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## Potential solid phases controlling dissolved aluminium and iron concentrations in acidic soils

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### Abstract

Acidic soils often have high concentrations of dissolved aluminium (Al) and iron (Fe) in their solutions. The objective of this study was to determine potential solid phases controlling dissolved Al and Fe concentrations in pyritic (FeS<sub>2</sub>) soils undergoing oxidation. Soil samples were extracted with distilled-deionised H<sub>2</sub>O after reacting for 14, 21 and 28 days (d) at 25±1°C. Soil water extracts were analysed for pH, Eh, total concentrations of Al and Fe as well as other cations and anions. From these, ion activities and ion activity products (IAPs) were calculated and compared with solubility products (K<sub>sp</sub>s). The importance of dissolved organic carbon (DOC) complexes of Al<sup>3+</sup> and Fe<sup>3+</sup> in soil extracts was also evaluated. The pH of the samples ranged from 6.6 to 2.3 and pe+pH ranged between 8.9 and 13.4. Aluminium concentrations ranged from 0.04 to 196 mg L<sup>-1</sup> and Fe from 0.38 to 337 mg L<sup>-1</sup>. The SO<sub>4</sub><sup>2-</sup> concentrations were found to be 253 to 4,924 mg L<sup>-1</sup>. As pyrite (FeS<sub>2</sub>) oxidised, pH decreased and soluble concentrations of Al<sup>3+</sup>, Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> increased in soil water extracts. Chemical speciation indicated that DOC complexes of Fe<sup>3+</sup> were significant in low pH soil water extracts. For near neutral to slightly acidic soils, the IAPs suggested saturation with respect to Al(OH)<sub>3</sub> (gibbsite). At extreme low pH, the IAPs were in equilibrium with Al(SO<sub>4</sub>)(OH).5H<sub>2</sub>O (jurbanite). Results obtained on iron solid phases indicated that Fe(OH)<sub>3</sub> (amorphous iron) before oxidation of FeS<sub>2</sub>, FeOOH (goethite) in slightly acidic environments, and FeSO<sub>4</sub>.7H<sub>2</sub>O (melanite) in extreme acidic environments may have potential for controlling Fe<sup>3+</sup> concentrations.

### Introduction

In a natural aerobic environment (i.e. in the presence of oxygen and water) there is potential for inorganic compounds to oxidise and produce acidity. The best example of this natural phenomenon is the oxidation of pyrite (FeS<sub>2</sub>) that occurs in acid sulfate soils (Van Breeman, 1973). Several plant and soil related problems are associated with the oxidation of pyrite in soils. For example, acidic conditions limit plant growth in soils by increasing the availability of Al and Fe that become more soluble at low pH (Armingier et al., 1976; Barnhisel, 1977; Kennedy, 1986; Tucker et al., 1987).

In acid environments, Al and Fe solubilities are often assumed to be governed by hydroxides (e.g. Al(OH)<sub>3</sub>, Fe(OH)<sub>3</sub>). The aqueous geochemistry of Al and Fe, however, is significantly modified by the oxidation of FeS<sub>2</sub>. To predict the availability of Al and Fe

to plants, it is important to determine the solid phase equilibria, i.e. potential solid phase (source) governing the solubilities of these elements in low pH environments. Such information is also essential for effective management of plant and soil interactions with Al and Fe in low pH environments.

Understanding these relationships in areas where soil disturbance (e.g. by surface coal mining) is a prevalent part of the land use is particularly important. However, chemical speciation and potential solid phases governing the concentrations of Al and Fe in acid environments have not been fully explored. Our objectives were to examine chemical speciation of Al and Fe in soil water extracts, to ascertain the importance of DOC complexes of Al<sup>3+</sup> and Fe<sup>3+</sup> on the determination of IAPs and Al and Fe solid phases and finally, to predict solid phases governing the dissolved Al and Fe concentrations in soils at low pH.

## Material and methods

Seven pyrite unoxidised and oxidised surface soil samples were collected from the Glenrock, which is located at the southern edge of the Powder River Basin, Wyoming, USA. The climate of the Powder River Basin is temperate and semiarid. The average daily temperature varies from a low of  $-15^{\circ}\text{C}$  in the winter to  $32^{\circ}\text{C}$  in July. Precipitation ranges from 27 cm in the southern part of the study area to 45 cm in the north (Martin et al., 1988). The geology of the Powder River Basin is the Fort Union and Wasatch formations of early Tertiary age and consist of continental-type sediments deposited in fluvial, lacustrine and swampy environments. Strata in these formations are lenticular and consist of alternating sandstone, siltstone and claystone, with occasional coal beds (Naftz and Rice, 1989).

Samples were sieved through a two mm screen and analysed for organic matter (OM),  $\text{CaCO}_3$  content and pyritic sulfur. Fifty grams of each sample, in triplicate, were suspended in 150 mL of distilled-deionised  $\text{H}_2\text{O}$  in 250 mL flasks for solubility measurements. Four drops of toluene were added to each sample suspension which were then closed tightly with a rubber stopper to minimise the oxidation of  $\text{FeS}_2$  during the shaking.

Sample suspensions were agitated on a rotary shaker at 200 rpm at  $25 \pm 1^{\circ}\text{C}$ . The pH of the sample suspensions was measured before and after each reaction period to determine the oxidation of  $\text{FeS}_2$ . After reacting for 14, 21 and 28 d sample suspensions were centrifuged and filtered through 0.45- $\mu\text{m}$  millipore filter. Each extract was divided into two subsamples. One was acidified with HCl to pH 4.0–4.5 and the other one was left unacidified and analysed for pH, Eh, total carbonate species, sulfate, fluoride and chloride. Acidified extracts were analysed for various cations, anions and DOC.

The pH was measured with an Orion combination electrode. The Eh was measured with an Orion platinum (Pt) electrode with a  $\text{Ag}/\text{AgCl}_2$  reference electrode. The Eh readings were taken over a period of 0.5 to two hours until the drift was less than three mV. Stable readings were always obtained within two hours. Stability of the readings was confirmed in selected extracts by monitoring the readings over a period of 24 h. From Eh measurements,  $p_e$  ( $-\log e^-$  activity) was calculated.

Carbonate species were measured by titrating extracts with standardised HCl to pH 4.5 end point. Calcium, Mg, Si, Al, Fe, Mn and B were measured

with inductively coupled plasma optical emission spectrometry (ICP-OES). Potassium and Na were measured with atomic emission. Ion chromatography was used to measure the concentrations of sulfate, fluoride and chloride. The DOC was analysed with a carbon analyser.

The speciation model GEOCHEM (Sposito and Mattigod, 1980) was used to calculate ion activities. This model uses total elemental concentrations and pH of extracts to calculate ion activities. From ion activities, ion activity products (IAPs) were calculated and compared with solubility products ( $K_{sp}$ s) to evaluate potential solid phases controlling the concentration of Al and Fe in soil water extracts. We assumed that IAPs within  $\pm 0.50$  log units of  $K_{sp}$ s of solid phases represented near saturation with respect to that solid phase. The variation within that range is accounted for by the uncertainty of IAP estimations and  $K_{sp}$  measurements (Stumm and Morgan, 1981). Ion activities were also calculated using MINTEQA2 (Brown and Allison, 1992) for comparison.

## Results and discussion

Selected properties of the soil samples showed that OM content varied from 0.4 to 1.6% and  $\text{CaCO}_3$  content was below 0.2%. The pH measurements before and after solubility experiments suggested that  $\text{FeS}_2$  did not oxidise during the reaction time (i.e. 14–28 d). Selected chemical data of soil water extracts (Table 1) suggested near steady state conditions. Therefore, day 28 data were selected for geochemical modelling.

The behaviour of Al and Fe in low pH soil environments is controlled by a number of chemical processes, including formation of soluble inorganic and organic complexes and solid phase equilibria. Several geochemical models, such as GEOCHEM, MINTEQA2, EQ3/EQ6, SOLMINEQ and WATEQFC are available to predict possible controls on chemical processes in soils. Among these models, GEOCHEM and MINTEQA2 are widely used to predict the chemical speciation and the solid phase equilibria. Therefore, these models were selected and evaluated for chemical modelling of soil water extracts (Tables 2 and 3).

Naturally-occurring DOC, comprised largely of fulvic acids released during microbial decomposition of organic matter, may complex with  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions (Antweiler and Drever, 1983) in soil solutions. Determination of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  in soil water extracts with ICP or AA probably includes both inorganic and

Table 1. Selected chemical data of soil water extracts for 28 d reaction period, mean of triplicate analyses

No.	pH	Eh (mV)	Al <sub>T</sub> <sup>a</sup> (log mol L <sup>-1</sup> )	Fe <sub>T</sub> <sup>a</sup>	S <sub>T</sub> <sup>a</sup>
Sample 1	6.6	321	6.10	5.15	2.57
Sample 2	5.6	220	5.80	4.16	2.07
Sample 3	5.4	211	5.35	5.12	2.38
Sample 4	5.1	410	5.47	3.84	2.41
Sample 5	2.5	602	2.37	4.06	1.37
Sample 6	2.4	605	2.32	3.94	1.34
Sample 7	2.3	624	2.14	2.24	1.30

<sup>a</sup> Al<sub>T</sub> = total dissolved Al concentration in soil water extracts, Fe<sub>T</sub> = total dissolved Fe concentration in soil water extracts, and S<sub>T</sub> = total dissolved SO<sub>4</sub><sup>2-</sup> concentration in soil water extracts.

Table 2. Comparison of Al<sup>3+</sup> activities calculated by GEOCHEM and MINTEQA2

No.	DOC (mg L <sup>-1</sup> )	Al <sup>3+</sup> activity (-log) <sup>a</sup>		Al <sup>3+</sup> activity (-log) <sup>b</sup>	
		with DOC	without DOC	with DOC	without DOC
Sample 1	56.9	11.18	11.90	10.30	10.30
Sample 2	26.2	8.19	8.18	7.42	7.42
Sample 3	37.2	7.28	7.29	6.62	6.62
Sample 4	12.7	7.07	7.08	6.76	6.76
Sample 5	11.4	3.88	3.87	3.93	3.93
Sample 6	14.4	3.82	3.81	3.88	3.88
Sample 7	28.4	3.52	3.53	3.60	3.60

<sup>a</sup> Calculations made by GEOCHEM.

<sup>b</sup> Calculations made by MINTEQA2.

Table 3. Comparison of Fe<sup>3+</sup> activities calculated by GEOCHEM and MINTEQA2

No.	DOC (mg L <sup>-1</sup> )	Fe <sup>3+</sup> activity (-log) <sup>a</sup>		Fe <sup>3+</sup> activity (-log) <sup>b</sup>	
		with DOC	without DOC	with DOC	without DOC
Sample 1	56.9	14.64	13.90	12.75	12.75
Sample 2	26.2	14.37	13.79	9.83	9.78
Sample 3	37.2	15.85	14.80	10.56	10.37
Sample 4	12.7	10.72	10.18	8.55	8.50
Sample 5	11.4	7.77	7.54	6.40	6.30
Sample 6	14.4	7.67	7.39	6.28	6.18
Sample 7	28.4	5.22	5.12	4.35	4.35

<sup>a</sup> Calculations made by GEOCHEM.

<sup>b</sup> Calculations made by MINTEQA2.

Table 4. Activities of selected elements in soil water extracts<sup>a</sup>

No.	Pyritic Sulfur %	pH	pe+pH	(-log)		
				Al <sup>3+</sup>	Fe <sup>3+</sup>	SO <sub>4</sub> <sup>2-</sup>
Sample 1	0.08	6.6	12.0	11.80	14.64	2.76
Sample 2	0.07	5.6	9.3	8.91	14.37	2.41
Sample 3	0.02	5.4	8.9	7.28	15.85	2.62
Sample 4	0.03	5.1	12.0	7.08	10.72	2.68
Sample 5	ND	2.5	13.4	3.88	7.77	1.99
Sample 6	ND	2.4	12.6	3.82	7.67	1.91
Sample 7	ND	2.3	12.8	3.52	5.22	1.90

<sup>a</sup> Calculations made by GEOCHEM.

ND= not detected (<0.01%).

Table 5. Potential solid phases controlling the solubilities of Al and Fe in soil water extracts. NS = near saturation, US = under saturation and OS = over saturation

Solid phase	log K <sub>sp</sub> pH	1	2	3	4	5	6	7
		6.6	5.6	5.4	5.1	2.5	2.4	2.3
Al(OH) <sub>3</sub> (gibbsite)	8.51	NS	NS	NS	NS	US	US	US
Al(OH)(SO <sub>4</sub> ).5H <sub>2</sub> O (jurbanite)	-17.80	US	US	US	US	NS	NS	NS
KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub> (alunite)	-85.40	US	OS	OS	OS	US	US	US
Fe(OH) <sub>3</sub> (amorphous iron)	4.89	NS	US	US	NS	US	US	US
FeOOH (goethite)	-0.70	OS	OS	OS	OS	NS	NS	OS
FeSO <sub>4</sub> .7H <sub>2</sub> O (melanite)	-17.70	US	US	US	US	US	US	NS
KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub> (jarosite)	-93.21	US	US	US	US	US	US	US

organic species of Al<sup>3+</sup> and Fe<sup>3+</sup>. The Al<sup>3+</sup> and Fe<sup>3+</sup> activities calculated using total concentrations of Al and Fe in these extracts, without correcting for organic complexes, would result in overestimation of Al<sup>3+</sup> and Fe<sup>3+</sup> activities.

DOC concentrations ranged from 11.4 to 57 mg L<sup>-1</sup> in our soil water extracts (Table 2). Two types of calculations were made with GEOCHEM and MINTEQA2 to determine the significance of DOC Al<sup>3+</sup> and Fe<sup>3+</sup> complexes and their effect on the determination of IAPs of Al and Fe solid phases. First, chemical speciation and IAPs were calculated without considering

DOC as input to the models. Second, chemical speciation and IAPs were calculated with considering DOC as input (fulvic acid) to the models by following the procedures of Mattigod and Sposito (1979).

Three important results were noticed from these calculations (Tables 2 and 3). One, both models predicted that Al<sup>3+</sup> fulvic complexes were not significant in soil water extracts examined in this study. Second, both models predicted that Fe<sup>3+</sup> fulvic complexes were significant in soil solutions. Finally, Fe<sup>3+</sup> ion activities calculated by GEOCHEM were always lower than MINTEQA2. A possible explanation is that

GEOCHEM computes more solution species when compared with MINTEQA2. These results suggested that MINTEQA2 probably lacks solution species that are important for low pH soil environments, resulting in overestimation of ion activities. Therefore, we use chemical speciation calculations made by the GEOCHEM for the following discussion.

Activities of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  in soil water extracts as well as pyritic sulfur in the soils, pH and pe+pH are summarised in Table 4. Pyritic sulfur content ranged from 0.08 to below detection limit of 0.01. The pH ranged from 6.6 to 2.3 and pe+pH varied from 13.4 to 8.9. These conditions represented somewhat acidic to highly acidic and moderately reduced to oxidised environments. Comparison between the pH of samples suggests that, as  $\text{FeS}_2$  oxidised, pH decreased from 6.6 to 2.3. Furthermore, as pH decreased activities of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  increased in soil water extracts.

In soils where pH is near neutral,  $\text{Al}^{3+}$  activities are generally low and are assumed to be controlled by  $\text{Al}(\text{OH})_3$  (gibbsite) (Nordstrom, 1982). However, in acid sulfate soils  $\text{Al}^{3+}$  activities are not controlled by gibbsite and it has been suggested that the solid phase  $\text{Al}(\text{OH})(\text{SO}_4) \cdot 5\text{H}_2\text{O}$  (jurbanite) may control  $\text{Al}^{3+}$  activities (Nordstrom, 1982; Van Breeman, 1973).

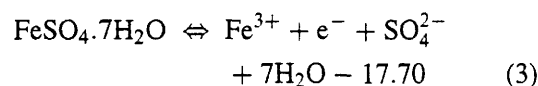
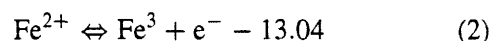
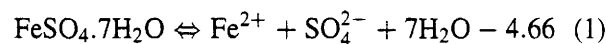
Potential solid phases controlling  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  activities in soil water extracts are shown in Table 5. The  $K_{\text{sp}}$  value for gibbsite was taken from Lindsay (1979) and for jurbanite and alunite,  $K_{\text{sp}}$  values were taken from Nordstrom (1982). Soil water extracts having a pH range between 6.6 and 5.1 suggested near saturation with respect to gibbsite. However, at low pH of 2.5 to 2.3 extracts were undersaturated with respect to this solid phase, and  $\text{Al}^{3+}$  activities were near saturation with respect to jurbanite. These extracts also suggested either a high degree of oversaturation (at high pH) or undersaturation (at low pH) with respect to alunite.

Acid water resulting from the oxidation of  $\text{FeS}_2$  may precipitate a number of secondary iron phases (Table 5), including  $\text{Fe}(\text{OH})_3$  (amorphous iron),  $\text{FeOOH}$  (goethite),  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$  (jarosite), and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (melanite) (Nordstrom, 1982). The log  $K_{\text{sp}}$  value used for amorphous iron is 4.89. This value was taken from Ball et al., (1981). From pH 6.6 to 2.3, samples 1 and 4 were near saturation with respect to amorphous iron and other samples suggested undersaturation with respect to this solid phase. The log  $K_{\text{sp}}$  value of 4.89 for amorphous iron is somewhat uncer-

tain. Chapman et al. (1983) used a value of 3.00 in their calculations. Our use of their value suggested undersaturation with respect to amorphous iron for all samples.

The log  $K_{\text{sp}}$  value used for goethite is -0.70. This value was taken from Nordstrom (1984). From pH 6.6 to 2.3, samples 5 and 6 were near saturation with respect to goethite and other samples suggested oversaturation with respect to this solid phase.

The log  $K_{\text{sp}}$  value for melanite in terms of  $\text{Fe}^{3+}$  is -17.70. This value was calculated from the following reactions:



The value for reaction 1 was taken from Ball et al. (1981) and value for reaction 2 was taken from Lindsay (1979). All extracts between pH of 6.6 and 2.4 suggested undersaturation with respect to melanite. However, at a low pH of 2.3 extracts were near saturation with respect to melanite. Again,  $K_{\text{sp}}$  value for melanite is also questionable, because  $K_{\text{sp}}$  value reported by Ball et al. (1981) for this solid phase is less soluble than the recent value of -2.20 at standard temperature and pressure (Reardon and Beckie, 1987), which makes all extracts in this study highly undersaturated with respect to melanite. Chapman et al. (1983) reported a  $K_{\text{sp}}$  value of -93.21 for potassium jarosite. Comparison of IAPs with this  $K_{\text{sp}}$  suggested that all extracts were undersaturated with respect to potassium jarosite.

Our results show that in  $\text{FeS}_2$  unoxidised samples, gibbsite will control the activity of  $\text{Al}^{3+}$ . However, in  $\text{FeS}_2$  oxidised samples pH decreased and  $\text{SO}_4^{2-}$  activity increased. Under such conditions, jurbanite will control  $\text{Al}^{3+}$  activities in soil water extracts. Results obtained on iron solid phases are not convincing, but indicate that amorphous iron in  $\text{FeS}_2$  unoxidised samples and goethite and melanite in  $\text{FeS}_2$  oxidised samples may have potential for controlling  $\text{Fe}^{3+}$  activities.

## Conclusions

The Al and Fe solubilities as affected by the oxidation of  $\text{FeS}_2$  in soil samples was examined in this study.

Evaluation of GEOCHEM and MINTEQA2 suggested that MINTEQA2 lacks solution species that are important for low pH environments. GEOCHEM was selected based on its more comprehensive capabilities.

Results suggested that oxidation of  $\text{FeS}_2$  decreased the pH and increased the activities of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  in soil water extracts. GEOCHEM predicted that fulvic acid complexes of  $\text{Al}^{3+}$  were not significant and  $\text{Fe}^{3+}$  fulvic complexes were found to be significant in soil water extracts examined in this study. The  $\text{Al}^{3+}$  activities from pH 6.6 to 5.1 suggested near saturation with respect to gibbsite. At low pH (2.5–2.3),  $\text{Al}^{3+}$  activities were controlled by jurbanite.

Saturation indices based on early estimation of solubility products reported in the literature suggest that amorphous iron may be near saturation in soil samples at high pH. The  $\text{Fe}^{3+}$  activities at low pH suggested near saturation with respect to goethite and melanite. All samples suggested a high degree of undersaturation with respect to potassium jarosite. Therefore, considerable uncertainty still prevails in the literature regarding the solubilities of amorphous iron, melanite and potassium jarosite. Further research regarding the solubilities of these solid phases in acid soil waters is needed.

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