

# HYDROTHERMAL ALTERATION ASSEMBLAGES AS A CONTROL ON WATER CHEMISTRY, UPPER ALAMOSA RIVER, COLORADO

By

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Water draining the Iron, Alum, and Bitter Creek (IABC) basins in the headwaters of the Alamosa River, upstream from influence of the Summitville mine, is extremely degraded (pH <3; conductivity >1,900  $\mu$ S/cm) and has been since the onset of stream downcutting nearly 5 million years ago (Steven, this volume). The presence of ancient iron-oxide cemented conglomerates many meters above modern drainages is strong evidence that metal-rich, acid drainage has been occurring in these basins for thousands, if not millions, of years. These highly altered and pyritized basins are underlain by igneous and volcanic rocks that underwent extensive hypogene hydrothermal alteration 29-26 million years ago (Lipman and others, in press). Geologic and aqueous geochemical studies from IABC drainages above the Wightman Fork/Alamosa River confluence document natural contamination and show the interrelationship between specific hydrothermal alteration assemblages and local stream and spring chemistry.

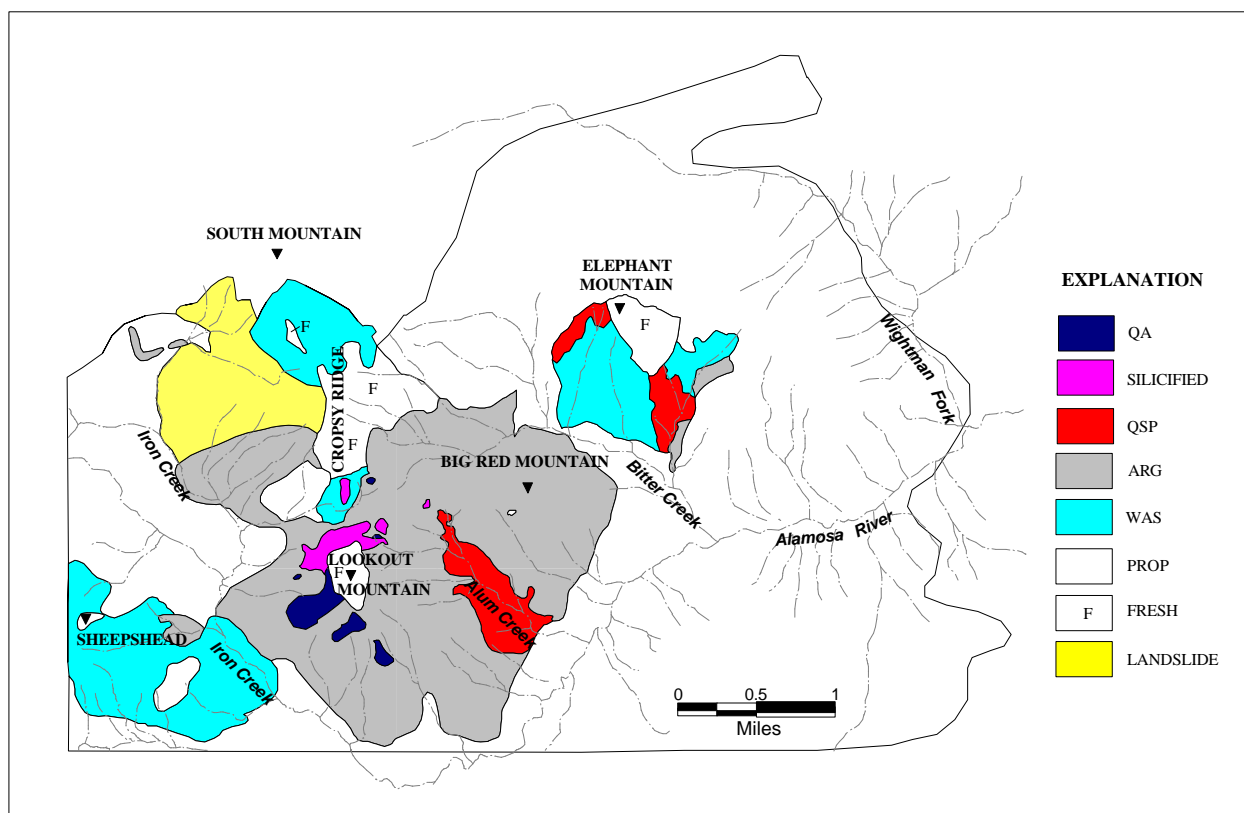
The IABC basins encompass roughly 11 km<sup>2</sup> of intensely altered and weakly mineralized rock on the northern margin of the Alamosa River stock, a large intrusive body. A later phase of this stock, the Alum Creek porphyry, is the focus of the most intense alteration in this area. A classic porphyry-style, quartz-sericite<sup>1</sup>-pyrite (QSP) alteration assemblage is centered around the Alum Creek porphyry (fig. 1) and is characterized by stockwork quartz-pyrite veinlets containing sparse molybdenite. Pyrite, which occurs ubiquitously throughout altered rocks in the IABC basins, is most prevalent in zones of quartz-sericite-pyrite alteration, where it averages about 3 to 5 volume percent of the rock.

The intensity of QSP alteration decreases outward and upward from the center in Alum Creek (fig. 1) as denoted mostly by a gradual decrease in both density of quartz-pyrite stockwork veinlets and silica flooding. Unpublished drill core data (Anaconda reference collection housed at the University of Wyoming, Laramie, Wyoming) indicate that QSP-altered rock extends several feet below the base of lower Alum Creek, with more than 70 percent of the rock containing greater than 1-2 volume percent pyrite. Several small centers of QA-altered rock crop-out on the south and western slopes of Lookout Mountain (fig. 1), nearly 600 m

above the QSP zone in Alum Creek. These QA centers grade upward into opaline ledges and siliceous sinter deposits that are remnants of an ancient hot springs environment. The QSP zones also grade laterally into weakly argillized (WAS) and finally into propylitized (PROP) assemblages. Pervasive argillic alteration (ARG), characterized by the presence of kaolinite, commonly in the absence of pyrite, is superimposed upon original QSP-altered rocks in the IABC basins (fig. 1). The argillic alteration assemblage was formed by extremely acid supergene fluids generated by the oxidation of pyrite by surface or meteoric water.

Figure 2 and table 1 depict geochemical data compiled from water sample sites affected by near end-member hydrothermal alteration assemblages. From these data it is apparent that the individual alteration assemblages produce distinctive aqueous geochemical signatures, especially when comparing the geometric mean or median of sample values. A plot of the sum of selected base metal concentration versus pH (fig. 2) illustrates that the most chemically-degraded water is produced by QSP-altered rocks, followed by argillic (ARG), weak argillic/sericitic (WAS), quartz-alunite (QA), propylitic (PROP), and unaltered (F) rocks. As summarized in table 1, water draining from QSP- and ARG-altered assemblages have the most degraded water with median pH values of 2.8 and 3.2, respectively. Geometric mean conductivity values for the same assemblages are 1915 and 595  $\mu$ S/cm, and sum of base metals (Zn+Cu+Cd+Ni+Co+Pb) is 1121 and 231 ppb, respectively. The QA, WAS, PROP, and unaltered assemblages, which contain progressively less pyrite due to either supergene or primary processes, have median pH values of 5.4, 4.5, 6.8, and 6.6, respectively. Specific conductivity (geometric mean) for these respective assemblages is 20, 207, 88, and 24  $\mu$ S/cm, whereas, the geometric mean sum of base metals is 11, 70, 15, and 6 ppb. Thus the type of alteration is directly related to the pH and metal content of the water.

Pyrite is of great environmental significance due to its role in the generation of acid waters and the liberation of heavy metals into the surrounding watersheds (Singer and Stumm, 1970; Forstner and Wittman, 1979). Pyrite



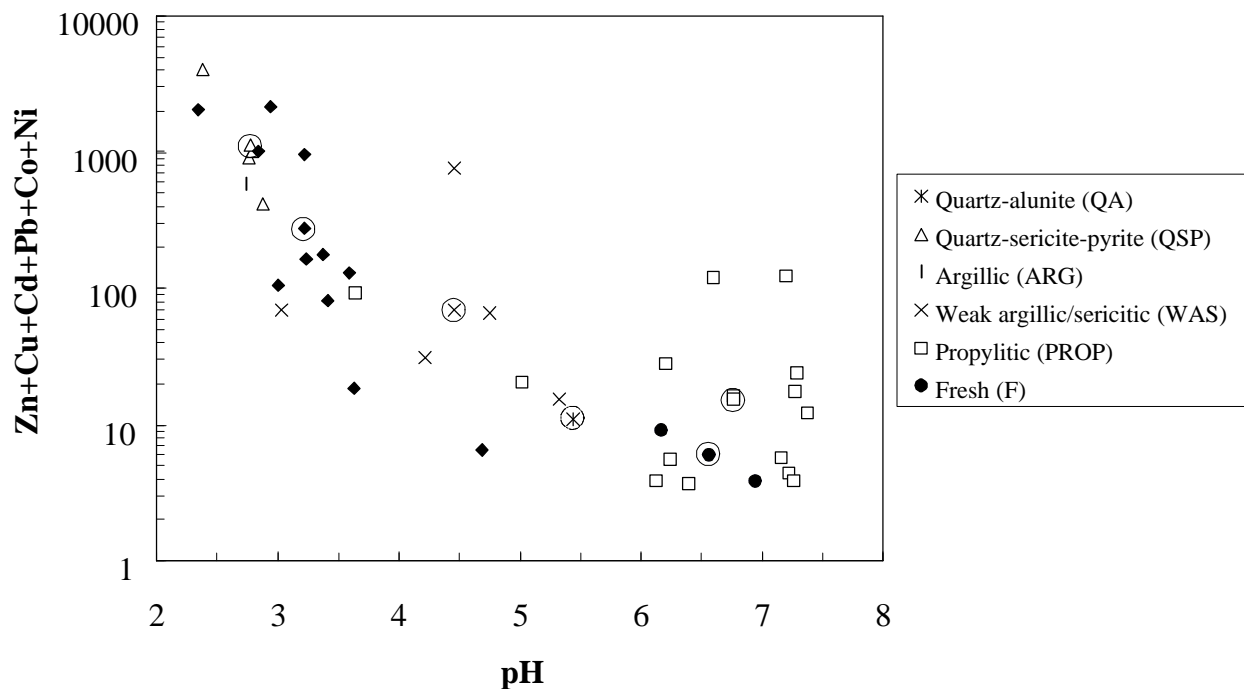
**Figure 1. Map showing distribution of hydrothermal alteration assemblages in the IABC study area. Alteration assemblages confirmed by X-ray diffraction analysis and characterized as follows: (QA) quartz and alunite replacement of volcanic rocks; (Silicified) fine-grained quartz and chalcedony replacement of volcanic rocks; (QSP) quartz-sericite-pyrite assemblage; includes quartz stockwork veinlets; (ARG) argillic assemblage, contains kaolinite and completely altered feldspars; (WAS) weak argillic/sericitic assemblage, contains kaolinite and (or) sericite; feldspars metastable; (PROP) propylitized rocks, weakly altered with chlorite, epidote, and calcite mainly after mafic minerals; (F) unaltered rocks; (Landslide) Quaternary landslide blocks, blocks are mostly propylitized and unaltered. Note: argillic (ARG) assemblage combines argillic (ARG) and (QSP-K) assemblages of Bove and others (1996). Map modified from Bove and others (1996).**

oxidation in and adjacent to QSP-altered rock generates extremely acid meteoric water that continues to react with sericite and pyrite within the QSP mineral assemblage. This chemical attack on QSP-altered rocks has resulted in the superimposition of a supergene argillic alteration assemblage (ARG) characterized by the presence of kaolinite, commonly in the absence of pyrite.

Mass balance calculations were performed on two sample pairs to ascertain chemical changes (net liberation to ground water) that took place during transformation from QSP- and WAS-altered rocks to a supergene ARG alteration assemblage. Samples within each pair were collected within a few feet of the other and in the same rock type to ensure limited chemical variability in the parent rock or protolith. In order to compare actual gains and

losses of elements during supergene transformation, the bulk rock density for each sample was determined by dividing the weight of the dry sample by its volume. As a result, the chemical compositions of the ARG-altered samples could be recalculated and compared to the equivalent QSP/WAS-altered parent on the basis of weight per unit volume of rock (Gresens, 1966). Preliminary mass balance calculations on both pairs indicate net losses of >75 percent Fe, K, Mn, Cu, Ni, Co, and pyrite, and between 20-40 percent Si, Al, and Mg during this supergene transformation. Water as a component of the mineral structure is the only major net gain, and Ti is relatively immobile.

<sup>1</sup> fine-grained muscovite



**Figure 2.** Plot showing the sum of selected base metal concentration (in ppb) versus pH from stream and spring water samples with the IABC basins. Circled symbols represent geometric mean of base metals versus median of pH. Dashed circle indicates data from only one sample.

**Table 1.** Geometric mean of waters draining specific alteration assemblages. N represents number of samples. See figure 1 for description of alteration assemblages. pH reported as median value.

Alteration assemblage	ARG	F	PROP	QA	QSP	W-AS
N	18	2	15	1	4	5
pH	3.22	6.56	6.77	5.44	2.78	4.46
Sp. Cond. ( $\mu$ S/cm)	595	24	88	20	1915	207
Fe-Tot (ppm)	19	0	0	1	187	2
Al <sup>3+</sup> (ppm)	10	0	0	0	65	1
Mg <sup>2+</sup> (ppm)	3	0	1	0	28	2
K <sup>1+</sup> (ppm)	1	2	1	1	1	2
Mn (ppm)	0	0	0	0	6	0
Ca <sup>2+</sup> (ppm)	8	3	9	3	54	10
Na <sup>1+</sup> (ppm)	2	2	3	2	3	5
Si <sup>4+</sup> (ppm)	21	13	5	14	30	15
SO <sub>4</sub> <sup>(2-)</sup> (ppm)	278	2	14	9	1404	77
Cl <sup>-</sup> (ppm)	1	0	0	0	1	0
F <sup>-</sup> (ppm)	0	0	0	0	2	0
PO <sub>4</sub> <sup>(3-)</sup> (ppm)	1	1	1	1	1	1
Pb (ppb)	0	0	0	0	1	0
Zn (ppb)	95	3	6	4	662	47
Cu (ppb)	45	1	2	5	215	1
Cd (ppb)	2	1	1	0	7	0
Ni (ppb)	17	1	1	1	73	6
Co (ppb)	35	0	1	1	144	6
Mo (ppb)	0	0	0	0	1	0
Cr (ppb)	3	1	1	1	7	1
Zn+Cu+Cd+Pb +Co+Ni	231	6	15	11	1121	70

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