Results of Chemical and Stable Isotopic Analyses of Water Samples Collected in the Patagonia Mountains, southern Arizona

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Abstract

Water samples were collected in the Patagonia Mountains in February, 1997. Most of the samples were collected from portals of abandoned mines, or from stream drainages immediately downstream from abandoned mines. Most of the samples have low pH (<4) and high total dissolved solids (> 1000 mg/L). Anion composition of the water samples is dominated by sulfate, while cation compositions range from calcium-dominated to mixed calcium-magnesium or calcium-sodium-dominated waters. Metals such as iron, manganese, copper, zinc, and aluminum contribute a significant portion (>10%) of the cation content to the water samples. Because of the low pH's, protons contribute up to several percent of the cation character of the waters in some of the samples. The data are presented in tabular and graphical formats, with descriptions of data quality and brief descriptions of results.

Introduction

The Patagonia Mountains are located in southern Arizona, between Tucson and Nogales (fig. 1). This area has a history of mining activity that extends back at least 100 years (Schrader, 1915). Primary production has included copper, lead, and zinc, with gold and silver produced from epithermal vein systems. Most of the mines in the area have been inactive and abandoned for many decades, but some continue to produce acidic, metal-rich drainage waters from mine portals or possibly from discharge of ground water that has passed through the mine workings. Drainage from these mines is mostly ephemeral.

The climate in southern Arizona is characterized by semiarid to arid conditions, with monsoon rains producing most of the average annual rainfall during the summer months. Only 25% of the average annual precipitation is historically experienced during the winter months.
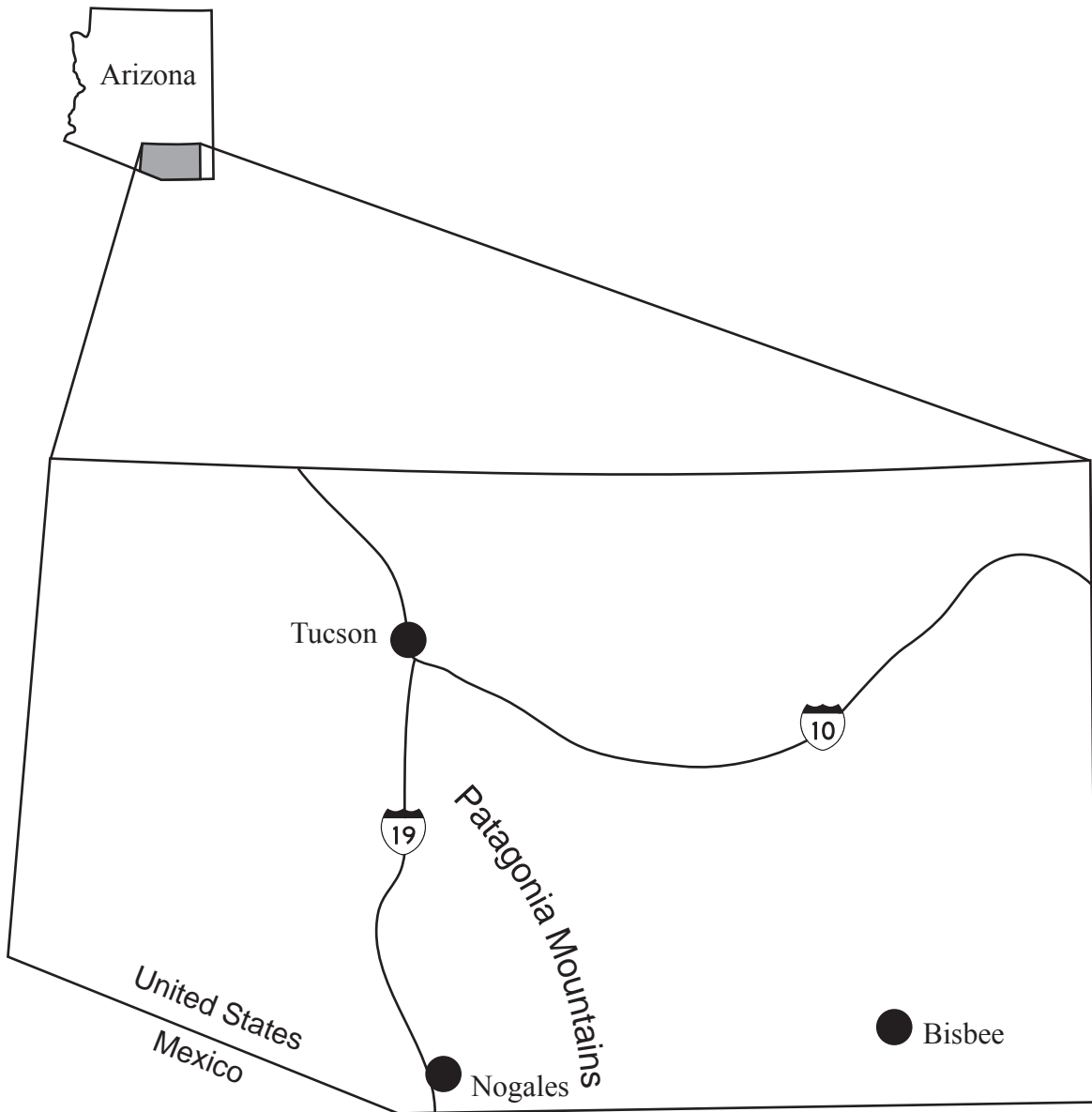
Figure 1- location map for this study.

Field Methods

Field sampling was conducted over a period of three days in February, 1997. During that time, air temperatures were 40-50ºF (approx. 5-15ºC). Rain fell during the third day of sampling, at the time that samples 14 through 17 were being collected.

Samples were collected using established methods (cf. Ficklin and Mosier, 1999, for a thorough review). Field analyses were performed for pH, temperature, dissolved oxygen, and electrical conductivity. The pH measurements were made at each site following a calibration using three known buffer solutions. Because the samples generally had low pH values, buffers from a similar pH range were used; usually pH 1.68, 3.00 or 4.00, and 7.00 (25°C values). The pH meter had an automatic temperature compensation device so that the pH calibrations and measurements are corrected for the listed water temperatures. Temperature was measured using a calibrated digital thermometer. Electrical conductivity was measured as equivalent total dissolved solids expressed as NaCl. At each site except 97AZ-13, a visual estimate of discharge was made; these are approximations only. Sample locations and results of field analyses are shown in Table 1. Other data shown in Table 1 include latitude, longitude, and elevation. These were determined after completion of field work from locations plotted on the USGS 1:24,000 scale topographic sheets for the Cumero Canyon and Harshaw quadrangles. The distribution of sample locations is shown in figure 2.

At each site, samples were collected for later laboratory analyses. These included samples for anions, cations, ferrous iron (for most samples), and for stable isotopes values of δD, $\delta^{18}O$, and $\delta^{34}S$ in water and in dissolved SO_4. The anion samples were filtered through a 0.45 μm nominal pore size cellulose acetate filter and stored in low-density polyethylene bottles. Cation samples were similarly filtered and acidified with concentrated Ultrex-grade nitric acid from J.T. Baker Chemical Company (0.5 mL acid per 30 ml sample) and stored in low-density polyethylene bottles. The ferrous iron samples were filtered and acidified with reagent grade hydrochloric acid (1 mL acid per 100 mL sample) and kept in amber (opaque) high-density polyethylene bottles to avoid photo-oxidation of iron. Anion and ferrous iron samples were kept on ice in a cooler from the time of sampling, then stored in a refrigerator in the laboratory until the time of analysis.

Table 1- Field analyses, locations and descriptive data for samples collected in the Patagonia Mountains, southern Arizona, in February, 1997. Elevations are given in feet above mean sea level (FAMSL) as determined from 1:24,000-scale topographic maps. Flow estimates were not made for samples 97AZ-13 or 97AZ-17.

Sample No.	description
97AZ-1	flowing well in Humboldt Canyon
97AZ-2	Humboldt Canyon, approx. 100m upstream of mine
97AZ-3	mouth of World's Fair mine
97AZ-4	World's Fair mine at base of tailings dump
97AZ-5	50 m downstream of site #4
97AZ-6	approximately 200 m downstream of site #5
97AZ-7	approximately 1 km downstream from W.F. mine in Alum Gulch
97AZ-8	approximately 500 m downstream of Three-R mine
97AZ-9	approximately 800 m downstream from site #8
97AZ-10	Ventura Mine mouth
97AZ-11	approx. 150 m downstream from European Mine
97AZ-12	flowing well down hill from European Mine
97AZ-13	Paymaster Spring
97AZ-14	Alum Gulch approx. 150 m downstream from Humboldt Canyon
97AZ-15	Same as site #7
97AZ-16	approx. 1 km downstream from site #15
97AZ-17	Alum gulch near Exposed Reef Mine

| Sample No.	Latitude	Longitude	elevation FAMSL	flow, visual estimate	pH	T°C	TDS, as NaCl
97AZ-1	31.4647	-110.7447	5150	30 gpm	3.45	19.3	160
97AZ-2	31.4686	-110.7331	4860	.1 - .3 gpm	2.89	9.6	650
97AZ-3	31.4797	-110.7377	4800	10 gpm	3.07	12.5	1300
97AZ-4	31.4802	-110.7363	4650	5 gpm	2.92	6.4	1300
97AZ-5	31.4812	-110.7363	4640	5 gpm	3.15	11.7	1860
97AZ-6	31.4831	-110.7367	4575	5 gpm	2.97	10.0	1820
97AZ-7	31.4857	-110.7373	4500	5 gpm	3.41	7.3	1750
97AZ-8	31.4767	-110.7729	4520	1-2 gpm	3.12	7.2	660
97AZ-9	31.4763	-110.7769	4390	<.5 gpm	3.05	8.6	680
97AZ-10	31.4572	-110.7640	5320	.1 gpm	2.89	9.7	1620
97AZ-11	31.4648	-110.7703	4800	0.02 - .04 gpm	2.88	7.6	1020
97AZ-12	31.4697	-110.7813	4415	.1 - .3 gpm	7.61	14.3	820
97AZ-13	31.4111	-110.7052	5500		6.86	7.3	140
97AZ-14	31.4766	-110.7327	4775	10 -20 gpm	3.8	7.6	1770
97AZ-15	31.4857	-110.7373	4500	25 gpm	3.45	7.1	1750
97AZ-16	31.4895	-110.7449	4390	5 gpm	3.77	9.6	1710
97AZ-17	31.4937	-110.7477	4350		3.47	9.0	1510
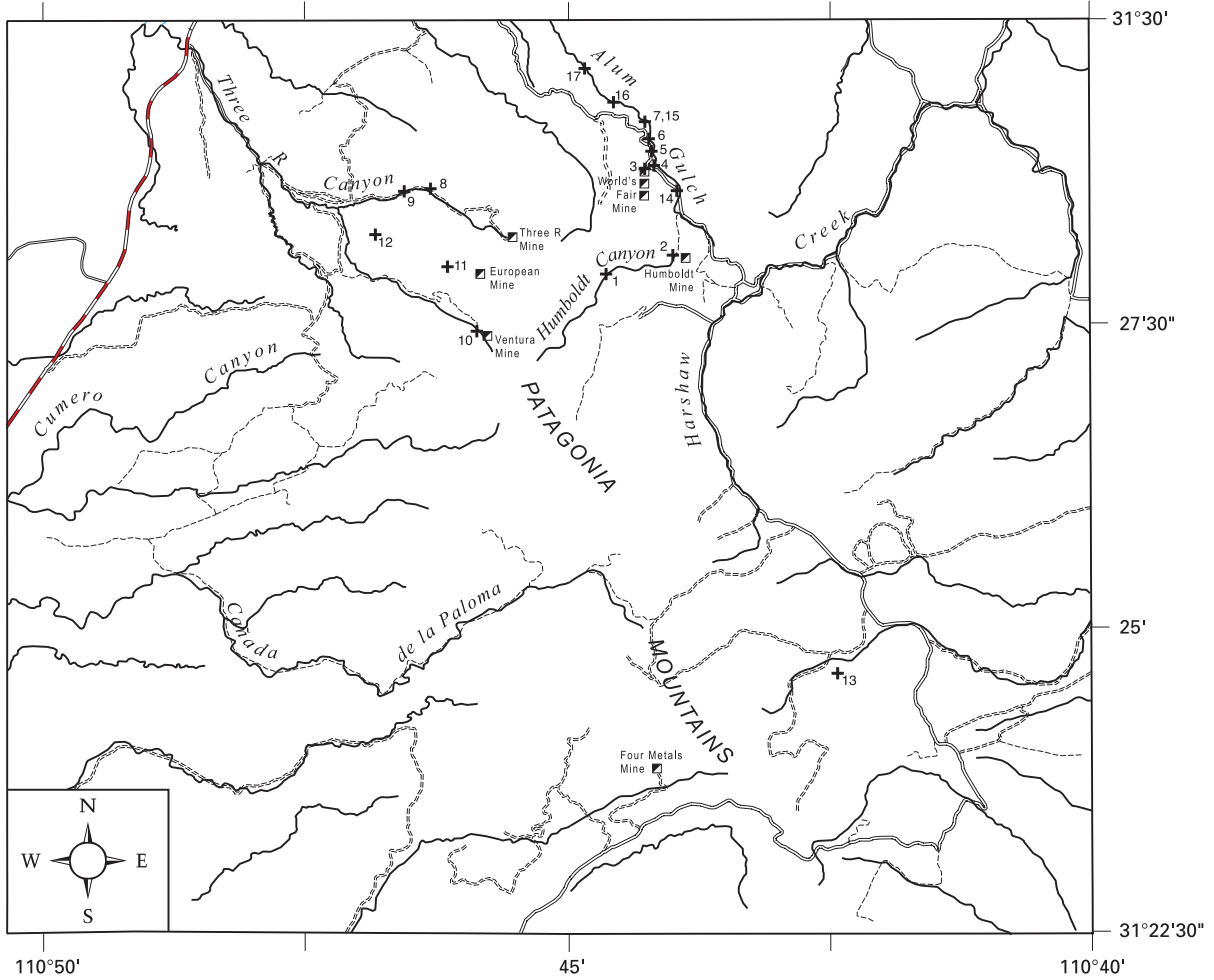
Figure 2- Base map of the Patagonia study area. Sample locations are indicated with a "+," and numbers correspond to sample numbers in the tables, each of which has the prefix, "97AZ-." Surface-water drainages are shown by the thin black lines. Roads are shown with double lines, dashed where not maintained.

Laboratory Methods

Ferrous iron determinations were made using Hach Accuvac® ampoules with a Hach DR-2000 spectrophotometer. The method involves drawing the sample into an evacuated ampoule that contains a proprietary reagent, then measuring the color development. The method is based on the 1,10 phenanthroline method as outlined in *Standard Methods for the Examination of Water and Wastewater* (Clesceri and others, 1998).

Anion determinations were made using a Dionex DX-500 ion chromatography (IC) system. Standard running conditions used an AS-4 chromatography column, with a mixed carbonate/bicarbonate eluent. With this method, fluoride and chloride determinations were made. Minor amounts of bromide were detected in most samples, and nitrate was detected in two samples. Sulfate analyses also were performed using the IC method, but the results of sulfate analyses from the ICP-AES are considered to be more reliable because of an analytical problem with the IC system. In the normal sequence of IC analyses, each sample was run, diluted with an equal volume of deionized water. This first sample run provided reliable analytical results for fluoride, chloride, bromide, and nitrate, but sulfate results were always much greater than the linear working range (all samples had SO_4^{2-} concentrations greater than 100 mg/L as SO_4^{2-}; the instrument is calibrated to 15 mg/L). Subsequently a greater dilution was run (usually 1:100, 1:200, or 1:500 *v:v*) for sulfate. However, a problem was discovered recently wherein there is a carryover effect following the injection of high-sulfate samples into the IC, so the sulfate numbers produced by the IC were spuriously high. Thus, the IC sulfate numbers are not reported herein, but rather, sulfate analytical results are reported from the ICP/AES. Further method development work with the IC has shown that dilution of samples with eluent, rather than deionized water, prevents this carryover effect in all but the most sulfate-rich samples.

Cations were determined by inductively coupled plasma / atomic emission spectroscopy (ICP/AES) and inductively coupled plasma / mass spectroscopy (ICP/MS). The ICP/AES method produces preferred values for major cations such as alkali metals and alkaline earths, as well as for some of the trace elements, including iron, aluminum, and manganese. The ICP/MS method has the advantage of greatly increased sensitivity, and is capable of detecting a greater number of elements, so most of the trace element values and rare-earth element analyses were determined by the ICP/MS method (Briggs and Fey, 1996; Lamothe and others, 1999).

Samples for isotopic determinations were placed in 20 mL glass scintillation vials, tightly capped, and returned to the USGS laboratories in Denver for analyses by isotope ratio mass spectrometry. Water samples were prepared for hydrogen isotopic analyses using the Zn reduction technique (Coleman et al., 1982) and for oxygen isotope analyses using an automated CO_2 equilibration technique. Values of $\delta^{18}O$ and δD are relative to the VSMOW standard and have reproducibility of approximately 1.0 and 0.7 ‰, respectively. Dissolved sulfate was precipitated in the laboratory as $BaSO_4$, filtered, dried, and reacted with BrF_5 to produce CO_2 for $\delta^{18}O$ analysis (Clayton and Mayeda, 1963) on a Finnigan 252 isotope ratio mass spectrometer. $\delta^{18}O$ error is estimated to be ±1‰. A split of each $BaSO_4$ precipitate

was analyzed for $\delta^{34}S$ using an automated elemental analyzer interfaced to a Micromass Optima isotope ratio mass spectrometer. $\delta^{34}S$ error is estimated to be ±0.2‰.

Results and Discussion

General results

Results of field analyses were given in Table 1. Ferrous iron determinations are shown in Table 2 for a subset of the samples collected. Anion results by ion chromatography (except sulfate) are shown in Table 3. Cation analyses were performed by ICP/AES on the same subset of samples for which ferrous analyses were performed. Those results are shown in Table 4. Cation analyses for the full suite of samples are shown in Table 5. Rare earth element analyses for the ferrous-iron subset are shown in Table 6. Results for stable isotopic analyses are shown in Table 7.

Data Quality

The primary test of the overall quality of the chemical data is indicated by the charge balance calculations, which are shown in Table 8. In all cases, charge balances are within ±8%. The analyses that contribute to the overall charge balances include, field (pH) and laboratory (anions by IC, cations plus sulfate by ICP/AES) methods. The results of cation-anion balances are in excellent agreement, indicating that the analytical results are reliable.

A second test of data quality is found in running field and laboratory blanks, using deionized or distilled water. A field blank was prepared using distilled water that was carried to a field site and treated as though it were a sample. Field-blank samples were run for anions (by IC) and cations (by ICP/MS) and in both cases, showed below-detection values for all components. This result demonstrates that the likelihood of sample contamination is very low.

A third test of data quality is given by running standards as though they are samples, and comparing the analytical results with most probable values given for the standards. For the IC, ICP/MS, and ICP/AES, at least 10% of the analyses were performed on standards run as unknowns. This test allows a check of analytical precision and accuracy through the data set. In addition, a minimum of 10% sample duplicates was run for the IC and ICP/AES as a further check of analytical precision.

Table 2- Summary of analytical results for ferrous and total iron. Sampling, preservation, and analytical methods are described above. All concentrations are given in milligrams per liter (mg/L). The Fe^{2+}/Fe^{tot} ratio is dimensionless.

	Fe^{2+}	total Fe	Fe^{2+}/Fe^{tot}
	(colorimetric)	(ICP/AES)	
97AZ-1	0.26	0.74	35%
97AZ-2	0.18	3.1	5.8%
97AZ-3	130	130	99%
97AZ-4	21	93	22%
97AZ-5	0.94	11	8.5%
97AZ-6	0.31	6.0	5.2%
97AZ-7	0.38	1.0	38%
97AZ-8	0.02	1.5	1.3%
97AZ-10	210	240	88%
97AZ-11	1.5	47	3.2%
97AZ-17	0.67	1.3	54%

Table 3- Results of anion analyses by ion chromatography (IC). Sampling, preservation, and analytical methods are described in the text. Nitrate is give as milligrams per liter as NO_3. To convert to milligrams per liter as N, multiply the result given by 0.23. A dash indicates no detectable quantity.

Sample Number	F mg/L	Cl mg/L	Br mg/L	NO_3 mg/L as NO_3
97AZ-1	0.35	4.7	-	-
97AZ-2	0.15	9.9	0.4	-
97AZ-3	1.8	10.	-	-
97AZ-4	2.0	13	-	-
97AZ-5	0.95	16.	0.2	-
97AZ-6	0.85	16.	0.1	-
97AZ-7	1.1	17.	0.2	-
97AZ-8	0.2	9.9	0.7	-
97AZ-9	0.33	13.	0.68	2.2
97AZ-10	0.33	22.	0.5	-
97AZ-11	0.6	14.	0.3	-
97AZ-12	0.61	7.4	-	-
97AZ-13	0.21	5	-	-
97AZ-14	0.83	17	0.6	0.6
97AZ-15	1	17	0.1	-
97AZ-16	2.1	17	0.1	-
97AZ-17	2.2	18.	0.2	-

Table 4- Results of cation analyses by ICP/AES. Values are given in the units indicated in each column. The following elements were reported as being below the lower limit of detection for all samples: Ag, Cr (< 10 µg/L); Mo (< 20 µg/L); and As, P, and Sb (all < 100 µg/L).

Field No	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	SO$_4$ mg/L	Si mg/L	Fe mg/L
97AZ-1	5.7	3.0	4.3	1.9	110	13.	0.74
97AZ-2	12.	9.8	8.5	3.0	680	29.	3.1
97AZ-3	170	100	11.	27.	1700	40.	140
97AZ-4	180	110	12.	24.	1700	40.	93.
97AZ-5	380	210	40.	7.3	2500	35.	11.
97AZ-6	390	210	40.	6.3	2500	35.	6.0
97AZ-7	400	200	41.	5.1	2500	34.	1.0
97AZ-8	15	8.5	22.	11.	730	49.	1.5
97AZ-10	260	130	60.	7.2	2500	37.	240
97AZ-11	90.	48.	36.	3.5	1200	51.	47.
97AZ-17	420	180	48.	4.4	2500	31.	1.3

Field No	Li µg/L	Be µg/L	B µg/L	Al mg/L	V µg/L	Mn mg/L	Co µg/L
97AZ-1	< 10	< 10	18.	12.	< 10	.33	26.
97AZ-2	16.	< 10	15.	98.	< 10	5.2	130
97AZ-3	110	19.	24.	50.	< 10	150	360
97AZ-4	101	19.	29.	52.	< 10	160	360
97AZ-5	120	12.	31.	75.	< 10	140	260
97AZ-6	120	15.	27.	73.	< 10	140	280
97AZ-7	110	14.	24.	73.	< 10	140.	270
97AZ-8	37.	< 10	16.	83.	< 10	2.0	180
97AZ-10	88.	15.	21.	130	23.	41.	430
97AZ-11	56.	< 10	16.	84.	< 10	19.	240
97AZ-17	110	15.	22.	86.	< 10	110	280

Field No	Ni µg/L	Cu µg/L	Zn µg/L	Sr µg/L	Cd µg/L	Ba µg/L	Pb µg/L
97AZ-1	22.	510	410	24.	< 5	24.	< 50
97AZ-2	110	4,200	7,400	59.	52.	18.	< 50
97AZ-3	310	96.	48,000	42.	29.	12.	< 50
97AZ-4	320	110	49,000	44.	29.	11.	< 50
97AZ-5	380	2,300	69,000	430	220	7.2	< 50
97AZ-6	370	2,300	70,000	440	220	14.	170
97AZ-7	360	2,600	68,000	460	230	11.	250
97AZ-8	91.	77,000	2,900	61.	130	16.	67.
97AZ-10	290	21,000	18,000	93.	62.	9.3	< 50
97AZ-11	58.	12,000	8,000	85.	39.	9.5	< 50
97AZ-17	360	2,600	59,000	550	220	13.	< 50

Table 5- Results of cation analyses by ICP/MS. All values are shown in µg/L. The following results are not shown: Au (all <0.01 µg/L);Bi (all <0.05 µg/L); Nb (all <0.1 µg/L); Ge (all < 0.2 µg/l, except 97AZ-12, which was 1 µg/L); Sn (all <1 µg/L); Se (all < 5µg/L); Sc (all <10 µg/L); P (all < 100 µg/L);

Sample Number	Ca	Mg	Na	K	SiO$_2$	Fe	Mn
detection limit	100	5.	100	100	500	500	10.
97AZ-1	4,500	3,000	3,600	1,900	16,000	250	280
97AZ-2	9,500	9,100	7,300	3,000	34,000	2,300	4500
97AZ-3	150,000	77,000	8,700	26,000	43,000	110,000	140,000
97AZ-4	150,000	80,000	9,000	24,000	44,000	78,000	150,000
97AZ-5	370,000	170,000	32,000	7,300	38,000	9,500	130,000
97AZ-6	380,000	170,000	32,000	6,400	39,000	4,900	130,000
97AZ-7	390,000	170,000	35,000	5,500	39,000	870	130,000
97AZ-8	11,000	7,100	18,000	11,000	56,000	900	1,300
97AZ-9	14,000	11,000	24,000	12,000	57,000	700	2400
97AZ-10	240,000	100,000	48,000	7,200	39,000	210,000	37,000
97AZ-11	77,000	38,000	31,000	3,600	64,000	40,000	17,000
97AZ-12	210,000	36,000	100,000	12,000	8,000	350	380
97AZ-13	28,000	4,500	15,000	4,000	29,000	80	34
97AZ-14	430,000	200,000	40,000	5,800	32,000	160	110,000
97AZ-15	400,000	170,000	35,000	5,500	39,000	930	130,000
97AZ-16	430,000	150,000	35,000	4,100	35,000	430	110,000
97AZ-17	420,000	150,000	39,000	4,500	34,000	860	100,000

Sample Number	Li	Be	Al	Ti	V	Cr	Co
detection limit	0.30	0.20	1.0	2.	10.	10.	0.50
97AZ-1	4	<0.2	9,800	<2	<10	<10	21
97AZ-2	16	3	81,000	3	<10	<10	100
97AZ-3	99	17	37,000	<2	<10	10	280
97AZ-4	100	18	39,000	<2	<10	<10	290
97AZ-5	120	11	57,000	<2	<10	<10	230
97AZ-6	120	15	56,000	2	<10	<10	240
97AZ-7	120	14	57,000	<2	<10	<10	240
97AZ-8	38	3	64,000	<2	<10	<10	130
97AZ-9	50	6	60,000	<2	<10	<10	110
97AZ-10	88	14	97,000	<2	24	15	330
97AZ-11	59	9	69,000	2	<10	<10	200
97AZ-12	260	<0.2	3	2	<10	11	<0.5
97AZ-13	53	<0.2	17	2	<10	10	<0.5
97AZ-14	99	4	36,000	<2	<10	<10	130
97AZ-15	120	14	58,000	2	<10	<10	240
97AZ-16	100	14	60,000	<2	<10	<10	230
97AZ-17	98	14	66,000	<2	<10	<10	240

Sample Number	Ni	Cu	Zn	Ga	As	Rb	Sr
detection limit	1.0	0.50	0.50	0.50	0.50	0.10	0.10
97AZ-1	19	450	350	<0.5	2.1	10	20
97AZ-2	91	3,800	5,700	1	<0.5	16	55
97AZ-3	240	100	39,000	1	0.5	170	42
97AZ-4	240	120	41,000	1	0.6	180	43
97AZ-5	290	1,900	57,000	1	6.5	44	430
97AZ-6	290	1,900	58,000	1	0.8	36	450
97AZ-7	290	2,300	58,000	1	<0.5	21	500
97AZ-8	63	140,000	1,600	<0.5	<0.5	44	52
97AZ-9	69	90,000	1,700	<0.5	<0.5	58	49
97AZ-10	230	21,000	13,000	3	1.6	87	91
97AZ-11	41	12,000	6,100	1	0.7	40	81
97AZ-12	<1	1	2	<0.5	61.	43	650
97AZ-13	1	2	20	<0.5	8.9	7	94
97AZ-14	260	1,800	58,000	1	<0.5	18	640
97AZ-15	300	2,300	59,000	1	<0.5	20	500
97AZ-16	270	2,100	53,000	1	<0.5	11	600
97AZ-17	280	2,100	50,000	1	<0.5	12	580

Sample Number	Zr	Mo	Ag	Cd	In	Sb	Te
detection limit	0.10	0.10	0.05	0.10	0.05	0.05	0.5
97AZ-1	<0.10	<0.10	0.05	2.8	<0.05	0.12	<0.5
97AZ-2	0.9	<0.10	<0.05	47.	0.33	0.22	<0.5
97AZ-3	<0.10	<0.10	<0.05	28.	<0.05	0.58	<0.5
97AZ-4	<0.10	<0.10	<0.05	30.	<0.05	0.36	<0.5
97AZ-5	0.1	<0.10	0.11	210	0.06	1.5	<0.5
97AZ-6	0.1	<0.10	0.35	220	0.08	1.7	<0.5
97AZ-7	0.1	<0.10	0.25	220	0.09	1.4	<0.5
97AZ-8	1.2	<0.10	<0.05	110	0.09	0.13	<0.5
97AZ-9	0.6	<0.10	<0.05	52.	0.07	0.08	<0.5
97AZ-10	0.2	<0.10	0.05	60.	0.45	0.40	2.0
97AZ-11	0.3	<0.10	<0.05	37.	0.18	0.16	<0.5
97AZ-12	<0.10	2.4	<0.05	<0.1	<0.05	0.86	<0.5
97AZ-13	<0.10	0.3	0.12	0.2	<0.05	0.38	<0.5
97AZ-14	0.1	<0.10	0.10	220	<0.05	0.25	<0.5
97AZ-15	0.1	<0.10	0.21	230	0.10	1.4	<0.5
97AZ-16	0.2	<0.10	0.18	220	<0.05	0.30	<0.5
97AZ-17	0.2	<0.10	0.15	210	<0.05	0.30	<0.5

Sample Number	Cs	Ba	Ta	W	Re	Tl	Pb
detection limit	0.05	0.05	0.05	0.05	0.05	0.10	0.05
97AZ-1	0.34	9.1	<0.05	<0.05	0.29	0.39	2.1
97AZ-2	0.36	6.4	0.09	<0.05	0.72	0.19	0.26
97AZ-3	7.7	0.63	0.22	<0.05	0.34	0.46	8.7
97AZ-4	8.3	0.45	0.21	<0.05	0.34	0.46	14.
97AZ-5	1.5	1.2	0.34	<0.05	0.53	0.25	42.
97AZ-6	1.1	1.9	0.22	<0.05	0.54	0.24	210
97AZ-7	0.41	4.3	0.30	<0.05	0.55	0.20	270
97AZ-8	2.2	5.6	0.09	0.18	1.9	0.44	0.47
97AZ-9	3.0	4.5	0.07	0.06	0.93	0.58	0.32
97AZ-10	6.9	0.06	0.43	<0.05	1.1	1.9	0.40
97AZ-11	3.4	0.21	0.14	<0.05	0.19	0.51	1.2
97AZ-12	24.	7.8	0.09	30.	<0.05	<0.1	0.17
97AZ-13	1.2	36.	<0.05	<0.05	<0.05	<0.1	0.49
97AZ-14	0.13	5.1	0.15	<0.05	0.49	0.14	61.
97AZ-15	0.39	4.1	0.20	<0.05	0.58	0.22	260
97AZ-16	1.1	5.0	0.17	<0.05	0.69	<0.1	16.
97AZ-17	0.60	4.4	0.15	<0.05	0.64	0.11	18.

Sample Number	Th	U
detection limit	0.05	0.02
97AZ-1	<0.05	2.0
97AZ-2	1.9	10.
97AZ-3	0.09	8.6
97AZ-4	0.10	8.9
97AZ-5	0.10	11.
97AZ-6	0.21	12.
97AZ-7	0.15	11.
97AZ-8	30.	69.
97AZ-9	13.	59.
97AZ-10	6.7	67.
97AZ-11	7.6	52.
97AZ-12	<0.05	3.9
97AZ-13	<0.05	0.13
97AZ-14	0.05	3.6
97AZ-15	0.14	11.
97AZ-16	0.08	9.4
97AZ-17	0.11	8.7

Table 6- Results of analyses of rare earth elements and yttrium, lanthanum, and hafnium by
ICP/MS. All values are given in µg/L.

Sample Number	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
detection limit	0.10	0.05	0.05	0.05	0.05	0.05	0.05	0.05
97AZ-1	4.9	0.26	1.4	0.34	1.8	0.46	0.13	0.62
97AZ-2	24.	9.3	26.	3.7	16.	3.6	1.0	4.1
97AZ-3	120	13.	59.	13.	71.	21.	5.8	26.
97AZ-4	120	14.	61.	14.	73.	21.	6.2	27.
97AZ-5	150	40.	130	22.	110	27.	7.4	32.
97AZ-6	150	42.	130	22.	110	27.	7.4	31.
97AZ-7	150	49.	140	23.	110	27.	7.3	31.
97AZ-8	51.	32.	79.	10.	39.	9.3	1.1	9.6
97AZ-9	67.	32.	85.	12.	47.	12.	1.4	13.
97AZ-10	190	17.	72.	15.	79.	23.	5.8	30.
97AZ-11	130	34.	100	16.	69.	18.	3.0	20.
97AZ-12	<0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
97AZ-13	<0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
97AZ-14	99.	32.	81.	12.	52.	13.	3.5	16.
97AZ-15	160	48.	140.	23.	110	27.	7.3	31.
97AZ-16	190	99.	260.	37.	160	37.	9.5	40.
97AZ-17	200	96	260.	37.	160	38.	9.7	41.

Sample Number	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf
detection limit	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
97AZ-1	0.13	0.87	0.16	0.50	0.06	0.41	0.06	<0.05
97AZ-2	0.69	4.3	0.76	2.1	0.30	1.8	0.25	<0.05
97AZ-3	3.9	21.	3.9	10.	1.3	7.1	0.94	<0.05
97AZ-4	4.0	22.	4.1	11.	1.3	7.3	0.95	<0.05
97AZ-5	4.8	27.	4.8	13.	1.6	8.8	1.1	<0.05
97AZ-6	4.8	27.	4.9	13.	1.6	8.8	1.1	<0.05
97AZ-7	4.8	27.	4.8	13.	1.6	8.7	1.1	<0.05
97AZ-8	1.7	10.	1.9	5.5	0.79	4.9	0.69	<0.05
97AZ-9	2.2	13.	2.4	6.8	1.0	6.3	0.91	<0.05
97AZ-10	5.2	32.	6.0	17.	2.4	14.	2.0	<0.05
97AZ-11	3.4	21.	4.1	13.	1.8	12.	1.8	<0.05
97AZ-12	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
97AZ-13	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
97AZ-14	2.7	15.	2.8	7.4	0.91	4.9	0.64	<0.05
97AZ-15	4.9	27.	4.9	13.	1.6	8.7	1.2	<0.05
97AZ-16	6.1	34.	5.9	15.	1.9	10.	1.3	<0.05
97AZ-17	6.	35.	6.2	16.	2.0	11.	1.3	<0.05

Table 7- Results of isotopic analyses of water samples. $\delta^{18}O$ and δD are reported in permil deviation relative to standard mean ocean water (SMOW); $\delta^{34}S$ is reported in permil deviation from Cañon Diablo troilite (CDT).

Sample No.	$\delta^{18}O$ in H_2O	δD in H_2O	$\delta^{18}O$ in SO_4	$\delta^{34}S$ in SO_4
97AZ-1	-8.5	-59.4		
97AZ-2	-8.1	-56.6	2.3	-6.2
97AZ-3	-8.9	-62.2	1.3	-5.2
97AZ-4	-4.5	-58.2	-1.0	-3.7
97AZ-5		-52	-0.4	-4.0
97AZ-6	-6.92	-50.4	0.0	-3.5
97AZ-7		-49.7	0.4	-3.5
97AZ-8		-55	-0.4	-3.3
97AZ-9		-64.2	0.3	-3.3
97AZ-10	-9.14	-59.3	0.9	-4.0
97AZ-11	-8.83	-64.6	1.2	-6.9
97AZ-12		-73.8	1.7	-1.3
97AZ-13	-8.32	-56.3	9.2	-2.4
97AZ-14	-7.53	-54	0.5	-2.8
97AZ-15	-6.81	-51.4	-0.2	-3.3
97AZ-16		-51.1	-0.2	-3.4
97AZ-17		-48.1	0.1	-3.1

Chemical character of the waters:

    The general chemical character of the waters can be depicted by a number of methods, including Piper diagrams, Durov plots, etc. (cf. Freeze and Cherry, 1979; Domenico and Schwartz, 1998). The data from Tables 3 and 4 are shown in a Piper diagram in figure 3. As seen in the figure, the cation composition of the waters ranges from Ca-dominated through a mix of Ca-Mg-Na+K dominated. The anion compositions, on the other hand, are nearly always sulfate dominated. The cation composition most likely varies as a result of the differences in the chemistry of the rocks with which the waters come into contact. The sulfate-dominated waters result from the oxidation of pyrite in the rocks, which produces sulfate.

    Stable isotope data indicate that all of the sampled waters are of meteoric origin. The waters from Alum Gulch, downstream from the World's Fair mine drainage, are somewhat evaporated, as indicated by δD and $\delta^{18}O$ enrichment. Sulfur isotope data for dissolved sulfate in mine drainage waters vary in $\delta^{34}S_{SO4}$ from −6.9 to −2.8‰. These values are similar to $\delta^{34}S$ values of primary sulfides in nearby ore deposits (Shanks and Lichte, 1996). Oxygen isotopes values of sulfate in mine drainage waters have $\delta^{18}O_{SO4}$ from −1.0 to 2.3‰, about 8-10‰ enriched relative to local meteoric water $\delta^{18}O$. These values would indicate isotopic equilibrium exchange between SO_4 and H_2O at a temperature of about 200ºC (Mizutani and Rafter, 1969), which is unrealistically high. More likely dissolved SO_4 that forms as a result of bacterial sulfide mineral oxidation in mine tailing and working has incorporated some atmospheric oxygen, as demonstrated experimentally by Krouse et al. (1991).

Conclusions

    Chemical analyses are presented for surface-water samples collected in 1997 in the Patagonia Mountains of southern Arizona. A full suite of inorganic chemical constituents is presented in this report. Data quality is assured by a variety of methods, which are oriented towards assuring accuracy and precision of the analytical results.

    Typical of acid mine drainage waters, the samples reported on here have low pH, and high concentrations of sulfate and metals. In most cases, sulfate constitutes >95% of the total anion composition, but the cation character of the samples is more variable. In some cases, pH is sufficiently low that hydronium ion (H_3O^+) figures significantly into the anion-cation charge balance.

    Oxygen and hydrogen isotopes indicate that mine drainage exiting underground workings is meteoric water and becomes somewhat evaporated as it moves downstream significant distances in drainages. Sulfur and oxygen isotope values of sulfate in mine drainage waters indicate sulfur is derived from sulfides and some atmospheric oxygen may be incorporated.
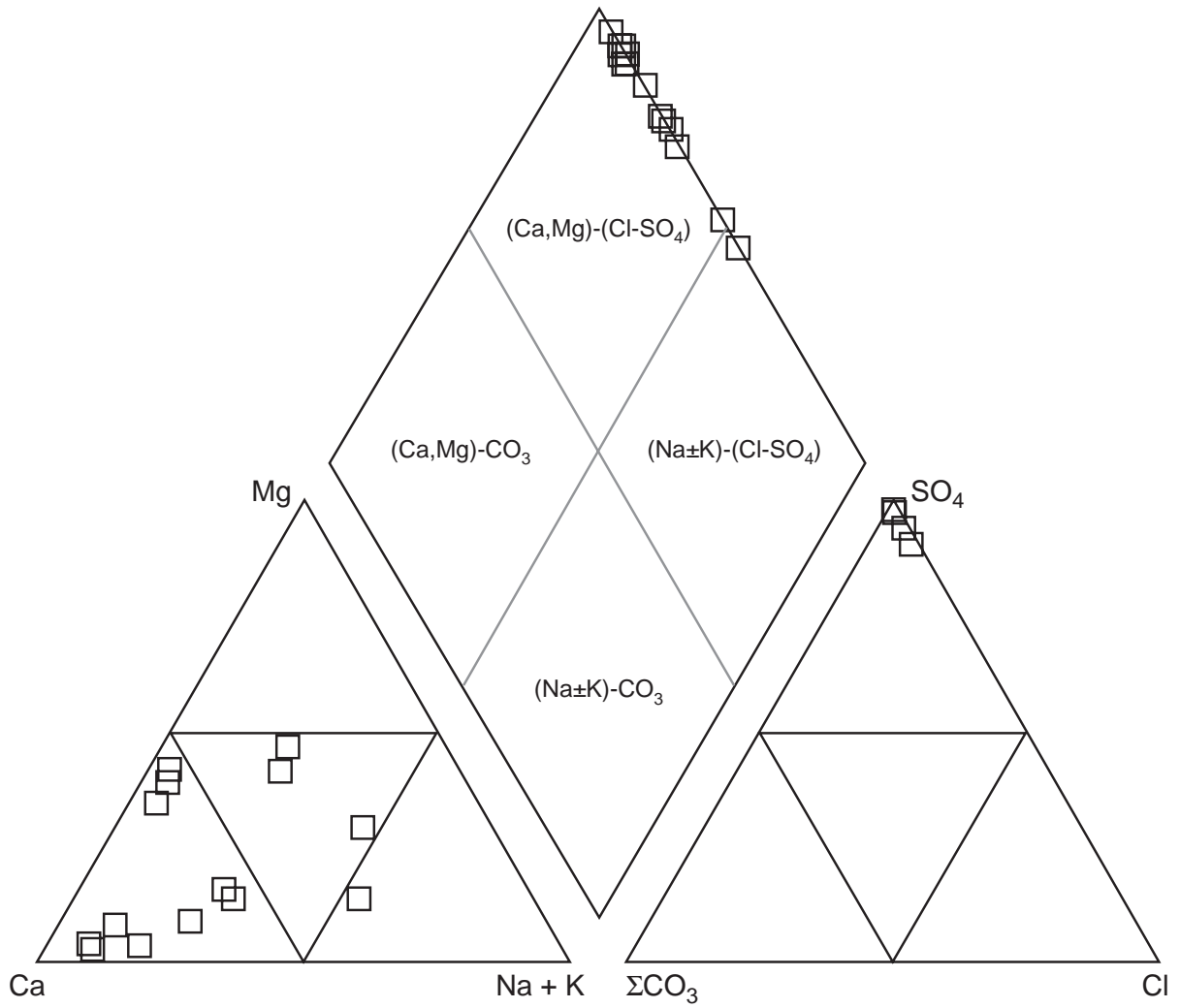
Figure 3- Piper plot for the water samples collected in the Patagonia Mountains study area.

References Cited

Briggs, P.H. and Fey, D.L., 1996, Twenty-four elements in natural and acid mine waters by inductively coupled plasma-atomic emission spectrometry, *in* Arbogast, B.F., ed., Analytical methods manual for the Mineral Resource Program, U.S. Geological Survey: U.S. Geological Survey Open-File Report 96-525, p.95-101.

Clayton, R.N., and Mayeda, T.K., 1963, The use of bromine pentafluoride in the extraction of oxygen in oxides and silicates for isotopic analysis.: Geochim. Cosmochim. Acta, v. 27, p. 43-52.

Clesceri, L.S., Greenberg, A.E., Eaton, A.D., eds., 1998, Standard Methods for the Examination of Water and Wastewater (20th ed.): Washington, D.C., American Public Health Association.

Coleman, M.L., Shepherd, T.J., Durham, J.J., Rouse, J.E., and Moore, G.R., 1982, Reduction of water with zinc for hydrogen isotope analysis: Analytical Chemistry, v. 54, no. 6, p. 993-995.

Domenico, P.A., Schwartz, F.W., 1998, Physical and Chemical Hydrogeology (2nd ed.): New York, John Wiley and Sons, Inc., 506 p.

Ficklin, W.H., and Mosier, E.L., 1999, Field methods for sampling and analysis of environmental samples for unstable and selected stable constituents, *in* Plumlee, G.S., and Logsdon, M.J., The Environmental Geochemistry of Mineral Deposits: Reviews in Economic Geology, Volume 6A, Society of Economic Geologists, Littleton, Colorado, pp. 249-264.

Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, Prentice-Hall, Inc., 604 pp.

Krouse, H.R., Gould, W.D., McCready, R.G.L., and Rajan, S., 1991, (18)O incorporation into sulphate during the bacterial oxidation of sulphide minerals and the potential for oxygen isotope exchange between O2, H2O and oxidized sulphur intermediates: Earth and Planetary Science Letters, v. 107, no. 1, p. 90-94.

Lamothe, P.J., Meier, A.L., and Wilson, S., 1999, The determination of forty-four elements in aqueous samples by inductively coupled plasma- mass spectrometry, U.S. Geological Survey Open-File Report 99-151, 14 p.

Mizutani, Y., and Rafter, T.A., 1969, Oxygen isotopic composition of sulphates; part 3, Oxygen isotopic fractionation in the bisulphate ion-water system: N.z. J. Sci., v. 12, no. 1, p. 54-59.

Schrader, F.C., 1915, Mineral deposits of the Santa Rita and Patagonia mountains, Arizona,, with contributions by J.M. Hill: U.S. Geological Survey Bulletin 582, 373 pp.

Shanks, W.C. III and Lichte, F.E., 1996, Trace element and stable isotope geochemistry of environmental minerals and acid rock drainage: Patagonia Mountains, Arizona: Geological Society of America, Annual Meeting, Abstracts with Program.