areas	3.5	100	0	5	4	.5	500	500

Table 8. Weighted percent (area x precipitation) assuming 10 percent greater mineralized area

	Weighted percent	
Drainage basin	Unmineralized rocks	Mineralized rocks
Cropsy Creek above Wightman Fork	69.4%	30.6%
Wightman Fork above Cropsy Creek	80.7%	19.3%
Wightman Fork above Alamosa River	89.8%	10.2%

derived from the Stunner altered area and altered areas in upper Cropsy Creek and Calico Peak area. The concentrations of copper and zinc in stream waters draining the mineralized areas in the Wightman Fork basin are estimated to be greater than what is derived from these altered areas because of the assumption that these metals were originally greater at the Summitville site. The assumption is made that 50 percent of the dissolved iron and aluminum from waters draining the mineralized areas is precipitated as hydrous metal oxides lowering the pH from 3.5 to 3.2. The calculated most likely pre-mining geochemical baselines for stream waters at the three junctions are shown in Table 9.

Comparison of calculated baselines with Calico Peak

The mineral system at Calico Peak is an acid-sulfate deposit, similar to Summitville, and occurs in a similar physical and geological setting. The observed attenuation of chemical species and geochemical baseline of this undeveloped area can provide a comparison of calculated geochemical baselines at Summitville. Mineralized rocks occur in the headwaters of Horse Creek. The streams draining the mineralized rocks have low pH values and high concentrations of sulfate, iron, aluminum, manganese, copper, and zinc. As the headwater streams mix with tributaries draining unmineralized rocks, the stream-water concentrations decrease for these species and pH rises (Table 3). The area of the drainage basin above site 23 (Fig. 3) is approximately the size of the Wightman Fork basin above Cropsy Creek. In addition, the percent of mineralized and unmineralized rocks is similar. A comparison of the calculated baseline of the Wightman Fork above Cropsy Creek and site 23 on Horse Creek is shown in Table 10. At site 23 on Horse Creek, the pH is higher and iron, aluminum, manganese, copper, and zinc concentrations are significantly lower compared to the calculated baselines at Summitville. An obvious difference is that the copper and zinc contents of surface and near surface rocks and consequently the surface waters generated at Summitville were significantly higher prior to development than at Calico Peak. But the pH, iron, aluminum, and manganese of the surface waters should be similar because both mineral systems contain abundant pyrite and occur in similar physical settings. The difference is probably because of more reactive rocks in the Horse Creek basin than at Summitville. The stream waters in Horse Creek basin are generally higher in bicarbonate than in the Wightman Fork basin. Calcite was observed to occur a gangue minerals associated with an earlier mineralization in the lower Horse Creek basin. Dissolution of calcite is probably the reason for the higher bicarbonate values, which would raise pH and lower metal contents in the stream waters.

Other considerations

Additional factors can be used to refine the geochemical baselines. The most significant factor, which is not taken into account, particularly during runoff periods, is ratio of mechanical erosion to chemical weathering. When chemical weathering exceeds mechanical erosion, underlying rocks are

Table 9. Pre-mining geochemical baselines at three stream junctions in the vicinity of Summitville, Colorado
[Species in mg/L except for Cu and Zn in µg/L]

Junction	pH	Sulfate	Fe	Al	Mn	Cu	Zn
Conservative scenario							
Cropsy Creek above Wightman Fork	3.67	68	15	2.3	0.19	460	309
Wightman Fork above Cropsy Creek	4.17	47	10	1.5	.12	290	196
Wightman Fork above Alamosa River	6.20	29	5	.9	.07	154	106
Most likely scenario							
Cropsy Creek above Wightman Fork	6.53	33	.70	.6	.15	139	142
Wightman Fork above Cropsy Creek	6.90	23	.45	.4	.09	88	91
Wightman Fork above Alamosa River	7.24	16	.30	.3	.06	47	50

Table 10. Comparison of chemical species of most likely and conservative scenarios for Wightman Fork above Cropsy Creek with site 23, Calico Peak
[Species in mg/L except for Cu and Zn in µg/L]

	pH	Sulfate	Fe	Al	Mn	Cu	Zn
Most likely scenario	6.9	23	0.45	0.4	0.09	88	91
Conservative scenario	4.17	47	9.7	1.5	.12	290	196
Site 23, Calico Peak	8.10	50	.03	<.1	<.1	<.6	<5

mantled by a zone of secondary products, thus most of the sulfides are out of contact with atmospheric oxygen. When mechanical erosion is greater than chemical weathering, sulfide minerals are continuously being exposed to oxygen, and generate natural acid drainage, akin to what happens during mining excavation. Areas of highly altered rocks occur in the Stunner altered area, south of Summitville, and consist of soft ground with steep slopes and little or no vegetation. These areas contribute large amounts of natural acid drainage, which is reflected by the stream-water chemistry of Alum, Bitter, and Iron Creeks. One method to estimate this factor would be to determine steepness of slope (using topographic maps) and amount of vegetation and altered ground (using aerial and remote sensing maps). The presence of steep slopes and altered areas and the lack of vegetation would indicate high rates of mechanical erosion. Removing vegetation to make roads and other construction activity will also increase the mechanical erosion within a basin and degrade stream-water chemistry.

Spring runoff and storm events

No attempt is made to calculate geochemical baselines during spring runoff and summer storm events. During these periods, the concentrations of species will be higher during the beginning of the runoff than during mean stream flow, mainly because of dissolution of easily dissolved salts that have accumulated during the winter and drier periods by processes such as capillary action/evaporation. After this initial increase, the concentration of species will decrease to less than mean stream flow. But the total amount of metals or loadings usually will be greater during the runoff period than during mean flow.

To estimate the geochemical baselines during spring runoff and storm events, a factor value above the calculated concentration of species during mean flow can be used. A factor of 10 would not be unusual and is a function of the amount of altered rocks, amount of runoff, and mechanical erosion. The greater the rate of mechanical erosion, which is a function of steepness of slopes and lack of vegetation, the greater this value will be. These factor values can be estimated from the study of streams draining geologically and physically equivalent areas with similar climates. Horse Creek drainages at Calico Peak during spring and storm runoff would be a good equivalent for the Wightman Fork drainages during spring and storm runoff.

CONCLUSION

Probable pre-mining geochemical baselines of stream waters in the vicinity of Summitville are calculated by combining chemical modelling of dominant in-stream reactions with mass balance calculations. This technique, which is developed for headland-type basins, consists of the mixing of two types of natural waters: 1)acid-sulfate waters derived from mineralized areas and 2) low-ionic strength-bicarbonate waters derived from unmineralized areas within a basin in which the calculation is desired. The calculations use as input, water chemistry of streams draining these two types of areas, along with other assumptions. Therefore, changing the input chemistry and/or the assumptions will change the calculated baselines. An example of an assumption is that 50 percent of the dissolved iron and aluminum is assumed to precipitate, lowering the pH. Consequently the dissolved iron and aluminum content plays a major role in the resultant pH.

This technique emphasizes the importance of using a process-orientated, water-shed approach to the calculations of pre-mining geochemical baselines.

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