Statistical and Geochemical Analyses of Vadose and Saturated Pore Waters in Sulfidic Mine Waste Tailings

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ABSTRACT

U.S. Bureau of Mines researchers conducted field studies at an abandoned copper-gold mine tailings impoundment in northern Washington State for over 2 years. Measurements of pore water quality were collected from the vadose and saturated zones. Principal component analysis (PCA) was used to calculate linear combinations of those water-quality variables that could account for the maximum correlation in each of the two zones. The PCA indicated that linear combinations of those variables reflecting sulfide oxidation and aluminum-silicate weathering best summarized the variability in each zone. A univariate analysis of variance (ANOVA) of seven of the 18 variables indicated that the groundwater chemistry of the two zones was significantly different, while multivariate analyses of variance (MANOVA) run on several sets of variables suggested that only one of these sets (Eh, Fe, Mn, S, Pb, and Zn) indicated a significant difference between the two zones. The geochemical computer model WATEQ4F was used to assess the solubility status (saturation index) of minerals with respect to the dissolved constituents. Saturation indices of the following minerals were different in the two zones: alunite, $Al(OH)SO_4$, anglesite, gypsum, K-mica, (K,Mg)-montmorillonite, kaolinite, and melanterite. Comparing statistical to geochemical analyses demonstrated that the statistical analysis produced similar or complementary results to the geochemical model.

INTRODUCTION

Sulfide oxidation is known to be influenced by chemical and physical factors. In sulfide mine waste tailings, differences in these factors as found between the vadose (unsaturated) zone and the saturated zone are important in characterizing mine waste-water quality and contaminant leaching. In this paper, the statistical techniques PCA, ANOVA, and MANOVA are used to distinguish the vadose and saturated zones of a copper-gold mine tailings impoundment, while WATEQ4F,(1) a computer code, is used to perform equilibrium thermodynamic geochemical computations. ANOVA calculations are made on a variable-by-variable basis. However, PCA, MANOVA, and WATEQ4F can take into account multivariate (as opposed to pairwise) correlations among water-quality variables. PCA and MANOVA account for multivariate correlations with no foreknowledge of the chemical relations, while WATEQ4F imposes chemical rules according to thermodynamically feasible group correlations. This study demonstrates that statistical and geochemical approaches can result in both similar and complementary descriptions of aqueous geochemical systems.

Background

Pore waters were sampled from the vadose and saturated zones of a 200- by 46-m (650- by 150-ft) tailings impoundment, which had been in use from 1939 to 1953. The impoundment had an average depth of about 3.7 m (12 ft) and a maximum depth of 6.1 m (20 ft). The unconfined phreatic surface was at a depth of approximately 3 m (10 ft). The source ore body was a massive sulfide deposit in igneous (andesitic-rhyolitic) rock.

The tailings consisted of 95% gangue minerals,(11) primarily plagioclase $[(Na,Ca)(Al,Si)AlSi_2O_8]$, quartz $[SiO_2]$, orthoclase $[KAlSi_3O_8]$, chlorite $[(Mg,Fe,Al)_6(Al,Si)_4O_{10}(OH)_8]$, and K-mica $[KAl_2(AlSi_3O_{10})(OH)_2]$. The remaining 5% were sulfide minerals, predominantly pyrite $[FeS_2]$, minor amounts of chalcopyrite $[CuFeS_2]$ and sphalerite $[(Zn,Fe),S]$, and trace amounts of galena $[PbS]$. No carbonate minerals were observed. The high boron [B] concentrations probably originated from tourmaline $[(Na,Ca)(Li,Mg,Al)_3(Al,Fe,Mn)_6(BO_3)_3(Si_6O_{18})(OH)_4]$, which is a common accessory mineral in igneous rocks. Dissolved concentrations of manganese [Mn] were probably originally substituted in chlorite and in other trace minerals, and the trace amounts of nickel [Ni] were probably substituted in pyrite and chlorite.

Procedure

The tailings impoundment water sampling devices (Figure 1, Table 1) were BAT hydroprobe samplers (B)[1] with cylindrical porous filter tips and piezometer wells (P). The BAT samplers were installed in the vadose and saturated zones of the impoundment in two clusters (Figure 1). Samples were withdrawn from the samplers by vacuum when an evacuated vial in a sampling housing was lowered down the hole, which forced a double-ended needle into a septum at the top of the downhole tip and into a septum in the evacuated vial. The P-wells were placed only in the saturated zone of the impoundment. Other details of sample collection, filtration, preservation, and analytical procedures are discussed in Stewart et al.(11)

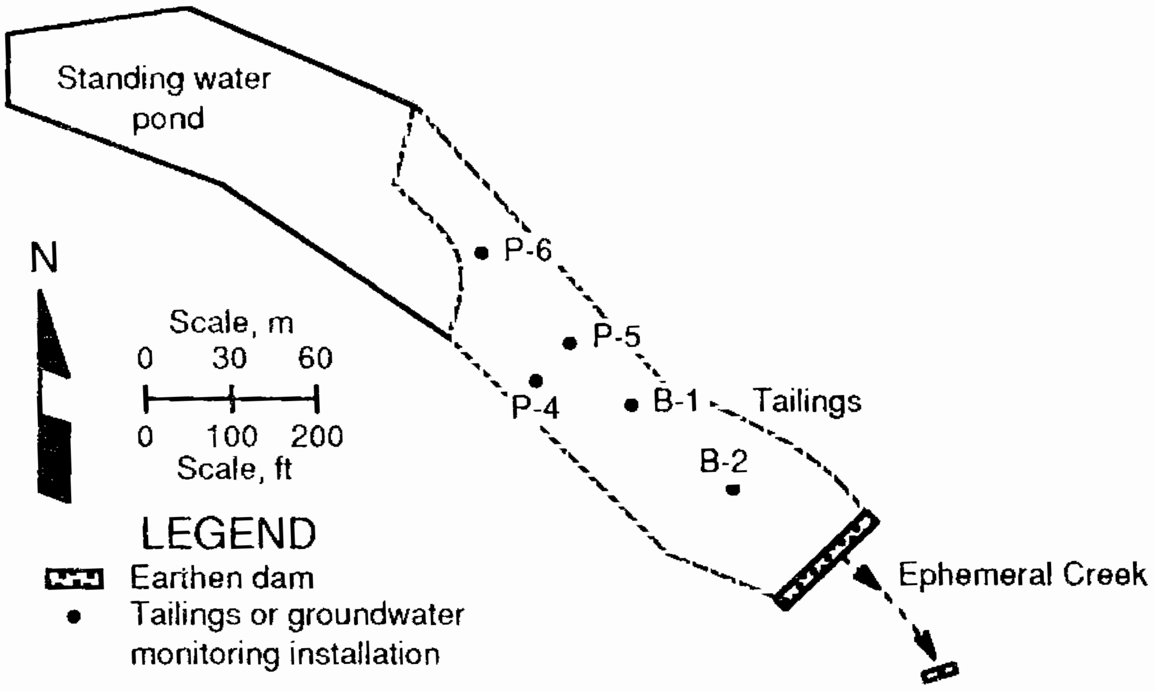

Figure 1.--Location of hydroprobe samplers and piezometer wells.

The data from this site were collected monthly over 2 years. The water-quality parameters measured were pH, redox potential [Eh], temperature, and dissolved concentrations of aluminum [Al], boron [B], barium [Ba], calcium [Ca], cadmium [Cd], copper [Cu], iron [Fe], magnesium [Mg], manganese [Mn], sodium [Na], nickel [Ni], lead [Pb], silicon [Si], sulfur [S], and zinc [Zn].

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[1] *Reference to specific equipment or trade names does not imply endorsement by the Bureau of Mines.*

Values of pH were found to be lower in the vadose zone, while values of Eh were higher, indicating that the vadose zone was more oxidizing than the saturated zone. However, dissolved constituents tended to be more highly concentrated in the saturated zone. These and other trends are discussed in Williams et al.(14) Dissolved oxygen [DO] was not measured in the B samples because the BAT sampling procedure exerts a strong enough vacuum to withdraw DO from solution in the sample fluid. Also, the influence of low levels of DO on redox status is insignificant in waters with low pH and large amounts of dissolved concentrations of iron. Therefore the variable DO was not considered in the statistical analyses or estimated for WATEQ4F input.

Table 1.--Depths and completion zones of water sampling devices

Sample location ID	Depth below surface, m	(ft)	Completion zone
Cluster B1:			
B-104	1.2	(4.0)	Vadose
B-107	2.1	(7.0)	Vadose
B-116	4.9	(16.0)	Saturated
Cluster B2:			
B-204	1.2	(4.0)	Vadose
B-208	2.4	(8.0)	Vadose
B-216	4.9	(16.0)	Saturated
P-wells:			
P4	4.7	(15.4)	Saturated
P5	4.5	(14.7)	Saturated
P6	5.0	(16.5)	Saturated

Data Preparation

Before the data were analyzed, all sample sets were tested for outliers using the Grubbs test.(12) The most conservative rejection probability available, that is, a 0.1% risk of false rejection, was used.

The normalities of the original sample distributions were then investigated, which is important because MANOVA and ANOVA are based on assumptions of normality. Because many water-quality data have been found to be log-normally distributed,(5) the normality of the original data from this site was compared to the normality of the log-transformed data. It was found that all variables except Eh tended to be either strongly log normal, or were as strongly log normal as normal. Therefore, for all statistical tests, all variables except Eh and pH (which, as the negative log of the concentration of H^+, is in log space already) were subjected to a log transformation.

All measurements were standardized or rescaled by using the equation $x^* = (x - x_m)/s$, where x^* = standardized measurement, x = measurement, x_m = variable mean over all measurements of that variable, and s = standard deviation over all measurements of that variable. Standardization was performed because the variables were measured in different units (e.g., mV and mg/L) and had widely different ranges.(4)

Principal Component Analysis

The first statistical procedure used was PCA, a multivariate procedure that calculates components that are linear combinations of original variables as based upon the variance-covariance structure of the data. This procedure is useful because usually system variability can be represented by a smaller number of principal components than there are original variables. The first principal component can be viewed geometrically as the rotation of the axes of all the variables that accounts for maximum variability as determined by multivariate (joint) correlations among the variables. Each subsequent principal component is calculated to be orthogonal, and therefore uncorrelated, to the previous one and is also calculated to maximize the remaining variability. Typically, the first few components account for most of the variability. A detailed presentation of PCA can be found in Johnson and Wichern.(4)

__Vadose Zone__--The principal components for the vadose zone are presented in Table 2. Three principal components account for 79% of the variation. Adding additional components does little to improve characterization of the zone.

The first principal component in the vadose zone appears to be a weighted average of Al, B, Ca, Cd, Cu, Fe, Mg, Mn, Na, S, and Zn because these variables have larger coefficients than the other variables. This list includes the dissolved constituents from oxidized sulfides such as pyrite and chalcopyrite. The role of Ca and Al in the component may be controlled by the dissolution of a plagioclase mineral such as anorthite [$CaO{\cdot}Al_2O_3{\cdot}2SiO_2$]; the presence of Ca in soils often depends upon plagioclase weathering.(3) The presence of Mg, Fe, and Al probably arises from the acid dissolution of alumino-silicates such as chlorite and montmorillonite [$(Al,Mg)_8(Si_4O_{10})_4(OH)_8{\cdot}12H_2O$], which degrade in acid sulfate environments.(2) The presence of Na is probably due to the acid sulfate weathering of albite [$NaAlSi_3O_8$], a sodium end member of the plagioclase solid solution series. The dissolved metals Cd and Zn are soluble in an acid environment, so they are probably most correlated to S and the sulfide metals.

The second principal component appears to relate Eh and Si inversely to pH and K. This is defensible because Eh and pH are inversely related in an oxidizing system. The inverse relation between Si and pH can be explained in terms of the weathering of chlorite, K-mica, and montmorillonite; these minerals are more soluble at lower pH levels.

The third principal component in the vadose zone appears to relate Pb inversely to Eh, Ba, and Si. This may reflect the inverse relationship between the solubility of some Pb species and Eh. (Most metals, although not Pb, are directly related to Eh).

__Saturated Zone__--Three principal components (Table 2) account for 70% of the variability in the saturated zone. Adding additional components does little to improve characterization of this zone.

The first principal component appears to weigh equally the variables B, Fe, Mg, Mn, Ni, S, and Zn. This suite is smaller than that of the first principal component in the vadose zone because Al, Ca, Cd, and Cu are absent; however, the variable Ni is included. The second principal component relates pH inversely to Eh, Al, and Cd. This suggests that the relationship between Al and Cd in the saturated zone is pH and Eh dependent. The third principal component in the saturated zone appears to relate Na and Pb inversely to Ba and Cu.

The following is a summary of the results of the PCA as well as some interpretations of the findings.

Table 2.--Principal components in vadose and saturated zones

Variable	Component coefficients					
	1	2	3	1	2	3
	VADOSE ZONE			SATURATED ZONE		
pH	-0.08	**0.53**	0.21	0.15	**-0.36**	0.08
Eh	.03	**-.43**	**.34**	-.23	**.34**	.06
Element:						
Al	**.29**	.001	.12	-.10	**.49**	.06
B	**.28**	-.09	.01	**.33**	.13	.10
Ba	-.005	.04	**.61**	.07	-.04	**.48**
Ca	**.29**	.07	.12	.11	-.24	-.12
Cd	**.29**	-.04	-.11	-.12	**.47**	-.15
Cu	**.29**	-.01	.05	-.12	.10	**.49**
Fe	**.30**	-.08	.04	**.34**	.15	.07
K	-.10	**.40**	.22	.24	-.07	-.20
Mg	**.29**	.07	.11	**.35**	.13	.04
Mn	**.30**	.12	.03	**.34**	.10	-.03
Na	**.26**	.25	.02	-.04	.01	**-.53**
Ni	.15	.11	.08	**.34**	.14	-.001
Pb	.16	-.14	**-.46**	.06	.20	**-.35**
S	**.30**	-.02	.06	**.33**	.16	.06
Si	-.08	**-.49**	**.37**	-.08	.25	.08
Zn	**.29**	-.01	-.05	**.35**	.10	.01
Proportion of variability	0.59	0.12	0.08	0.44	0.16	0.10
Cumulative variability	.59	.71	.79	.44	.60	.70

NOTE: Bolding indicates component coefficients with the largest absolute values relative to other variable coefficients. Significance is discussed in the text.

1. The principal components, with three variables each, account for 70 to 80% of the variability in each zone. In both zones, these three variables point to two or three key mechanisms: Sulfide oxidation, aluminum-silicate weathering, and cation exchange.

2. The first principal component in the vadose zone appears to include weighted averages of variables resulting from sulfide oxidation and aluminum-silicate weathering.

3. The first principal component in the saturated zone appears to be dominated only by variables of sulfide oxidation and not by those from aluminum-silicate weathering; aluminum is a part of the second component in the saturated zone.

4. The second component in the vadose zone reflects an acidic, oxidizing environment, because pH is inversely related to Eh. This inverse relation is not as pronounced in the second component of the saturated zone (the coefficients for these two variables are not as large), probably because the saturated zone is not as acidic or as oxidizing as the vadose zone.

5. The second component in the vadose zone relates Si inversely to K and Na in addition to inversely relating Eh and pH. This result reflects cation exchange and/or the operation of aluminum-silicate aqueous equilibria mechanisms.

6. The second component in the saturated zone indicates a pH- and Eh-dependent relationship between Al and Cd.

7. The third component in the vadose zone reflects an inverse relationship between the solubility of some Pb species and Eh.

8. The third components in both zones relate Pb inversely to Ba.

Univariate Analyses of Variance

With ANOVA, the means of a single variable measured under two or more conditions can be compared to test whether the variable is significantly different under the different conditions. In this study, separate analyses using the two zones as the independent classification variables, location within each zone as the second-level classification variable, and time as the repeated measure were run on 18 water-quality variables to test the hypothesis that the saturated and vadose zones were statistically the same for each variable. ANOVA depends upon calculation of an F test, which is a generalized case of the Student's *t* test. The appropriate format of ANOVA for this database included calculation of a zone-comparison F statistic that consisted of a ratio of the between-zone variance to the within-zone variance. The denominator of the zone-comparison F statistic was designed to account for nested variation attributable to the location in each zone because in this study, each location was sampled several times rather than several locations being sampled only once. Another F statistic represented the zone-time interaction. If a significant zone-time interaction were present (i.e., if it were impossible to distinguish the variation resulting from time from the variation resulting from zone), the zone-comparison F statistic would not necessarily be valid. For both F tests, the calculated probability of a Type I error was compared at a level of significance of $\alpha = 0.05$. This level of significance is used frequently in the natural sciences.

The results of the ANOVA for the interaction effect of zone-with-time are presented in Table 3. The zone-with-time interaction is found to be insignificant for the majority of variables, but Ba, Ca, and Pb appear to have an interaction effect. ANOVA comparisons of the two zones are presented in Table 4. The two zones were found to be significantly different for seven of the variables (Eh, B, Fe, K, Mn, Ni, and Zn) at the $\alpha = 0.05$ level of significance. The other eight variables (pH, Al, Cd, Cu, Mg, Na, S, and Si) were not significantly different at $\alpha = 0.05$. Note, however, that if a level of significance of $\alpha = 0.1$ had been used rather than $\alpha = 0.05$, then pH, Mg, S, and Si would have been significantly different in the two zones.

Table 3.--Univariate F tests of zone and time interaction
(Hypothesis: zone-time interaction shows no significant effect)

Reject hypothesis[1]			Cannot reject hypothesis[2]		
Variable	F statistic	Probability	Variable	F statistic	Probability
Element:			pH	1.56	0.0891
Ba	2.66	0.0017	Eh	1.01	.4472
Ca	1.92	.0208	Element:		
Pb	3.60	.0001	Al	1.01	.1082
			B	1.45	.1340
			Cd	.85	.6401
			Cu	.62	.5847
			Fe	.97	.8772
			K	1.02	.4402
			Mg	.97	.5022
			Mn	.82	.6681
			Na	1.41	.1387
			Ni	1.65	.0702
			S	.67	.8362
			Si	.88	.5891
			Zn	.50	.9548

[1] Zone-time interaction is significant.
[2] Zone-time interaction is not significant.

Table 4.--Results of univariate F tests of zone comparisons
(Hypothesis: means of each variable are the same in the two zones)

Reject hypothesis[1]			Cannot reject hypothesis[2]		
Variable	F statistic	Probability	Variable	F statistic	Probability
Eh	9.18	0.0191	pH	3.63	0.0986
Element:			Element:		
B	5.91	.0453	Al	.10	.7562
Fe	6.57	.0374	Ba[3]	.91	.3724
K	5.74	.0478	Ca[3]	1.01	.3480
Mn	8.83	.0208	Cd	.97	.3574
Ni	5.33	.0542	Cu	.11	.7475
Pb[3]	62.42	.0001	Mg	4.63	.0685
Zn	6.98	.0333	Na	.01	.9269
			S	4.91	.0622
			Si	4.91	.0623

[1] Zones are significantly different.
[2] Zones are not significantly different.
[3] Zone comparisons are not necessarily valid for these variables because their zone-time interactions are significant (Table 3).

The following is a summary of the levels of each constituent in the two zones using ANOVA.

1. A zone-time interaction is significant for Ba, Ca, and Pb. Therefore, the between-zone comparisons for these three variables are not necessarily valid.

2. The two zones appear to be significantly different on the basis of several sulfide oxidation variables (Eh, Fe, Mn, and Zn), two aluminum-silicate weathering variables (B and K), and the metal Ni.

3. The two zones appear marginally different on the basis of the sulfide oxidation variable S and the aluminum-silicate weathering variables Mg and Si.

4. The two zones appear to be effectively the same on the basis of concentrations of aluminum-silicate variables Al, Ca, and Na, and metals Ba, Cd, and Cu.

5. Overall, the zones appear to be more different on the basis of sulfide oxidation than on the basis of aluminum-silicate weathering or any other mechanism.

Multivariate Analysis of Variance

In MANOVA, the means of several variables measured under two or more conditions are co-evaluated to determine whether the conditions are significantly different. As with ANOVA, F statistics are calculated; however, in MANOVA, the computations are based upon matrix calculations that incorporate shared sources of variation. MANOVA and other multivariate techniques have been applied to water-quality databases by Williams,(13) Steinhorst and Williams,(10) Riley,(8) and Riley et al.(9)

Several MANOVA's were performed using the two zones as the independent variables to test the hypothesis that the multivariate water-quality "fingerprints" in the two zones were significantly different. MANOVA has a similar structure to ANOVA in that the zone-time interaction F statistic is evaluated as an indication of the validity of the zone-comparison F statistic. Because of the sampling network design, there were insufficient degrees of freedom to consider all 18 water-quality variables at the same time in one MANOVA. Several combinations of variables were tested, but only one combination (Pb, Mn, Eh, Zn, Fe, and S) had an insignificant zone-time interaction and a significant zone comparison. The canonical coefficients for the variables (Table 5) result from a technique called canonical discriminant analysis and identify linear combinations of variables that maximize the between-zone variation in the same manner as PCA maximizes within-zone variation. Note that the most important variables (as indicated by the magnitudes of the canonical coefficients) of the MANOVA are Pb, Zn, and S, even though the ANOVA for Pb was not necessarily valid because of an interaction effect and S failed the univariate test.

Thus, given the structure of the database, the two zones were significantly different only when a shared distribution was based upon Pb, Mn, Eh, Zn, Fe, and S. This is a very specific statement of significant difference between the two zones and is consistent with the finding from the ANOVA, in which the zones appeared to be more different when sulfide oxidation was considered than when aluminum-silicate weathering was considered.

Table 5.--Results of multivariate F tests

	F statistic	Probability	Significant
Zone-time interaction	1.26	0.0858	No
Zone comparison	122.5	.0081	Yes

Canonical coefficients: Eh = −3.8, Fe = −1.9, Mn = −0.8, S = 5.9, Pb = 9.4, and Zn = −7.8

NOTE: Six other combinations of variables were considered, but in each case, the zone-time interaction was unacceptable or the zone comparison was insignificant. These combinations were:

1. pH, Eh, B, Fe, Mn, Pb, Zn
2. pH, Eh, Fe, Mn, Pb, Zn
3. pH, Eh, B, Mn, Pb, Zn
4. pH, Eh, Fe, Mn, S, Zn
5. pH, Eh, K, Mn, Pb, Zn
6. pH, Al, Cd, K, Mn, Pb

Saturation Index Results

The computer code WATEQ4F, recently updated by Nordstrom et al.,(7) contains thermodynamic data for the solubility products of hundreds of minerals and calculates the saturation indices of all possible minerals, given the dissolved constituents. The saturation index is defined as the log of the ratio of (1) the solubility product of the mineral based on ionic activity and computed from the input sample data to (2) the maximum solubility product of the mineral at equilibrium under the same conditions. Therefore, when the mineral saturation index is 0, the mineral is in equilibrium; when the index has a negative sign, the mineral is undersaturated; and when it has a positive sign, the mineral is supersaturated. An undersaturated mineral has a tendency to dissolve and a supersaturated mineral to precipitate, but whether a phase change will actually occur depends upon the kinetics of the system. The code WATEQ4F does not include kinetic data nor algorithms. The accuracy of the model's predictive ability depends on reaction kinetics, the quality of the field and laboratory data, and the matrix mineralogy of the host rock. The defensibility of model output is also diminished for waters of extremely high ionic strength (dissolved concentrations), such as the water sampled in this study. Therefore, the interpretations based upon WATEQ4F output are expressed herein in qualitative, rather than quantitative, terms.

The mineral species tracked for changes in solubility status are presented in Table 6. The status of each mineral is based on the range of saturation indices for that mineral in all locations at different sampling times. For example, the saturation index for chalcedony at different locations in the vadose zone at several different sampling times ranges from 0.8 to 1.3, and so the mineral's status is noted as oversaturated. WATEQ4F indicates that seven minerals of the 24 considered undergo a discernable change in saturation index between the vadose and saturated zones; these are alunite, the aluminum hydroxysulfate $Al(OH)SO_4$, anglesite, gypsum, melanterite, K-mica, and (K,Mg)-montmorillonite. These minerals are all either sulfates (which are sulfide oxidation products) or aluminum silicates.

Table 6.--Status of saturation indices of several minerals in vadose and saturated zones based on WATEQ4F calculations

Mineral	Mineral equation	Zone status	
		Vadose	Saturated
Albite	$NaAlSi_3O_8$	U	U
Boehmite	$Al_2O_3 \cdot 3H_2O$	U	U
Chlorite	$(Mg,Fe)_3(Si,Al)_4O_{10}$- $(OH)_2 \cdot (Mg,Fe)_3(OH)_6$	U	U
Gibbsite	$Al(OH)_3$	U	U
(K,Mg)-montmorillonite	$(K,Mg,Fe)Al(AL,Si)_4$- $O_{10}(OH)_2 \cdot 10H_2O$	U	UU
Sepiolite	$Mg_2Si_3O_8 \cdot 2H_2O$	U	U
Melanterite	$FeSO_4 \cdot 7H_2O$	U	UE
Anglesite	$PbSO_4$	U	E
Gypsum	$CaSO_4 \cdot 2H_2O$	UE	OE
K-mica	$KAl_3Si_3O_{10}(OH)_2$	UE	E
Kaolinite	$Al_2Si_2O_5(OH)_4$	UE	O
Ca-montmorillonite	$Ca(Mg,Fe)Al(Al,Si)_4$- $O_{10}(OH)_2 \cdot 10H_2O$	E	E
Ferrihydrite	$Fe(OH)_3$	E	E
H-jarosite	$(H_3O)Fe_3(SO_4)_2(OH)_6$	E	E
Na-jarosite	$NaFe_3(SO_4)_2(OH)_6$	E	E
Amorphous SiO_2	SiO_2	E	E
Barite	$BaSO_4$	OE	OE
$Al(OH)SO_4$	$Al(OH)SO_4$	O	OO
Alunite	$K(AlO)_3(SO_4)_2 \cdot 3H_2O$	O	OO
Chalcedony	SiO_2	O	O
Cuprousferrite	$CuFeO_2$	O	O
Cupricferrite	$CuFe_2O_4$	O	O
Goethite	$Fe(O)(OH)$	O	O
K-jarosite	$KFe_3(SO_4)_2(OH)_6$	O	O

O = Oversaturated. E = Equilibrium. U = Undersaturated.
UE = Ranging from undersaturated to equilibrium.
OE = Ranging from oversaturated to equilibrium.
OO = More oversaturated than in the other zone.
UU = Less undersaturated (closer to equilibrium) than in the other zone.

Metal oxides other than the iron oxides are not included in Table 6 because they do not exist in low-pH, highly oxidizing systems. In both zones, iron oxides in equilibrium or are oversaturated, with a tendency to precipitate. Several of the minerals in equilibrium in one or both zones are those associated with acid sulfate environments:(6) melanterite, ferrihydrite, and jarosite.

Comparative Results

PCA identified highly correlated groups of variables on the basis of sulfide oxidation and aluminum-silicate weathering. ANOVA and MANOVA distinguished the two zones on the basis of approximately nine sulfide oxidation variables. WATEQ4F indicated that the minerals that underwent phase changes between the vadose and saturated zones were sulfate (alunite, $Al(OH)SO_4$, anglesite, gypsum, and melanterite) and aluminum-silicate (K-mica and (K,Mg)-montmorillonite) minerals. Of the critical variables identified by the MANOVA (Eh, Fe, Mn, S, Pb, and Zn) as differentiating the two zones, Eh, Fe, S, and Pb were constituents of minerals that WATEQ4F predicted would undergo changes in saturation status. Although Mn and Zn were not directly represented in the list of phase-changing minerals, it is common for most available metals to be coprecipitated with iron hydroxides. The minerals identified by WATEQ4F to be in equilibrium in both zones had constituents (Al, Ca, Fe, Mg, Na, and S) that were represented in the first principal component of one or both zones.

The findings from the statistical analyses and WATEQ4F were consistent because all analyses identified sulfide oxidation and aluminum-silicate variables as critical to characterizing and distinguishing the two hydrologic zones. Although the statistical analyses were unbiased with respect to chemical reactions, they successfully identified changes in concentrations resulting from the hydrogeochemical environments in the zones.

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