

Similarities in hydrogeochemical processes between ore deposition formation and acid mine drainage. Example near a porphyry copper mine

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Abstract

Acid Rock Drainage (ARD), or Acid Mine Drainage, is a naturally occurring process often accelerated by mining activity. ARD may be misinterpreted as mining related, when in fact, it relates to natural hydrogeochemical processes associated with existing mineral deposits or mineralization under formation. An example of these processes occurs at Gold Gulch in the western part of the Morenci Mining District, Arizona. This area is characterized by low pH springs and manganocrete (manganese oxide precipitates) formation.

Manganocrete, a conglomerate consisting primarily of manganese and iron oxide/hydroxide precipitates cementing alluvial material, is actively forming from spring water in the bottom of Gold Gulch. The existence of this process is demonstrated by older manganocrete deposits existing on the hillsides above Gold Gulch. The element composition of the spring water indicates that the source of metals is from the nearby undisturbed bedrock and not from the mine related development stockpile. Geochemical modeling of the spring water and the similarity in chemistry between the actively forming manganocrete and the older manganocrete indicate that the spring water quality has been consistent for a long period and has not been affected by Morenci mining activity.

1 Introduction to ore formation processes

ARD processes are essential in the formation of several types of ore deposits, particularly supergene enrichment of porphyry copper deposits, where chalcopyrite and pyrite oxidation form an acidic environment allowing for copper transport downward or outward (Evens, 1992; Chavez, 2000). Primary mineralization occurs during emplacement and cooling of an intrusion which may range in geochemical composition from monzonitic to granitic. This primary (or hypogene) mineralization, near the core of the intrusion, will contain chalcopyrite/molybdenite/pyrite +/- bornite. Base metal skarn or vein

deposits containing galena, sphalerite, chalcopyrite and pyrite, may form in the surrounding rocks. Manganese oxide (+/- pyrite) veins and veinlets may occur further away from the source rock. This zonation is due to the mobility difference of the metals, primarily in response to changing temperature and pH.

Fluctuations in the water table expose the sulfide mineralization to unsaturated, oxidizing conditions, resulting in sulfide oxidation, acid generation, and release of metals. Depending upon water chemistry and mineralogy, released elements may re-precipitate *in-situ* or be transported. If the iron-copper sulfide mineralization is oxidized *in-situ* (due to neutralization or lack of acid generation), copper minerals like chrysocolla, tenorite, malachite, azurite, and brochantite will be present. Precipitation of chalcocite/covellite and enrichment of copper at the water table in a reducing environment indicates transportation of copper.

If transport becomes more distal from the deposit, the copper precipitation may occur together with manganese oxide precipitation as seen at Mine Sur, Excotica, Chile and El Abra, Chile (Chavez, 2000).

2 Site characterisation

Gold Gulch, located on the outskirts of the Morenci Mine, Arizona, is an example of transported copper and manganese mineral precipitation, where these processes are currently occurring from springs with low pH and high TDS.

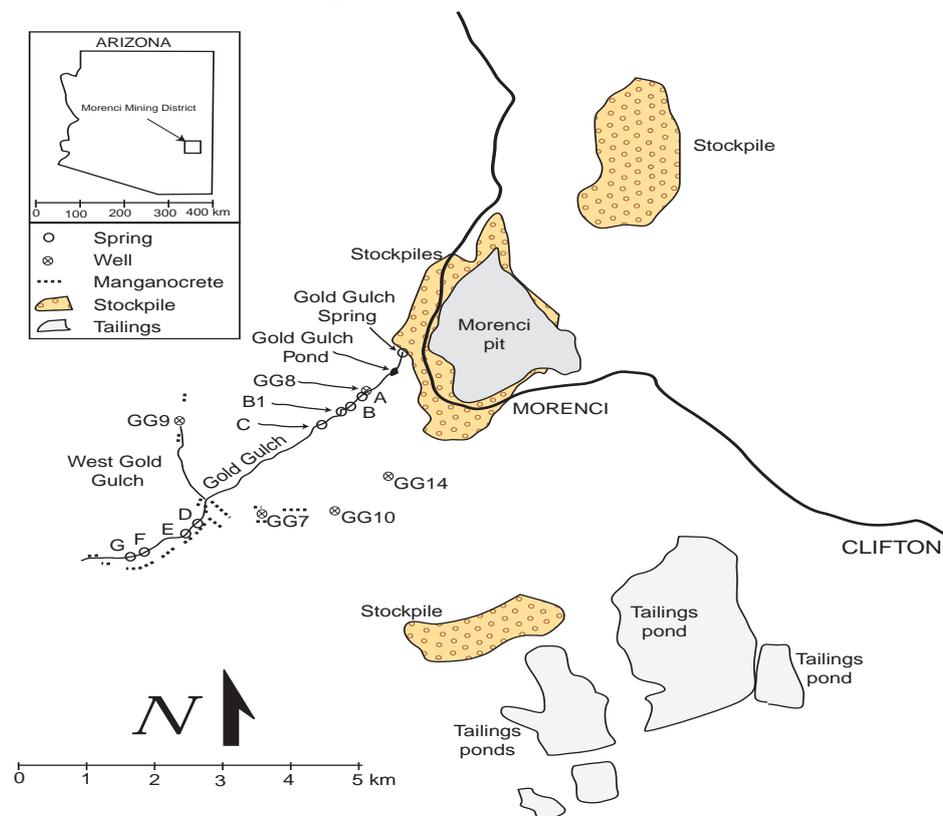
Gold Gulch is located in the western part of the Morenci Mining District. Upgradient of Gold Gulch is the Producer Stockpile, a development rock stockpile constructed in the 1940s during the opening of the Morenci Pit (Fig. 2). At the base of the stockpile is a collection impoundment (GGI) containing water with low pH and high metal concentrations, derived from storm-water runoff and Gold Gulch Spring (GGS) discharging from the base of the stockpile. Downgradient of the impoundment are another eight springs also with low pH and high metal concentrations. Detailed geologic mapping, spring water and groundwater sampling and analysis, manganocrete mapping, sequential extraction analysis, and geochemical modeling were performed to evaluate the source(s) of the poor quality water in the Gold Gulch springs.

Bedrock in the study area is composed of Precambrian granodiorite basement overlaid by a highly faulted section of Paleozoic to Cretaceous sedimentary units. These rocks were intruded by Eocene monzonite and quartz monzonite porphyries related to the Morenci mineralization. Alteration in the Gold Gulch area is dominated by propylitic assemblages cut by local phyllic veining. Quartz-sulfide and manganese oxide veins crosscut the intrusive rocks. Quaternary alluvial deposits consisting of unconsolidated sand and gravel are located along the hillsides and in the bottom of Gold Gulch

2 Results and Discussion

2.1 Spring Water Quality

Springs A, B and C closest downstream from GGI show a similar major ion chemistry to one another (Appendix) while springs D, F, and G (located further downstream) show more variation and have higher sulfate content. Spring E falls outside these two groups.



Discharge from GGI and GGS are similar in major ion chemistry and are most similar to the three most distal downgradient springs (D, F, and G).

Magnesium, aluminum, zinc, cadmium, iron, nickel, manganese, copper, silica, sulfate and hydrogen ion concentrations are lower in the upper springs, A, B and C, relative to GGI (Fig. 2). Sodium, calcium, chloride, and bicarbonate ion concentrations are higher in the upper springs compared with GGI (Table 1).

The lower springs, however, have higher nickel, manganese, zinc, and magnesium concentrations (Table 1), and lower chloride and potassium concentrations, than GGI. Sodium concentrations and pH values in the lower springs lie between the upper springs and GGI concentrations. Copper, iron, calcium, and alkalinity values are similar for the upper and lower springs, while sulfate, sodium and silica concentrations are similar for the lower springs and GGI.

	Higher	Equal	Lower
Upper Springs	Mg, Al, Zn, Cd, Fe, Ni, Mn, SO ₄ , H ⁺	SO ₄ , Na, Si	Ni, Mn, Zn, Mg, Ca, Alk
Lower Springs	Ni, Mn, Zn, Mg, Cu, Fe		Cl, K, Ca, Alk

Table 1. Upper Springs and Lower Springs concentrations relative for Gold Gulch Impoundment.

The pH relative to the concentrations of total dissolved solids (TDS), sodium, calcium, sulfate, copper, manganese, fluoride, and aluminum, have been plotted to evaluate relations between the water qualities (Figure 2). A distinct spread in the data is evident, with pH vs. species concentration for GGS (Spring) and GGI (pond) very similar. Spring G plots relatively close to GGI and GGS, but is clearly different for TDS, copper and manganese.

The pH vs. species concentration data from springs A, B, and B1 show many similarities and are primarily clustered together. Spring C data are clustered together with data for springs A, B, and B1, while springs E, F, and G show fewer overlapping data with springs A, B, and B1.

2.2 Groundwater Quality

Groundwater (as seen in the spring waters) is dominated by calcium and sulfate and to lesser extent magnesium (Appendix). Sulfate concentrations and TDS are generally higher in the southern part of Gold Gulch (downgradient, wells GG7, 10 and 14), 2200-3100 mg/l TDS and 1200-2000 mg/l SO₄, respectively, than in the northern part (upgradient, wells GG8 and 9), 600-800 mg/l TDS and 330-440 mg/l SO₄, respectively. All wells analyzed have a pH around 7 (6.8-7.4). Manganese is detected in all monitoring wells in the Gold Gulch in the range of 0.4-2.0 mg/l, where wells GG8 and 9 are in the lower range.

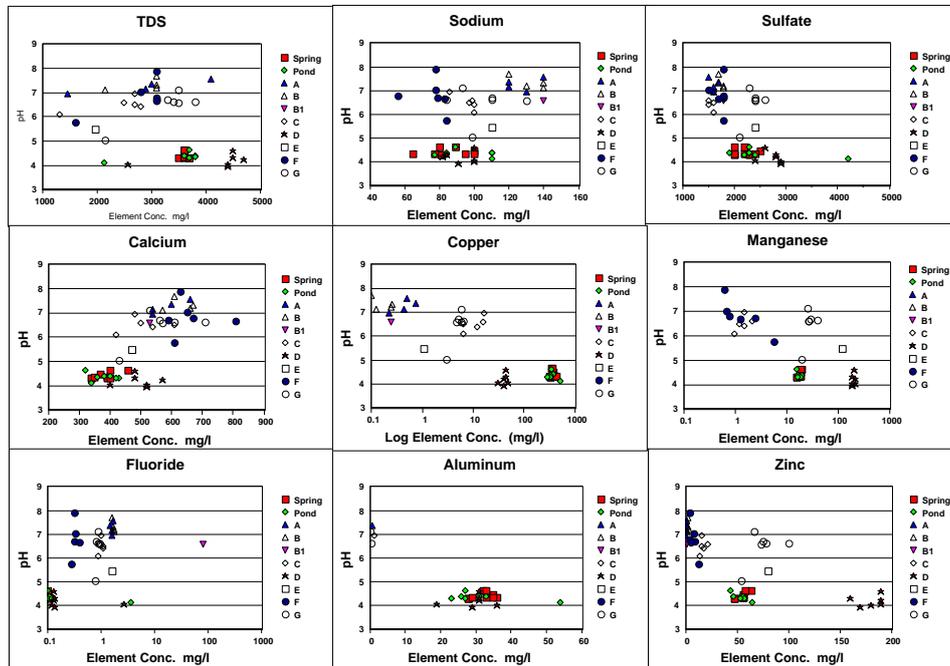


Figure 2. Element concentrations in spring water and GGI plotted versus pH.

2.3 Manganese Mineralization

Manganese mineralization within the Gold Gulch area has been mapped and consists of: primary hydrothermal manganiferous veins and skarns; fracture coatings with thin film of MnOx; and black agglomerates of sand and gravel material cemented together with iron and manganese oxide minerals - manganocrete (Lee and Herdrick, 2002). The chemistry and mineralogy of the manganese mineralization are discussed in the following few paragraphs.

2.3.1 Veins and Fractures

Vein and skarn mineralization is found throughout the study area. The veins are found in the quartz-sericite alteration zone and consist of quartz, MnOx, pyrite and minor concentrations of chalcopyrite, galena and sphalerite. The skarn mineralization contains garnet epidote and magnetite as gangue minerals, in addition to, the sulfides and MnOx. The chemical analysis of the veins and skarn show (as expected) high metals concentration.

Fracture mineralization consists of greenish-black neotocite associated with variable amounts of jarosite, goethite, and hematite. The host rocks have commonly been subjected to phyllic alteration consisting of quartz-sericite-pyrite with or without other sulfides. Fracture coatings, containing high

concentrations of base and precious metals, are chemically similar to the vein and skarn mineralization.

2.3.1 Manganocrete Chemistry

Manganocrete is found in the bottom of Gold Gulch associated with the springs and on the hillsides of Gold Gulch. Some of the lenses have partly been eroded. Bulk manganocrete chemistry is similar to the vein and fracture mineralization, but with lower lead content.

The manganocrete was analyzed using sequential extraction with seven steps (Dold, 1999) with the following first four steps related to the manganocrete mineralization: 1) water soluble extraction; 2) sorption extraction from oxides and clay minerals; 3) dissolution of iron oxy- hydroxides and manganese oxides, secondary jarosite and schwertmannite; and 4) extraction of iron oxides like goethite, jarosite, Na-jarosite,

Extr. Step	Major	Minor but distinct	Minor	Trace
1	None	None	Mg, Ca	Sr, Mo, Mn, Zn, Ni, K
2	Cu, Zn, W, Cu	Cd, Ni, Y	Be, Sr, Mn	Mg, Cr, La, K
3	Mn, Cu, Ni, Zn, Mo, P, Y, Co, Cd, Pb, La, As, W, Ag	Cr, Li	Fe, Sr	Al
4	Fe, Pb, As, P	Cr, Cd, Ba	Sr, Mn, La, Mg, V, Y, Ba	Cu, Ni, Zn, Mo, Al
5	None	None	Mg, Cr	Fe, Sr, Al
6	Sn, La, Ag, Mg	Pb, Sr, Fe, P	Cr, V, Y	Al, Ni, Cd, Zn, Cu
7	Na, Al, K, Ti, Bi, V, Sc, Zr, Li, Mg, Be, Sr, Cr	Ag, Y, Pb, Fe, La, Ba	None	Ca, Ni, Cu, Zn

Table 2. Summary of the seven step sequential extraction result. The categories major, minor but distinct, minor and trace are based on a visible distinction from the graphs without a fixed concentration grouping.

hematite, magnetite and higher order ferrihydrite. As expected, only a few of the 32 analyzed elements showed any leaching in the first step (Table 2). The majority of extraction occurred during steps 3 and 4. Table 2 summarizes the element extraction and Figure 4 illustrates element distribution of some of the metals.

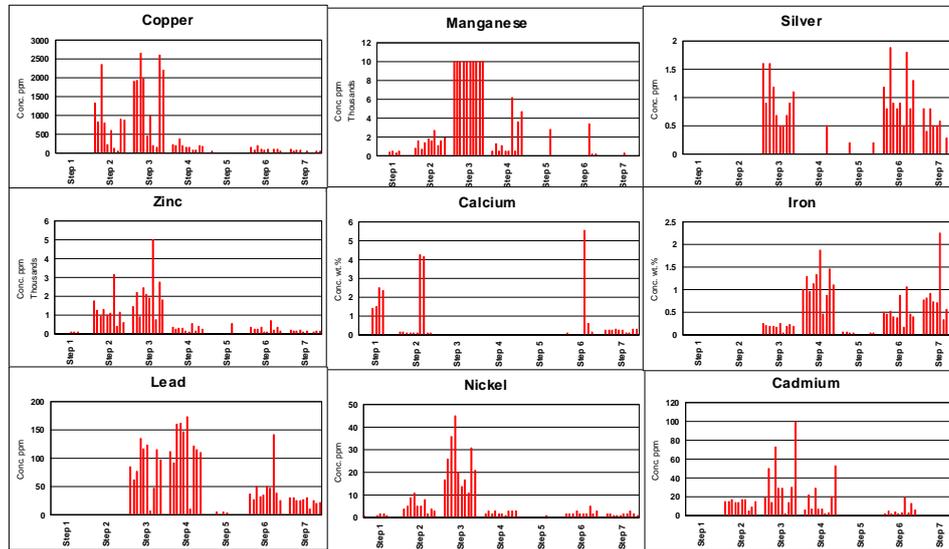


Figure 4. Sequential extraction data

3 Conclusions

The hydrochemistry of all eight springs is similar to hydrochemistry typically associated with groundwaters related to sulfide mineralization, (i.e. dominated by calcium, magnesium and sulfate), with subordinate concentrations of bicarbonate, potassium and chloride (Plumlee, 1999). Groundwater shows similar trends, however, with lower elemental concentrations.

The water in Gold Gulch forms two distinct groups of water qualities, with the GGS and the GGI in one group and Springs A, B, and B1 in the other group (Fig. 2). Many element concentrations in Spring D are similar to the first group but differ distinctly for TDS, manganese and copper. The other springs (C, E, F and G) show greater variation with no distinct grouping. The chemistry of the water indicates that GGI is primarily made up of the GGS water, with variations on a seasonal basis due to evapoconcentration and surface runoff mixing with impoundment water.

3.1 Spring Water Evaluation

Three possible scenarios were evaluated for the origin of the spring water quality along Gold Gulch from GGI and downgradient (Fig. 4): 1) GGI recharges the groundwater and thereby mixes with the groundwater. This mixed GGI and groundwater discharges in all the springs, however, with different source amounts; 2) GGI recharges the groundwater and mixes as in scenario 1. However, this mixed groundwater impoundment water discharges

in the upper three springs A, B, and B1, while the more distal springs, the Lower springs, have another groundwater source; and 3) none of the springs are influenced by GGI.

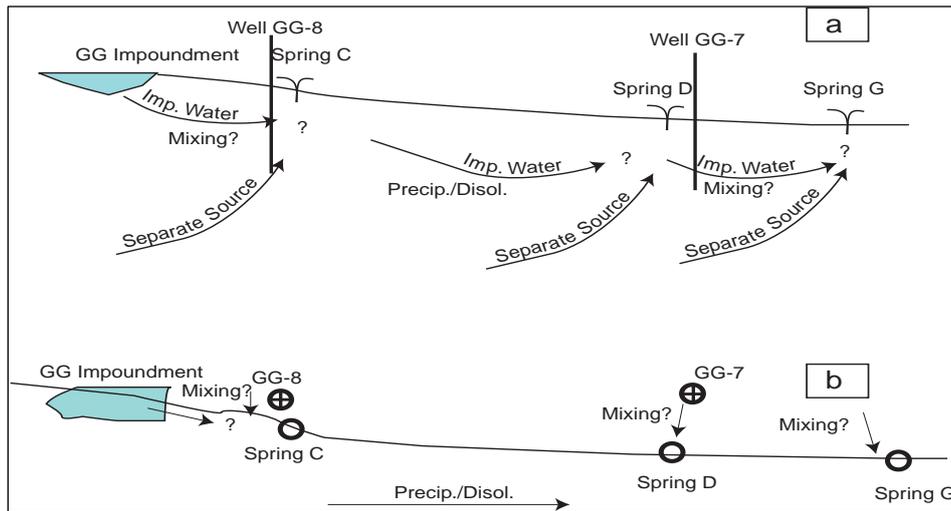


Figure 4. Illustration of possible scenarios evaluated using NETPATH with a cross section (a) and a plan view (b). GGI is used as the initial water, with possible evaporation prior to groundwater recharge.

Scenario 1

GGI mixed with groundwater from monitor well GG-8 would result in reduction of chloride, sulfate, TDS, sodium, potassium, nickel and zinc, and an increase of fluoride. Chloride and fluoride concentrations are higher in Springs A, B, and B1 than in groundwater and GGI. GGI mixed with GG-7 gives too high sulfate concentration. This suggests that straight mixing of GGI with groundwater is not possible for producing the spring water qualities.

Scenario 2

If the lower springs were geochemically connected with GGI, those springs would also show reduction in most elements while increasing in fluoride. The fluoride concentrations in springs C through G are lower than in springs A, B, and B1, but still higher than in GGS and the groundwater. Sulfate concentrations are higher in these lower springs than in the upper springs. This suggests that the spring water chemistry found in springs C through G is not produced by mixing of GGI with groundwater. Therefore, it is unlikely that this

second scenario represents the hydrochemical processes observed via water quality data.

Scenario 3

Speciation concentrations relative to pH for samples with pH above 5 (Fig. 5) have a 1:1 correlation between pH, cadmium and zinc, while the samples with lower pH (GGS, GGI and Spring D) are plotting off this 1:1 correlation. The pattern indicates zinc and cadmium are controlled by sorption for samples with pH above 5.

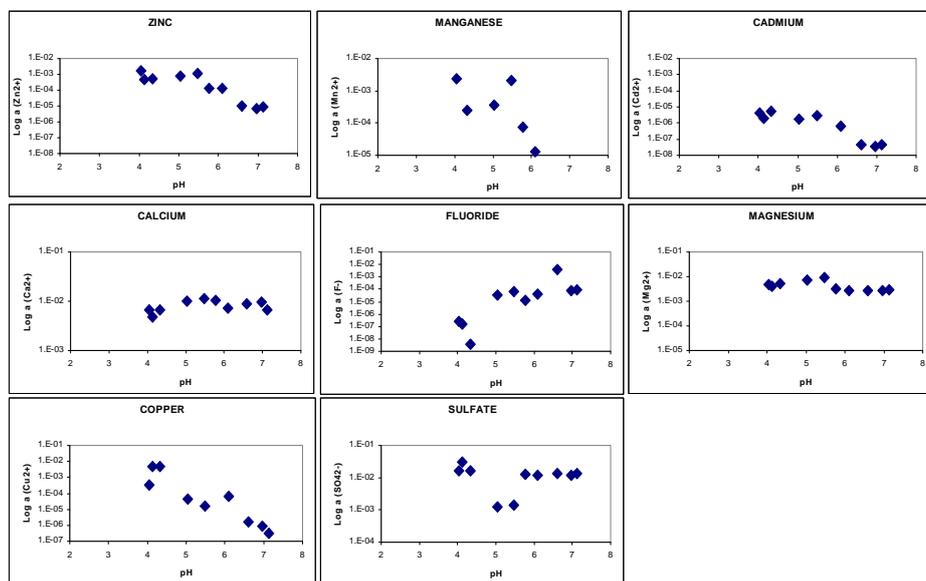


Figure 5. Speciation concentration based on element speciation calculations relative to pH. See text for explanations.

The Mn^{2+} shows a weak correlation with pH. The slope of a linear correlation is 0.7. If groundwater transports manganese as Mn^{2+} , the slope and poor correlation could be explained by a slow oxidation of Mn^{2+} to Mn^{3+} . Most of the sampled spring water is, therefore, supersaturated in manganite.

Copper, as Cu^{2+} , is negatively correlated with pH with a slope of 1.2, tenorite precipitation would give a slope of 2. It is, therefore, likely that the copper concentration is controlled by sorption.

Fluoride has a positive correlation with pH indicating that the source is the mineral fluorite (CaF_2).

The major species, Ca^{2+} , Mg^{2+} , and SO_4^{2-} , appear to be independent of pH (Fig. 5) and could be controlled by gypsum and magnesium sulfate that are near saturation for most of the springs.

Therefore, the element composition of the spring water indicates that the sources of the elements are from the nearby bedrock and not from the development rock which would affect GGI.

3.2 Manganocrete Formation

Sequential extraction and saturation index calculations of water from the springs indicate that elements are distributed in the manganocrete in the following phases, Ca, SO_4 – gypsum; K – jarosite (traces); Al - bauxite (traces); Mn – manganite/pyrolusite/nsutite; Fe - ferrihydrite (and other iron oxides and hydroxides); Cu - copper sulfate, tenorite, sorbed to manganese and iron hydroxides; and Ba, Mo, Zn, Cd, Pb, Ag – sorbed.

Manganese occurs primarily in three oxidation stages in nature: Mn(II), Mn(III) and Mn(IV) (Stumm and Morgan, 1988). In an acidic environment ($\text{pH} < 4$), Mn^{2+} may occur under both aerobic and anaerobic conditions. Nsutite/pyrolusite (Mn(IV)O_2) precipitates at $\text{pH} > 4$, under oxidizing conditions, while under less oxidizing conditions, manganite (Mn(III)OOH) is more common. Both pyrolusite and manganite have large surface areas relative to mass with large sorption capacity.

Iron occurs in nature primarily as Fe(II) and Fe(III). Iron is mobile as Fe(II) in acidic to neutral conditions. Fe(III) is dominating under oxidizing acidic ($\text{pH} < 3.5$) conditions. With $\text{pH} > 3.5$, iron oxide and hydroxide minerals are stable, making iron less mobile than manganese. Iron minerals are supersaturated in the two samples where iron was detected. However, the brown-orange water in GGI indicates suspended iron hydroxide minerals, which would result in an over-estimation of dissolved iron concentration by the analytical method.

Manganese in the lower springs can only come from a source different than the impoundment water, a source with reduced manganese. When this spring water enters the atmosphere, manganese oxidizes from two valent to three or four valent and precipitates, forming the manganocrete. Therefore, the source of the spring water quality is from oxidizing veins and skarns (generating a low pH environment) transported in fractures and discharging at the surface with manganocrete formation.

References

Allison, J.D., Brown, D.S., and Nova-Gradac, K.H., 1990: MINTEQA2, a geochemical assessment model for environmental systems: Version 3.0

- user's manual. U.S. Environmental Protection Agency, Environmental Research Lab., Athens, GA.
- Chavez, W.X., 2000: Supergene enrichment processes in porphyry copper deposits. SEG Newsletter.
- Dames and Moore, 1999: Hydrogeology and Potential Sources of Poor Quality Groundwater in the Gold Gulch Area of the Morenci Mining District: prepared by Dames & Moore for Phelps Dodge Morenci, Inc., May 7, 1999, 26 pp.
- Dold, B., 2001: A 7-step sequential extraction for geochemical studies of copper sulfide tailings. In Proceedings, Securing the Future, Intern. Conf. on Mining and Environ., Skelleftea, Sweden, 2001. pp 158-170.
- Evens, 1994: Ore Deposits.
- Lee, J. S. and Herdrick, M. A., 2002: Manganese Mineralization of the Gold Gulch Drainage Basin, Morenci Mining District, Arizona: prepared by Phelps Dodge Morenci, Inc., Geology Department, May 2002, 29 pp.
- Plumlee, G., 1999: The environmental geology of mineral deposits. In the Environmental geochemistry of mineral deposits. Rev. Econ. Geol. 6A, 71-116.
- Plummer, L.N., Prestmon, E.C. and Parkhurst, D.L., 1991: An interactive code (NETPATH) for modeling net geochemical reactions along a flow path. U.S. Geol. Serv. Water-Resource Invest. Report 91-4078.
- Stumm, W. and Morgan, 1988: Aquatic chemistry. 2nd. Edition. John Willey & Son., New York.
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	GGSPR	POND	A	B	B1	C	D	E	F	G	GG-7	GG-8
Dist. ft	0	350	1,000	1,150	1,200	1,550	3,750	3,900	4,400	4,500		
TDS	3,640	3,406	2,867	2,865		2,404	4,116	1,980	2,802	3,272	3,100	812.5
pH	4.39	4.34	7.21	7.3	6.6	6.43	4.14	5.48	6.4	5.77	6.76	7.49
Temp. C	13.54	14.62	12.98	18.5	17.3	14.52	16.76	10	12.84	17.1	18.9	20.8
Diss. Ox.		12.78	12.47	12.3	8.28	11.65	8.15	1.98	3.81	12.0		
Sodium	83.6	88.8	127.5	132	140	96.4	91.4	110	76	103	120	44.2
Potass.	13.4	13.2	13	15.2	15	14.4	4.52	7.9	2.88	11.2	9.95	6.63
Calcium	374	374	585	627	530	510	498	470	662	570	545	152
Magnes.	162	146	100	122	100	108	196	230	108	196	175	28.2
Chloride	36.2	39	126	143	84	91.4	26.6	nd	31.8	37.6	10.35	15.5
Bicarb.	17	14.2	192.5	172	150	77.8	7.4	150	248	44.6	285	137
Fluoride	0.07	0.83	1.6	1.73	84	1	0.65	1.6	0.27	0.89	0.8	0.26
Sulfate	2,180	2,680	1,600	1,750	1,800	1,560	2,760	2,400	1,780	2,360	1,950	440
Alum.	32.2	31.4	0.38	nd	nd	0.34	29.2	nd	nd	0.17	0.09	0.1
Barium	0	0.02	0.03	0.03	0.04	0.02	nd	nd	nd	0.02	0.02	0.02
Cad.	0.75	0.65	0.02	0.02	0.01	0.17	1.25	0.33	nd	0.27	nd	nd
Copper	380	368	0.48	0.19	0.25	11.62	41.2	1.1	0.03	5.24	nd	nd
Iron	nd	4.82	0.23	0.03	nd	0.27	0.04	nd	0.04	0.04	6.95	1.89
Lead											nd	.0069
Mangan.	17.8	13.85	0.03	nd	nd	1.48	202	120	2.18	28	1.6	0.4
Nickel	0.19	0.21	nd	nd	nd	0.1	0.76	0.5	0.07	0.38	nd	nd
Silica	77.8	66	30	32.75	22	51.2	77.8	34	55.2	65.4	34.5	46.5
Zinc	54.2	53.2	1.44	2.3	1.1	17.2	178	80	7.14	74.6	1.22	nd

Appendix. Average water quality values for springs along Gold Gulch, GGI, and two wells GG7 and GG8. The average non detected concentrations, using ½ of detection limit, when at least one sample is above detection limit. Otherwise, it is listed as non detected –(nd).