

## Chapter I

# **A GEOENVIRONMENTAL MODEL FOR POLYMETALLIC VEIN DEPOSITS: A CASE STUDY IN THE COEUR D'ALENE MINING DISTRICT AND COMPARISONS WITH DRAINAGE FROM MINERALIZED DEPOSITS IN THE COLORADO MINERAL BELT AND HUMBOLDT BASIN, NEVADA**

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### ABSTRACT

A case study on drainage from polymetallic vein deposits in the world-class Coeur d'Alene mining district in northern Idaho is presented. The initial discussion focuses on our conceptual geoenvironmental model for these deposits, and then proceeds to examine the composition of waters, particularly those draining from adits and tailings piles within the district. The relative importance of the amount of reacting pyrite and carbonate minerals on drainage composition is discussed from a theoretical viewpoint and then compared with observed compositions from the district. Comparisons of drainage composition and reacting pyrite to carbonate ratios are made with diverse types of ore deposits, including polymetallic vein deposits, in Colorado and with polymetallic vein deposits in Nevada.

The results indicate that drainage from polymetallic vein deposits has highly variable pH (i.e., acidic to basic) and concentrations of sulfate, metals, and arsenic. These observations are largely due to variable amounts and types of sulfide minerals and predicted ratios of reacting pyrite to carbonate minerals that range from near zero to just under 20/1. The dominant dissolved base metal in these waters is zinc (Zn).

### INTRODUCTION

Initial mineral deposit models classified ore deposits based on their geological, geophysical, geochemical, and genetic characteristics (Cox and Singer, 1986; Bliss, 1992). The next generation of models, defined as geoenvironmental models and discussed in du Bray (1995), built upon and expanded the definition of mineral deposit models to include their environmental signature or environmental behavior. Plumlee and Nash (1995) define this signature to be "the suites, concentrations, residences, and availabilities of chemical elements in soil, sediment, airborne particulates, and water at a site that result from the natural weathering of mineral deposits and from mining, mineral processing, and smelting".

Our development of a geoenvironmental model for polymetallic vein deposits in the Coeur d'Alene (CdA) mining district has been strongly influenced by the impact of these deposits on the overall health of the ecosystem. Examples include high concentrations of lead (Pb) and zinc (Zn) in sediments not only in the mining district, but also 150+ miles downstream of the district, higher than recommended levels of Pb in the blood of children living outside of the Superfund site, poisoning of migrating, endangered water fowl in the lower valley by ingestion of Pb-enriched sediment during feeding, and the absence of a viable fisheries in the upper CdA River and its tributaries due to high dissolved Zn concentrations. Therefore, our conceptual geoenvironmental model has components similar to mineral deposit and geoenvironmental models, but expands the definition to include impacts on bio-receptors.

Our geoenvironmental model has three basic components: 1) sources of elements (primarily metals and metalloids) from mineralized deposits and associated mine wastes, 2) zones of reaction and transport including identification of the reservoirs or residences of metals and the pathways or processes that transfer elements between reservoirs, and 3) impacts on the health of humans and other biota. The source component of our geoenvironmental model entails characterization of minerals deposits and mine wastes to define such things as the geologic structure of the deposits, mineralogy of the deposits and host phases, and solid phase speciation of toxic elements. The second component includes identifying and describing all of the physical, chemical, and biological processes that act to transform or re-distribute elements between dissolved and particulate phases or between locations within the system and the parameters that force those transformations (e.g., hydrologic transport, pH, redox state, or microbial activity). This component also includes determining the concentration and locations of elements in different parts of the eco-system. For example, defining whether Zn and Pb reside primarily in sediment or in water or identifying how much Pb exists in riverbed sediments, in over bank deposits, or in marshes within the floodplain. The third

model component entails targeting the critical physical and biogeochemical pathways or processes that influence the bioavailability and bioaccumulation of toxic elements.

This paper discusses a very small portion of our geoenvironmental model for the polymetallic vein deposits in the CdA mining district. We examine the geochemical characteristics of waters, primarily drainage from adits and tailings piles, and key parameters and processes that influence their composition. Specifically, we address the effect of reacting pyrite and carbonate minerals on drainage composition. Comparisons are made with drainage from diverse types of ore deposits, including other polymetallic vein deposits, in the Colorado Mineral Belt and with polymetallic vein deposits in the Humboldt Basin in northern Nevada.

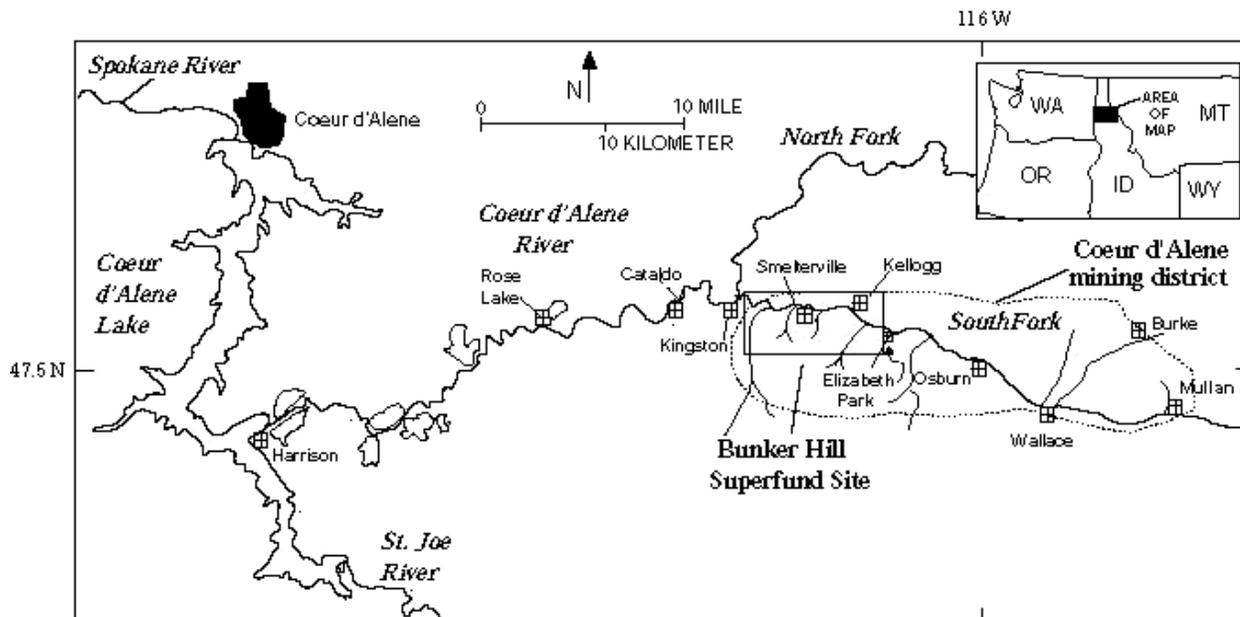


Figure 1. Location of the Coeur d'Alene mining district within the Coeur d'Alene River basin.

## STUDY AREA

The CdA mining district is located in northern Idaho and western Montana in the northwestern United States (Fig. 1). Total production records indicate that deposits in this district rank as super giants (top 1% of world producers) for Ag (34,300 metric tons) and Pb (7,288,300 metric tons) and as giants (top 10% of world producers) for Zn (2,870,000 metric tons) (Singer, 1995; Long, 1998a). Ore deposits are steeply dipping, stratigraphically controlled Pb-Zn-Ag veins occurring in Precambrian rocks of the Belt Supergroup (Fryklund, 1964; Hobbs et al., 1965; Zartman and Stacey, 1971; Bennett and Venkatakrishnan, 1982; Reid, 1984; Leach et al., 1988; Criss and Fleck, 1990). The two major types of veins are galena (PbS)-sphalerite (ZnS) and argentiferous tetrahedrite ( $[(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}]$ ). They are spatially separated, most likely of differing ages, and are a distinct type unique to the district (Leach et al., 1998; Long, 1998b). Most veins contain small amounts of chalcopyrite ( $\text{CuFeS}_2$ ). Pyrite ( $\text{FeS}_2$ ) is ubiquitous, but variable in abundance, in the veins. Minor minerals include arsenopyrite ( $\text{FeAsS}$ ) and pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ). Host rocks are primarily quartzite and argillite with lesser amounts of interbedded carbonate and carbonate bearing rocks. The galena-sphalerite veins with the highest grade of Zn are located in the argillaceous middle Prichard formation, while galena-sphalerite veins with moderate amounts of Pb-Zn-Ag are in the Prichard-Burke formations. The stratigraphically higher Revett-St. Regis formations host the largest tonnage and highest Ag grade of the galena-sphalerite deposits. Tetrahedrite veins contain the highest Ag and Cu grades in the district and are only found in the Revett-St. Regis formations (Long, 1998b). The predominant gangue minerals are siderite ( $\text{FeCO}_3$ ) and quartz ( $\text{SiO}_2$ ). The absolute and relative abundance of sulfide and gangue minerals varies significantly between different vein systems.

Mineralogical work done at several mines in the district indicate that wall rocks around veins are concentrically zoned with respect to three carbonate minerals – siderite ( $\text{FeCO}_3$ ), ankerite [ $\text{CaFe}(\text{CO}_3)_2$ ], and calcite ( $\text{CaCO}_3$ ) (Gitlin, 1986). The carbonate mineral closest to the veins is siderite. The outer edge of the siderite zone grades to a

much wider zone of ankerite either in assemblages of ankerite and siderite or ankerite and calcite. Wall rocks typically contain 10 to 15%, but can have as much as 62%, carbonate minerals.

Historical milling and tailings disposal practices have had a significant effect on the environmental impacts of mining in the CdA basin. Initial ore separation methods were not very efficient. Jig tailings produced before 1915 were highly enriched in metals, especially Zn. Development of more efficient flotation methods between 1915 and 1925 resulted in tailings with lower metal concentrations. Most tailings were deposited directly into the CdA River and its tributaries before environmental regulations required the installation of tailings ponds in 1968. Physical transport, including major flood events, subsequently re-distributed metal enriched tailings 150+ miles downstream throughout the channel of the South Fork and main stem of the CdA River and its floodplain, into Lake Coeur d'Alene, and into the Spokane River.

#### DATA SOURCES

The compositions of several types of waters are discussed in this paper. Drainage data from adits and tailing seeps in the CdA mining district were obtained from Balistrieri et al. (1998) and Box et al., (unpublished data). Information on the composition of waters from wells located within the CdA mining district either in floodplain soils covered by jig tailings (i.e., Woodland Park and Smelerville Flats) or in tailings piles at mill sites (i.e., Interstate-Callahan and Success) is from McCulley, Frick, and Gilman, Inc. (1994, 2000), Golder Associates, Inc. (1998), and Terragraphics Environmental Engineering, Inc. (1998). Historical data from the South Fork and main stem of the CdA River are from Mink et al. (1971) and U. S. Geological Survey (1973). Porewater data that were collected from the upper 30 cm of metal-enriched sediment near the river and in marshes in the lower CdA River valley (i.e., between Cataldo and Harrison; Fig. 1) are from Balistrieri et al. (2000). The composition of adit and tailings seep water draining diverse deposit types in the Colorado Mineral Belt (qCMB) and other polymetallic vein deposits in Colorado and Nevada was obtained from Plumlee et al. (1993, 1999) and Nash (2000).

#### DISCUSSION

##### *Concentrations of dissolved Zn in waters within the Coeur d'Alene River basin*

Water quality within the Coeur d'Alene River basin is largely governed by dissolved Zn concentrations. The chronic aquatic life criteria for dissolved Zn for the State of Idaho are a function of the hardness of the water and range from 32.2 µg/L at a hardness of 25 mg/L to 188.3 µg/L at a hardness of 200 mg/L (Code of Federal Regulations, 1999). Water quality criteria for pH as set by EPA (1986) for freshwater range from 6.5 to 9 (chronic). As a benchmark, hardness in the CdA River varies from 15 to 65 mg/L depending on the season and pH is near neutral.

Dissolved Zn concentrations as a function of pH for a variety of waters impacted by ore deposits or mining wastes within the CdA River basin are plotted in Fig. 2. Both pH and dissolved concentrations of Zn show large variations, and many, particularly groundwaters, fall outside of the aquatic life criteria. Values of pH range from a low of 2.72 at the Kellogg Tunnel (adit) to a high of 9.1 in the CdA River. Dissolved Zn concentrations vary from 1.2 ppb to 759 ppm. Table 1 summarizes the range and median values for pH and dissolved Zn concentrations in the various waters. Except for waters from the Kellogg Tunnel, groundwaters and tailing seeps have the lowest pH values and highest dissolved Zn concentrations. Porewaters in metal contaminated sediment tend to be acidic and can have moderately high dissolved Zn concentrations. Most adits, except the Kellogg Tunnel, have pH values near neutral with moderately high dissolved Zn concentrations. Most river waters are near neutral and tend to have the lowest dissolved Zn concentrations, although the median value is still above the aquatic life criteria. The acidic and Zn-enriched groundwaters and tailings seeps likely occur because acid-generating (e.g., pyrite) and Zn sulfide minerals (and their subsequent oxidation) are separated from buffering carbonate minerals during mining, processing, and disposal.

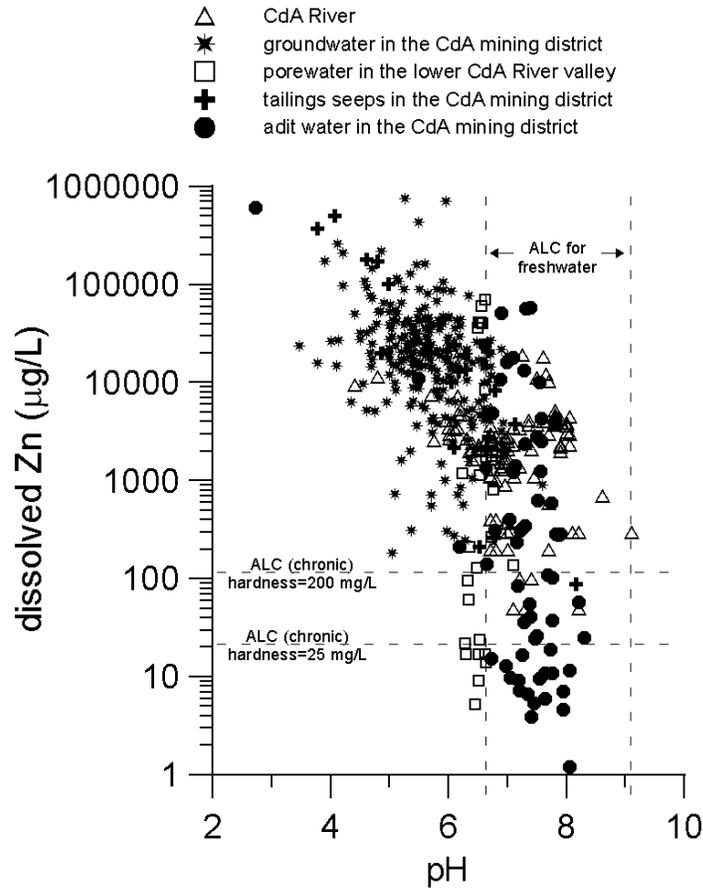


Figure 2. Values of pH and dissolved zinc (Zn) concentrations in waters from the Coeur d'Alene River Basin. ALC = aquatic life criteria.

Table 1. Range and median values of pH and dissolved Zn concentrations in waters in the Coeur d'Alene (CdA) River Basin.

Water type	No. of samples	Range pH	Median pH	Range dissolved Zn mg/L	Median dissolved Zn mg/L
groundwaters	246	3.5-7.6	5.61	0.18-759	38
tailings seeps	26	3.8-8.2	5.93	0.09-498	66
porewaters	30	6.2-7.1	6.57	0.005-70	10
adits:					
Kellogg Tunnel	1	2.7		615	
all other adits	61	5.5-8.3	7.34	0.001-58	5.8
CdA River	117	4.4-9.1	7.05	0.05-21	3.4

*Values of pH and concentrations of metals, metalloids, and other species in adits and tailings seeps in polymetallic vein districts*

Drainage from adits and tailings piles in polymetallic vein deposits in the CdA mining district, in the Colorado Mineral Belt, and in the Humboldt Basin in northern NV are illustrated on a plot developed by Ficklin et al. (1992) (Fig. 3). This plot shows the sum of dissolved base metal (Cd, Co, Cu, Ni, Pb, and Zn) concentrations as a function of pH. The sum of dissolved base metal concentrations is dominated by Zn concentrations in nearly all drainage. Drainage data from polymetallic deposits in northern NV have the greatest range in pH and dissolved base metal concentrations. Although drainage from Au-quartz-pyrite and carbonate-rich polymetallic deposits in Colorado has a similar range in dissolved base metal concentrations as observed in drainage from the CdA mining district, values of pH tend to be higher in drainage from CdA versus CO. As expected, drainage from pyrite-rich polymetallic vein deposits in CO that are poor in base metals (Zn, Pb, and Cu) has lower dissolved base metal concentrations and lower pH values relative to drainage from other polymetallic deposits in CdA. The comparison of drainage from CO and NV suggests that certain polymetallic deposits in NV are also rich in pyrite but poor in base metals.

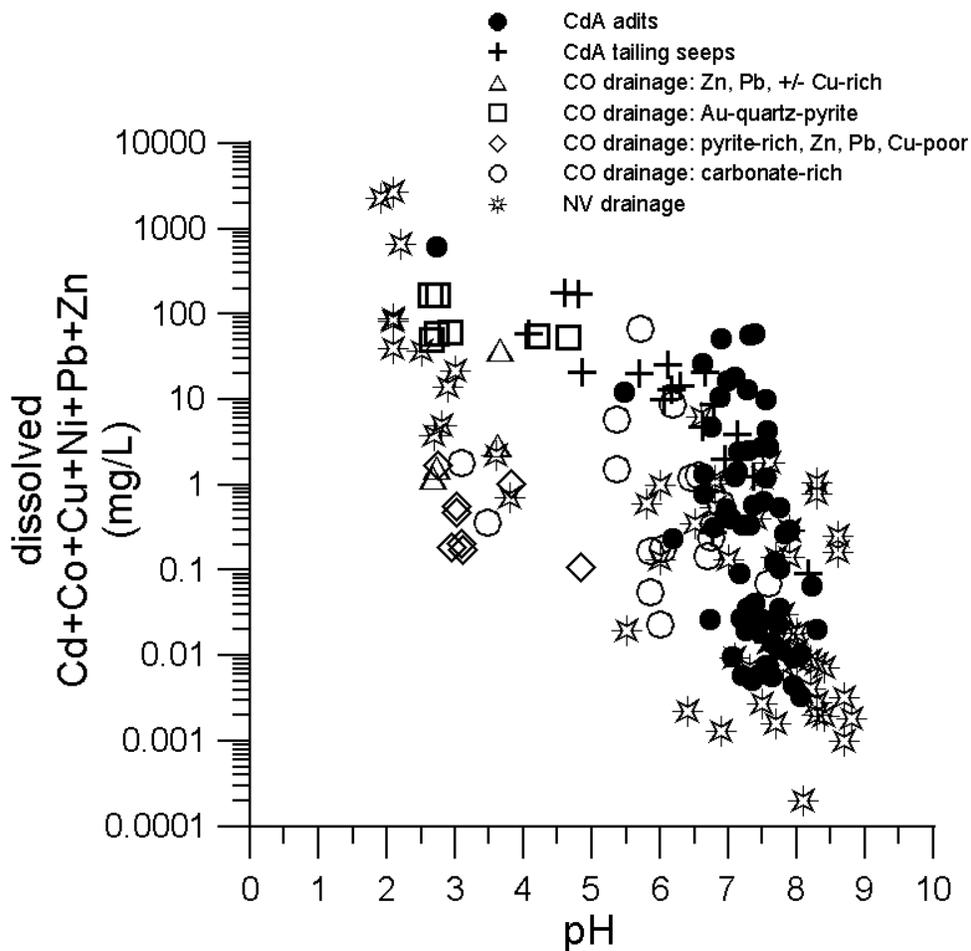


Figure 3. A Ficklin plot (i.e., sum of dissolved base metal concentrations versus pH) for drainage from polymetallic vein deposits in the Coeur d'Alene mining district, in the Colorado Mineral Belt, and in the Humboldt Basin in northern Nevada.

Comparisons between dissolved concentrations of sulfate, As, Mn, and Fe and values of pH in mine drainage from polymetallic deposits CdA, CO, and NV are shown in Fig. 4. Only those concentrations of As, Mn, and Fe greater than the detection limits of the analyses are plotted. Drainage from most of the polymetallic deposits in CO and many of the same type of deposits in NV has higher concentrations of sulfate than almost

all of the adit drainage in CdA (Fig. 4A). This observation suggests that greater amounts of metal sulfides are being oxidized in the CO mining districts and in some NV districts relative to the CdA district. Concentrations of As in drainage from polymetallic deposits in CdA, CO, and NV range from 0.05  $\mu\text{g/L}$  to 3,800  $\mu\text{g/L}$  (Fig. 4B). The highest concentrations of As are observed in drainage from some sites in

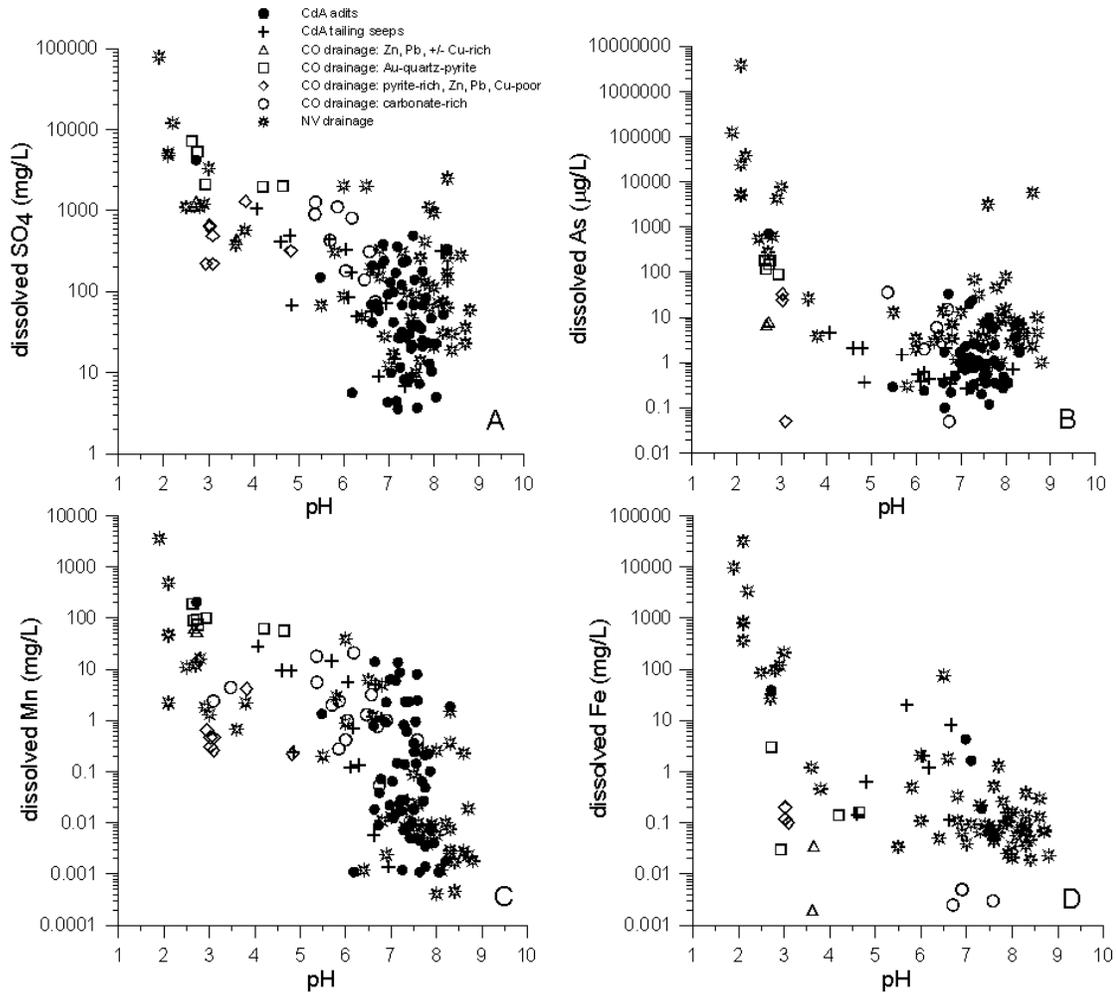


Figure 4. Dissolved concentrations of A) sulfate ( $\text{SO}_4$ ), B) arsenic (As), C) manganese (Mn), and D) iron (Fe) versus pH in drainage from polymetallic vein deposits in the Coeur d'Alene mining district, in the Colorado Mineral Belt, and in the Humboldt Basin in northern Nevada.

NV, from the Kellogg Tunnel in CdA, and from Au-quartz-pyrite polymetallic deposits in CO. Concentrations of Mn in drainage as a function of pH show some similarities to plots for total dissolved base metal concentrations as a function of pH (Fig. 4C). Dissolved Mn concentrations in drainage from NV vary by 7 orders of magnitude, while concentrations in CdA drainage vary by 5 orders of magnitude. The highest concentrations of Mn occur in drainage from certain sites in NV, from the Kellogg Tunnel (pH 2.7) in CdA, and in drainage from Au-quartz-pyrite and Zn, Pb, +/- Cu-enriched polymetallic deposits in CO. Drainage from pyrite-rich and Zn, Pb, and Cu-poor polymetallic deposits in CO tends to have lower concentrations of Mn compared to drainage of the same pH from other polymetallic deposits. Drainage from adits and tailings with the highest pH values tends to have the lowest dissolved Fe concentrations (Fig. 4D), while the drainage with the lowest pH (i.e., sites in NV, Kellogg Tunnel in CdA, Au-quartz-pyrite and pyrite-rich, base metal-poor polymetallic deposits in CO) has the highest Fe concentrations. These trends are consistent with the solubility of Fe minerals (Bigham et al., 1996; Langmuir, 1997). The data in Figs. 3 and 4 indicate that mine drainage is not necessarily acidic and that near neutral mine drainage can have high concentrations of metals and other species (Plumlee et al., 1993).

Studies in the Colorado Mineral Belt (CMB) examined the relationship between mine drainage composition and mineralogy of diverse ore deposit types (including, but not limited to, polymetallic deposits) and host rocks (Plumlee et al., 1993). One of the key parameters that influenced drainage composition was the relative abundance of sulfide minerals, especially pyrite, and carbonate minerals. Their adit data and classification of deposits with respect to their relative abundance of pyrite and carbonate minerals in deposits and host rocks are compared with drainage data from polymetallic deposits in mining districts in CdA, ID and the Humboldt Basin in NV in Fig. 5.

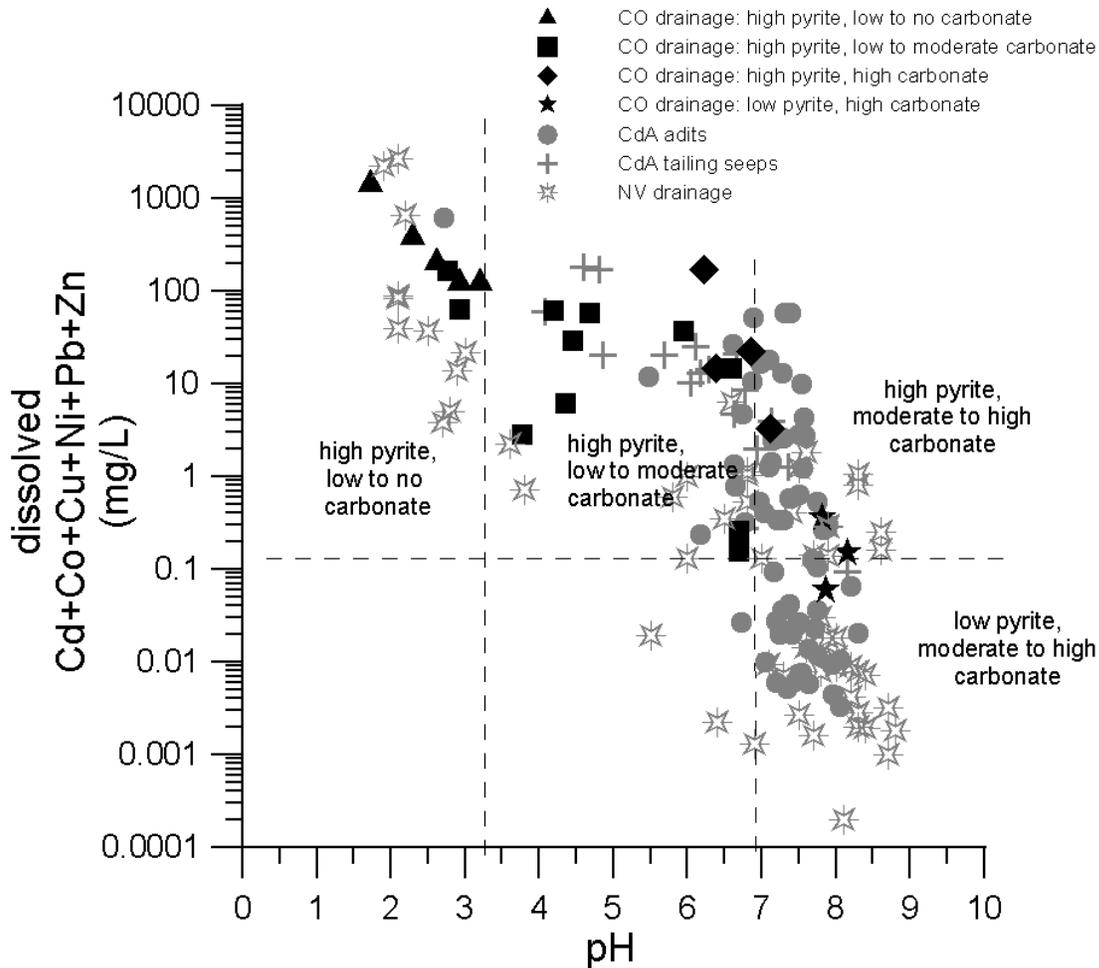


Figure 5. Relationship between the sum of dissolved base metals (Cd, Co, Cu, Ni, Pb, and Zn) and pH in mine drainage from diverse deposit types in the Colorado Mineral Belt and from polymetallic vein deposits in the Coeur d'Alene mining district and in the Humboldt Basin in northern Nevada.

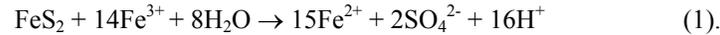
This comparison indicates that the wide ranging pH and metal concentrations found in drainage from polymetallic deposits in CdA and NV likely are due to variable amounts of sulfide and carbonate minerals in the individual deposits and host rocks. The dominance of acid generating minerals (e.g., pyrite) results in acid pH values and the mobilization of metals into solution, whereas significant amounts of acid neutralizing minerals (e.g., calcite) increase the pH and possibly result in the precipitation of oxides and hydroxysulfates that scavenge metals from solution. Thus, low pH values and high dissolved metal concentrations are found in drainage from deposits

with high pyrite to carbonate ratios. Deposits that are enriched in both pyrite and carbonate minerals produce drainage that has high dissolved metal concentrations and near neutral pH values. The lowest dissolved metal concentrations are found in near neutral drainage from deposits that contain low pyrite to carbonate ratios.

### *Reacting pyrite to carbonate ratios*

Why is there such a range in pH and metal concentrations in drainage from these mineralized terranes? Comparisons in Fig. 5 are based on empirical observations of drainage composition and mineralogy of the deposits and host rocks. In reality, the composition of drainage is a function of the amount of reacting sulfide and carbonate minerals, not the absolute abundance of the minerals in the deposits and host rocks. A more quantitative approach can be used to assess the relative abundance of reacting pyrite and carbonate minerals on drainage composition (Balistrieri et al., 1999). This approach compares relationships between selected dissolved ion concentrations and alkalinity (or acidity) in drainage with stoichiometric relationships between these variables predicted from chemical reactions. The predictions are derived from reactions describing the oxidation of pyrite, precipitation of hydrous Fe oxide or Fe hydroxysulfate minerals, and dissolution of carbonate minerals, and from the definitions of alkalinity and acidity. As only a few samples from the CO and NV datasets have measured alkalinity, most of the following discussion will focus on drainage from CdA.

It is well known that a major source of acid to waters in mineralized areas is the oxidation of pyrite. Although the overall oxidant that drives pyrite oxidation is O<sub>2</sub> from the atmosphere, dissolved Fe(III) appears to be the primary oxidant that attacks the pyrite surface to form Fe(II), SO<sub>4</sub>, and protons (Taylor et al., 1984; Reedy et al., 1991):



The Fe(II) that is produced in reaction 1 can oxidize in the presence of O<sub>2</sub> to Fe(III):



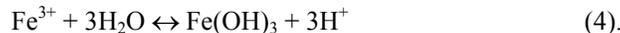
This reaction is the rate-determining step and is usually catalyzed by autotrophic bacteria (Singer and Stumm, 1970).

The Fe(III) produced in reaction 2 can either further oxidize pyrite (reaction 1) or hydrolyze and then precipitate as hydrous Fe oxide (goethite [ $\alpha\text{FeOOH}$ ] or ferrihydrite [ $\sim\text{Fe}_5\text{OH}_8 \cdot 4\text{H}_2\text{O}$ ]) or as Fe hydroxysulfate minerals (jarosite [ $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ] or schwertmannite [ $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ ]) depending on kinetic factors, pH, and concentrations of Fe(III), SO<sub>4</sub>, and bicarbonate (Nordstrom et al., 1979; Bigham et al., 1996). Bigham et al. (1996) indicates that although goethite and jarosite ultimately control the concentration of Fe(III) in mine drainage, the metastable phases of ferrihydrite or schwertmannite are frequently found in such systems. Both mineralogical and thermodynamic data suggest that jarosite controls the activity of dissolved Fe(III) in drainage with pH values less than about 2.7, schwertmannite for pH values from about 2.8 to 4.5, mixtures of schwertmannite and ferrihydrite for pH values between 4.5 and 6.5, and ferrihydrite for higher pH values. Given the pH range of drainage in CdA, schwertmannite, mixtures of schwertmannite and ferrihydrite, or predominantly ferrihydrite likely control dissolved Fe(III) concentrations.

The precipitation of Fe(III) as schwertmannite consumes SO<sub>4</sub> and produces protons:



whereas the precipitation of ferrihydrite [hereafter denoted by the formula Fe(OH)<sub>3</sub>] only produces protons:



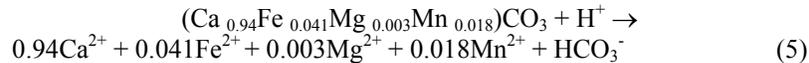
The principal reactions that generate base, in sequential order based on reactivity, are the dissolution of carbonate minerals (calcite [ $\text{CaCO}_3$ ], dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ], or ankerite [ $\text{CaFe}(\text{CO}_3)_2$ ]), oxides and hydroxides of Al and Fe, and aluminosilicates (feldspars, chlorite, and muscovite) (Blowes and Ptacek, 1994; Sherlock et al., 1995). The most important acid neutralizing reactions are the dissolution of carbonate minerals. The carbonate minerals of importance in the CdA mining district are calcite, ankerite, and siderite. Several analyses of the composition of these minerals for the district have been done and are summarized in Table 2.

Table 2. Composition of carbonate minerals in the Coeur d'Alene mining district.

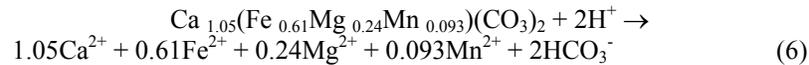
Mineral	Mine	Ca moles	Fe moles	Mg moles	Mn moles	CO <sub>3</sub> moles	Reference
calcite	Lucky Friday (n = 8)						Gitlin, 1986
	average	0.94	0.041	0.003	0.018	1	
	standard deviation	0.01	0.008	0.002	0.002		
ankerite	Lucky Friday	1.07	0.7	0.13	0.097	2	Gitlin, 1986
	Sunshine	1.04	0.68	0.17	0.1	2	Fryklund, 1964
	Coeur d'Alene (n = 2)	1.07	0.49	0.38	0.068	2	Fryklund, 1964
	Merger	1.05	0.63	0.22	0.098	2	Fryklund, 1964
	Bunker Hill	1.02	0.56	0.32	0.098	2	Fryklund, 1964
	average	1.05	0.61	0.24	0.093	2	
	standard deviation	0.02	0.08	0.09	0.013		
siderite	Lucky Friday (n = 8)	0.024	0.83	0.07	0.077	1	Gitlin, 1986
	Sunshine (n = 7)	0.006	0.87	0.04	0.078	1	Fryklund, 1964
	Bunker Hill (only ranges given)	0.02-0.06	0.75-0.85	0.06-0.10	0.08-0.10	1	Fryklund, 1964
	average	0.023	0.84	0.06	0.082	1	
	standard deviation	0.014	0.03	0.02	0.006		

The carbonate phases are not pure and analyses are limited to only a few locations in the district. The calculations that follow assume that the average compositions of carbonate minerals at these locations are representative of the entire district. The dissolution of these minerals results in the release of divalent metal (Ca<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup>, and Mn<sup>2+</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>) ions to solution. The dissolution reactions for the CdA carbonates are written as follows:

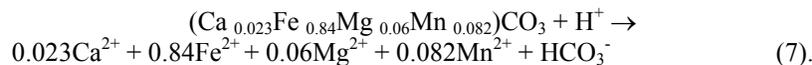
for calcite:



for ankerite:



for siderite:



The Fe(II) that is released during dissolution of the carbonate minerals can oxidize and precipitate either as Fe oxide or Fe hydroxysulfate minerals.

Alkalinity [Alk] is the acid neutralizing capacity of water (Stumm and Morgan, 1996). For most waters alkalinity can be defined in terms of the carbonate ions (HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) as the concentrations of other proton acceptors (e.g., NH<sub>3</sub>, HS<sup>-</sup>, or B(OH)<sub>4</sub><sup>-</sup>) are negligible:

$$[Alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (8)$$

Acidity [Acy] is the base neutralizing capacity of water (Stumm and Morgan, 1996). Acidity is measured by titrating water with a strong base to a designated pH, typically pH 8.2 or 8.3 (US EPA, 1974; APHA, 1976). For mine drainage waters, reactions that contribute to acidity during a base titration to pH 8.3 include the neutralization of strong and weak acids (H<sup>+</sup>, HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>CO<sub>3</sub><sup>0</sup>), the hydrolysis of metal ions (Fe<sup>3+</sup>, Al<sup>3+</sup>), and the oxidation and hydrolysis of redox sensitive metals (Fe<sup>2+</sup>, Mn<sup>2+</sup>) (Langmuir, 1997). Thus, acidity is defined as:

$$[\text{Acy}] = [\text{H}^+] + [\text{HSO}_4^-] + [\text{H}_2\text{CO}_3^0] + 3[\text{Al}^{3+}] + 3[\text{Fe}^{3+}] + 2[\text{Fe}^{2+}] + 2[\text{Mn}^{2+}] \quad (9).$$

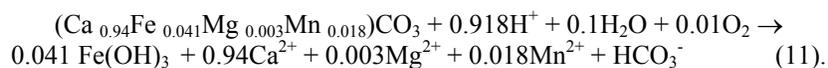
It should be noted that acidity, as defined above, is not strictly the negative of alkalinity as other species besides carbonate species are included in the acidity definition.

The above reactions and definitions for alkalinity and acidity can be used to predict the relative amounts of pyrite and carbonate minerals that react to form drainage. Concentrations of dissolved  $\text{SO}_4$  are the net result of oxidation of all sulfide minerals and the precipitation of secondary sulfate minerals such as Fe hydroxysulfates. Dissolved Ca and Mg concentrations represent the net concentration of Ca and Mg produced during the dissolution of carbonate minerals and Ca and Mg consumed during the precipitation of secondary minerals. Alkalinity is the net result of protons consumed and bicarbonate produced during the dissolution of carbonate minerals and protons generated during pyrite oxidation and precipitation of Fe oxide or Fe hydroxysulfate minerals. Acidity accounts for the strong acids and metals generated during pyrite oxidation, for the consumption of protons and production of metals during carbonate mineral dissolution, and for protons generated during the precipitation of Fe oxides or Fe hydroxysulfate minerals.

The stoichiometric relationships between the sum of dissolved Ca and Mg, dissolved  $\text{SO}_4$ , and alkalinity or acidity are derived from the reactions and definitions given above. We consider the oxidation of pyrite, dissolution of average CdA calcite, ankerite, or siderite, and either no oxidation of Fe(II) produced from the previous reactions or oxidation of Fe(II) with subsequent precipitation of schwertmannite and ferrihydrite. The stoichiometry for the various cases is determined by combining the appropriate reactions given above. For example, the reaction describing the oxidation of pyrite and precipitation of ferrihydrite is determined by combining reaction 1 plus 15 times reaction 2 plus reaction 4:



The dissolution of average CdA calcite and oxidation and precipitation of released Fe(II) as ferrihydrite is determined by combining reaction 5 plus 0.041 times reaction 2 plus 0.041 times reaction 4:



These reactions are used to predict relationships between dissolved Ca and Mg, dissolved  $\text{SO}_4$ , and alkalinity for variable ratios of reacting pyrite to carbonate minerals for the case where Fe(II) oxidizes and precipitates as ferrihydrite. Assuming comparable oxidation and dissolution rates, a reacting pyrite to calcite mineral ratio of 1 to 4, considering precipitation of ferrihydrite, would yield 2 moles of dissolved  $\text{SO}_4$  and 4 moles of protons for every mole of oxidized pyrite (equation 10), while 4 moles of average CdA calcite would consume 3.672 moles of protons and produce 3.76 moles of dissolved Ca, 0.012 moles of dissolved Mg ions, 0.072 moles of dissolved Mn ions, and 4 moles of dissolved bicarbonate ions (equation 11; coefficients multiplied by 4). Thus, 3.672 moles of alkalinity (i.e., 4 moles of bicarbonate – 0.328 moles of protons; equation 8) and 0.472 moles of acidity (i.e., 0.328 moles of protons + 0.144 moles of Mn; equation 9) are generated for this system. The stoichiometries for other cases are summarized in Table 3.

Table 3. Stoichiometric coefficients for reactions describing pyrite oxidation and dissolution of average Coeur d'Alene (CdA) carbonate minerals considering no precipitation (ppt) of Fe, precipitation of ferrihydrite (ppt F), or precipitation of schwertmannite (ppt S).\*

oxidation of 1 mole of pyrite				dissolution of 1 mole of average CdA calcite			
	no ppt	ppt F	ppt S		no ppt	ppt F	ppt S
SO <sub>4</sub>	2	2	1.875	Ca	0.94	0.94	0.94
Fe(II)	15	0	0	Mg	0.003	0.003	0.003
Fe(III)	14	0	0	SO <sub>4</sub>	0	0	-0.005
H <sup>+</sup>	16	4	3.75	Fe(II)	0.041	0	0
				Mn	0.018	0.018	0.018
				H <sup>+</sup>	-1	-0.918	-0.928
				HCO <sub>3</sub> <sup>-</sup>	1	1	1
				dissolution of 1 mole of average CdA ankerite			
					no ppt	ppt F	ppt S
				Ca	1.05	1.05	1.05
				Mg	0.24	0.24	0.24
				SO <sub>4</sub>	0	0	-0.077
				Fe(II)	0.61	0	0
				Mn	0.093	0.093	0.093
				H <sup>+</sup>	-2	-0.77	-0.93
				HCO <sub>3</sub> <sup>-</sup>	2	2	2
				dissolution of 1 mole of average CdA siderite			
					no ppt	ppt F	ppt S
				Ca	0.023	0.023	0.023
				Mg	0.06	0.06	0.06
				SO <sub>4</sub>	0	0	-0.104
				Fe(II)	0.84	0	0
				Mn	0.082	0.082	0.082
				H <sup>+</sup>	-1	0.67	0.46
				HCO <sub>3</sub> <sup>-</sup>	1	1	1

\*See text for example calculation. Positive numbers indicate production of species and negative numbers indicate uptake of species.

The moles of dissolved Ca and Mg, dissolved SO<sub>4</sub>, and alkalinity or acidity resulting from the calculations for variable ratios of reacting pyrite to average CdA carbonate minerals are normalized to 100%. Normalization involves calculating the proportion of one of the components relative to the sum of all components [e.g., % SO<sub>4</sub> = moles of SO<sub>4</sub> / (moles of SO<sub>4</sub> + moles of (Ca + Mg) + moles of alkalinity) times 100] and reflects the relationships between components. The example above (i.e., a reacting pyrite to calcite ratio of 1 to 4 with precipitation of ferrihydrite) yields 2 moles of dissolved SO<sub>4</sub>, 3.77 moles of Ca + Mg, and 3.672 moles of alkalinity. The normalization results in 21% SO<sub>4</sub>, 40% (Ca + Mg), and 39% alkalinity. The ratio of the normalized values for SO<sub>4</sub> and (Ca + Mg) are plotted versus the normalized values for alkalinity or acidity for different reacting pyrite to carbonate ratios in Figs. 6 and 7. These diagrams indicate how variations in the reacting solid phase ratios and either no precipitation or precipitation of various Fe minerals influence solution compositions. Drainage that leaches rocks with relatively very low reacting pyrite to carbonate (i.e., calcite, ankerite, or siderite) ratios is predicted to have lower ratios of dissolved SO<sub>4</sub> to (Ca + Mg) concentrations, higher proportions of alkalinity, and lower proportions of acidity. This type of drainage plots near the bottom of the diagrams. Waters draining ore deposits with higher reacting pyrite to carbonate ratios are predicted to have higher ratios of SO<sub>4</sub> to (Ca + Mg) concentrations, lower proportions of alkalinity, and higher proportions of acidity. These waters plot near the top of the diagrams. The locations of the specific carbonate minerals are uniquely defined in the diagrams by the relative amounts of Ca and Mg that are released during their dissolution. Predictions with siderite as the buffering carbonate are clearly separated from calcite and ankerite, except for the acidity diagram with no precipitation of Fe minerals. Although predictions for calcite and ankerite are close to each other in the alkalinity diagrams (Fig. 6), there is better separation between these carbonates in the acidity diagrams with precipitation of Fe minerals (Fig. 7). In addition, there are clear differences in the relationships if Fe(II) does not oxidize and precipitate or if it oxidizes and precipitates as Fe hydroxysulfate or Fe oxide minerals.

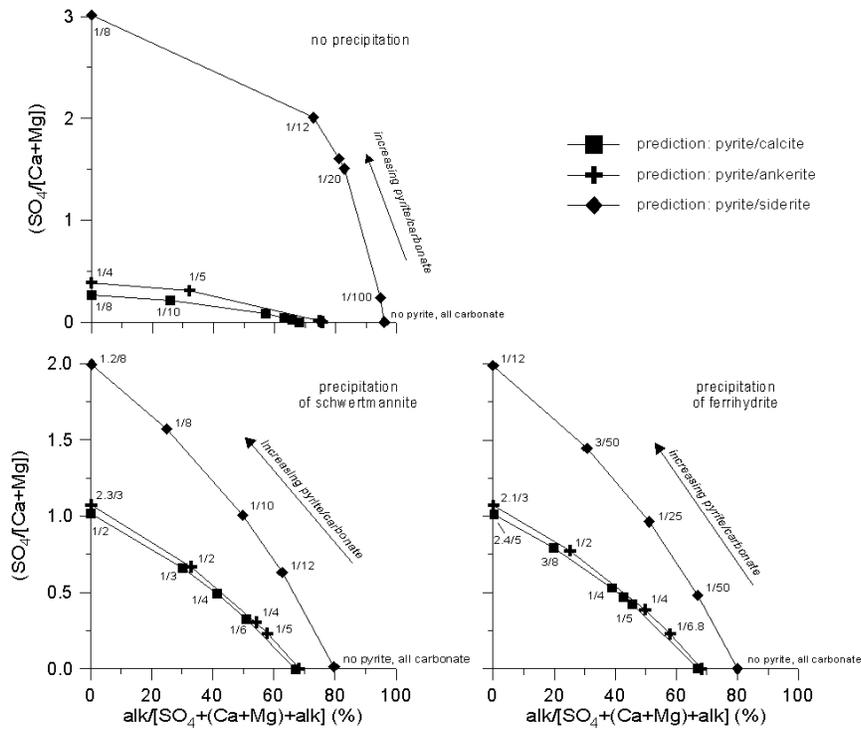


Figure 6. Predicted relationships between the ratio of sulfate ( $SO_4$ ) to the sum of dissolved calcium (Ca) and magnesium (Mg) and normalized alkalinity (alk) for various ratios of reacting pyrite to carbonate (i.e., calcite, ankerite, or siderite) considering no precipitation of Fe or precipitation of schwertmannite or ferrihydrite.

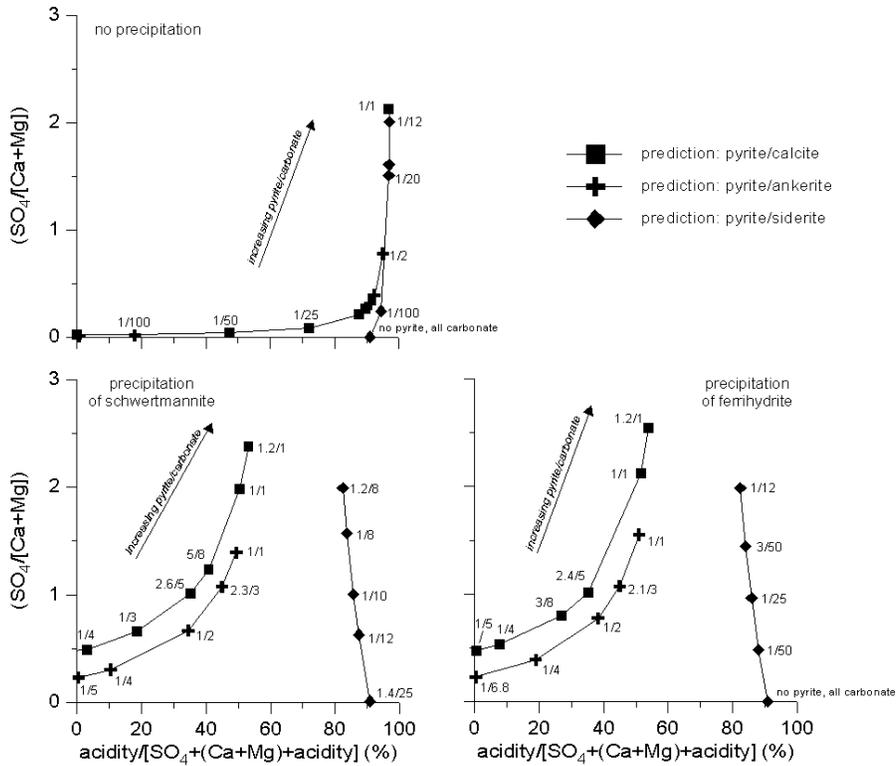


Figure 7. Predicted relationships between the ratio of sulfate ( $SO_4$ ) to the sum of dissolved calcium (Ca) and magnesium (Mg) and normalized acidity for various ratios of reacting pyrite to carbonate (i.e., calcite, ankerite, or siderite) considering no precipitation of Fe or precipitation of schwertmannite or ferrihydrite.

These diagrams do not clearly distinguish between schwertmannite and ferrihydrite because differences in the moles of protons and  $\text{SO}_4$  produced per mole of pyrite oxidized or consumed per mole of carbonate mineral dissolved are too small during precipitation of the two Fe phases (Table 3). Successful predictions of the exact ratios of reacting pyrite to carbonate minerals from drainage data require an understanding of the particular Fe phase that is precipitating. This point is demonstrated by the different locations of the same pyrite/carbonate ratios for the precipitation of schwertmannite and ferrihydrite phases. However, an estimate of the ratios can be made because the locations for the reacting mineral ratios are nearly the same for the precipitation of these Fe minerals.

The next step is to use the predictions of the relationships between  $\text{SO}_4$ , Ca and Mg, and alkalinity or acidity to interpret drainage data from the CdA mining district. Dissolved  $\text{SO}_4$  concentrations in drainage from the district represent the oxidation of various sulfide minerals. However, only a portion of these minerals (i.e., pyrite) produces acidity during oxidation. In order to predict how the relative ratios of acid generating and acid consuming minerals vary throughout the district, we correct dissolved  $\text{SO}_4$  concentrations in drainage from the district for contributions from the major sulfide minerals that do not produce acidity during oxidation (i.e., sphalerite and galena) by assuming that all dissolved Zn and Pb concentrations are derived from the oxidation of these minerals. The dissolved concentrations of  $\text{SO}_4$ , Zn, and Pb are converted to a molar basis. Then dissolved  $\text{SO}_4$  derived from pyrite (i.e., pyritic  $\text{SO}_4$ ) is calculated as the difference between dissolved  $\text{SO}_4$  and the sum of dissolved Zn and Pb concentrations.

Thermodynamic speciation calculations using MINTEQA2 (Allison et al., 1991) indicate that drainage in the CdA mining district is undersaturated with respect to secondary Ca and Mg minerals. Thus, it is assumed that Ca and Mg concentrations are not affected by the precipitation of secondary minerals.

All adit waters, except the Kellogg Tunnel, and almost all tailings seeps collected in the CdA mining district contain alkalinity with values ranging from 0.1 to 7.2 mM. Because acidity was not measured by titration for the drainage waters from the CdA mining district, we calculated [Acy] for a subset of the data using equation 9. We used measured dissolved concentrations of Al, Fe(III), Fe(II), and Mn(II) to include the free metal ion as well as its solution complexes. Concentrations of  $\text{H}^+$ ,  $\text{HSO}_4^-$ , and  $\text{H}_2\text{CO}_3^0$  were determined from solution speciation calculations done for the drainage waters using MINTEQA2. The calculated [Acy] range from 0.02 to 41 mM. These calculations assume that titrations of drainage samples would result in complete oxidation and precipitation of Fe(II) and Mn(II). Furthermore, the calculations assume that filtration results in the accurate partitioning of Fe(III) between dissolved and particulate or colloidal forms. If particulate or colloidal Fe(III) passes through the filter and is considered to be dissolved, then the calculated acidity would be too high. These assumptions are only critical for drainage from the Kellogg Tunnel where 64% of the calculated acidity is due to Fe species. Because of their higher pH values, carbonic acid generally is the primary contributor to the calculated acidities of the remaining drainage samples. In addition, because reactions that contribute Al to acidity (e.g., buffering by Al oxides and aluminosilicate minerals) are not considered in our theoretical approach, we correct the calculated acidity values for the Al contribution. This correction is less than 5%. Finally, the corrected or pyritic dissolved  $\text{SO}_4$ , the sum of dissolved Ca and Mg, and alkalinity (or corrected acidity) data are converted to a molar basis, normalized to 100%, and plotted on the same diagram as the predictions (Figs. 8 and 9).

Comparisons between the predictions and drainage from CdA indicate that these waters drain mineralized areas with reacting pyrite to carbonate ratios ranging from near zero (i.e., very, very little pyrite to carbonate) to about 1/2 to 2/3 for most of the drainage in the district to about equal portions of reacting pyrite and carbonate (i.e., ~1/1) for the very acidic drainage from the Kellogg Tunnel. The relative concentrations of dissolved Ca and Mg in these waters suggest that, depending on location within the district, either calcite or ankerite appear to buffer the waters. The acidity diagram shows a clearer distinction between drainage that is buffered by calcite or ankerite. The location of CdA drainage within the diagrams indicates that Fe(II) oxidizes and precipitates. Drainage data are consistent with the precipitation of schwertmannite or ferrihydrite.

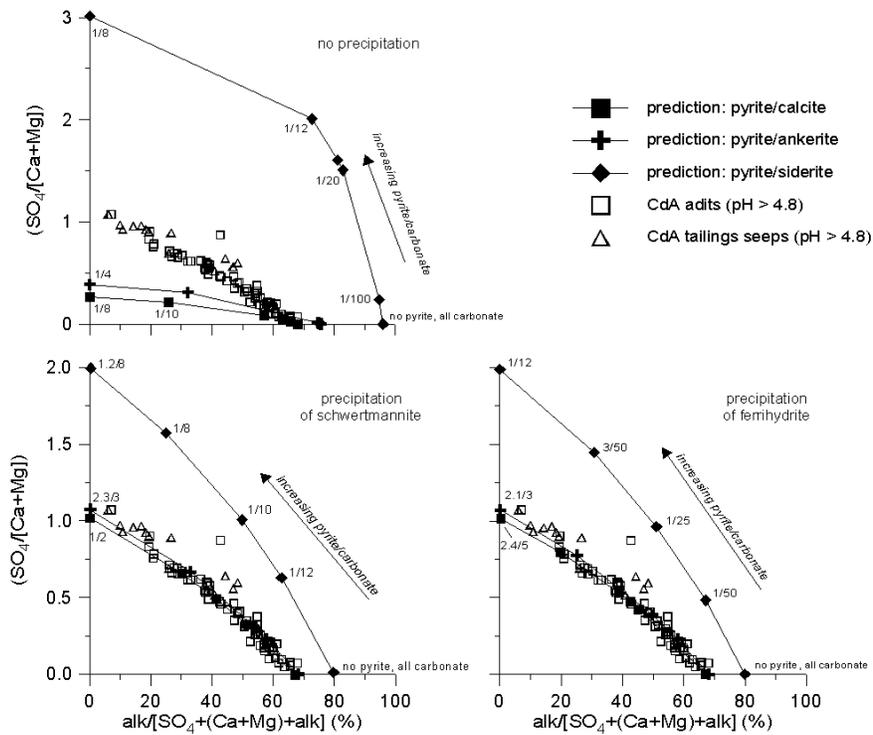


Figure 8. Comparisons between the predictions presented in Figure 6 and the composition of drainage from adits and tailings piles in the Coeur d'Alene (CdA) mining district.

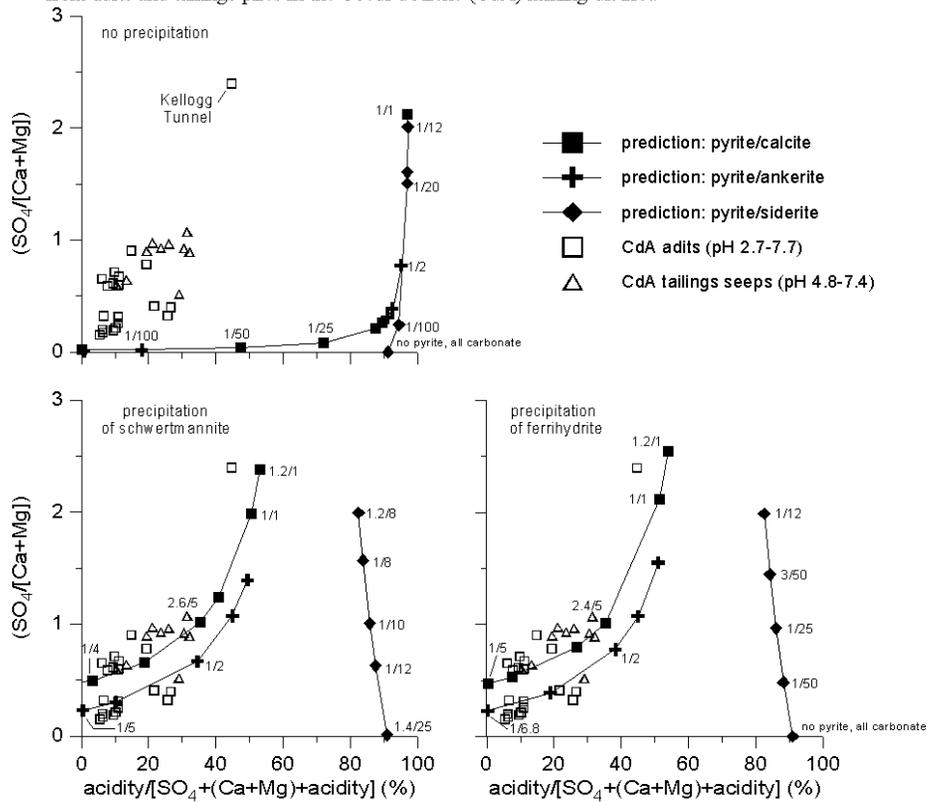
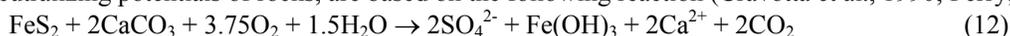


Figure 9. Comparisons between the predictions in Figure 7 and the composition of drainage from adits and tailings piles in the Coeur d'Alene (CdA) mining district.

### *Reacting pyrite to carbonate ratios and pH*

What is the relationship between the pH of drainage and the relative amounts of pyrite and carbonate minerals that have reacted in a mineralized deposit? Using the theoretical approach presented above, we can estimate the reacting pyrite to calcite or reacting pyrite to ankerite ratios of the deposits from the measured pyritic  $\text{SO}_4$  to (Ca + Mg) ratios in the drainage. If we consider precipitation of ferrihydrite, the reacting pyrite to calcite ratio is equal to  $[\text{pyritic } \text{SO}_4 / (\text{Ca} + \text{Mg})] / 2.12$ , while the reacting pyrite to ankerite ratio is equal to  $[\text{pyritic } \text{SO}_4 / (\text{Ca} + \text{Mg})] / 1.55$ . The predicted reacting pyrite/calcite ratios, considering ferrihydrite precipitation, for the polymetallic vein deposits in CdA, CO, and NV are plotted versus the pH of the drainage in Fig. 10. Note that the results would be very similar if the reacting pyrite to ankerite relationship is used. As expected, drainage from deposits and host rocks with the highest reacting pyrite to calcite ratios, as determined by pyritic  $\text{SO}_4$  to (Ca + Mg) ratios in drainage, have the lowest pH values. The results indicate that the pH of drainage is near neutral or slightly basic when the polymetallic deposits and their host rocks have reacting pyrite to calcite ratios less than 3/10. The pH of drainage is very acidic ( $\text{pH} \leq 3$ ) when the reacting pyrite to calcite ratios of the deposits and host rocks are near or greater than about 6/10. The transition between neutral and acidic pH values occurs in drainage when the reacting pyrite to calcite ratios of the deposits and host rocks are between 3/10 and 6/10.

What values of drainage pH should be expected based on the stoichiometry of the pyrite oxidation and calcite dissolution reactions? Acid-Base Accounting (ABA) measurements, which determine the relative acid generating and acid neutralizing potentials of rocks, are based on the following reaction (Cravotta et al., 1990; Perry, 1998):



That is, for each mole of pyrite that is oxidized, two moles of calcite are required for acid neutralization, assuming loss of  $\text{CO}_2$  to the atmosphere. If  $\text{CO}_2$  is not lost, but is retained within the system resulting in additional acid generating capacity, then up to 4 moles of calcite are needed for neutralization of one mole of pyrite (Cravotta et al., 1990):



Hence, neutralization of acid generated during oxidation of one mole of pyrite theoretically requires between 2 and 4 moles of calcite (i.e., reacting pyrite to calcite ratios ranging between 2.5/10 and 5/10). Thus, drainage data from polymetallic deposits in CdA, CO, and NV are consistent with the theoretical predictions as predicted reacting pyrite to calcite ratios  $< 3/10$  for the deposits and host rocks result in near neutral to basic drainage.

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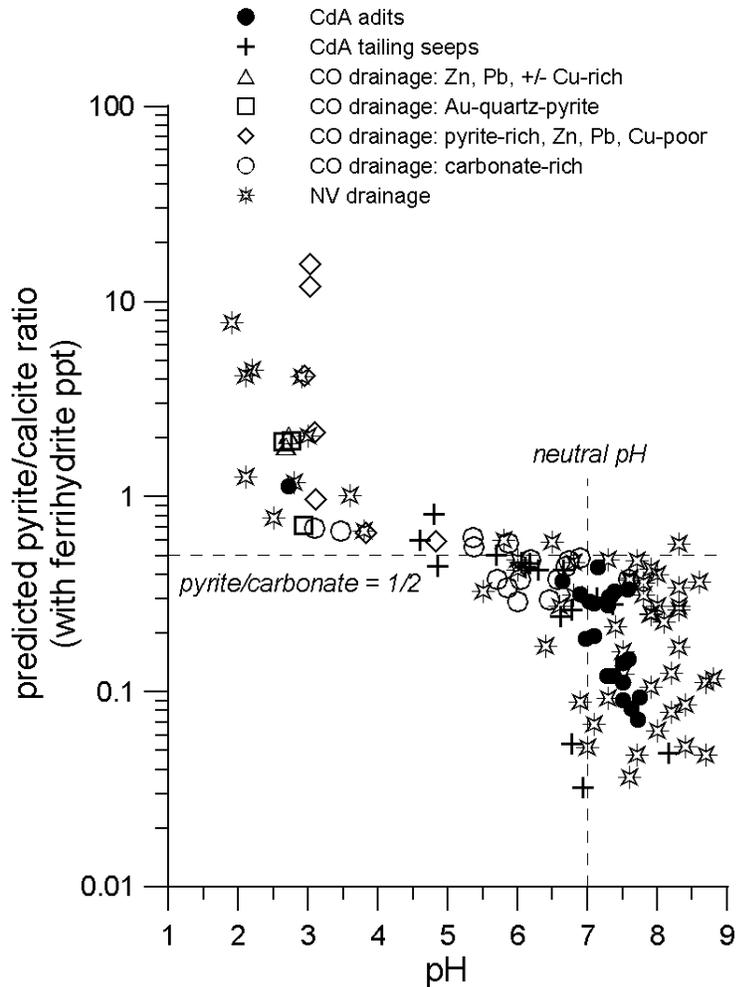


Figure 10. Comparisons between the predicted ratios of reacting pyrite to calcite, considering precipitation of ferrihydrite and calculated as pyritic  $\text{SO}_4/(\text{Ca} + \text{Mg})$  in drainage, versus the pH of drainage from polymetallic vein deposits in the Coeur d'Alene mining district, in the Colorado Mineral Belt, and in the Humboldt Basin in northern Nevada.

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