

## Speciation of Aluminum in Acidic Natural Water Equilibria with Mineral Phase Kaolinite by Chemical Equilibrium Calculation

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**Abstract:** This paper presents a computer model using thermodynamic relationships and mass balance to investigate the speciation of aluminum in acidic natural water equilibria with mineral kaolinite. Factors affecting the distribution are discussed. Compared with the case of equilibria with gibbsite, some unique characteristics are discovered. The model is verified by analyzing practical water samples. Effect of errors in thermodynamic data on calculation is evaluated by the Monte Carlo simulation.

**Keywords:** Kaolinite, aluminum speciation, Monte Carlo simulation.

Aluminum is largely associated with aluminosilicate minerals such as kaolinite  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  within the earth's crust<sup>1</sup>. During the weathering, especially when the acid rain hastens the process, aluminum is released and thus becomes available to biogeochemical processes. The elevated concentrations of aqueous aluminum cause detrimental consequences to plants, aquatic organisms and humans. Therefore, there have been considerable growing concerns in the aqueous chemistry of aluminum these years.<sup>2</sup>

In natural waters, it has been known that different species of aluminum differ in toxicity markedly. It is imperative to know the concentrations of various aluminum species rather than simply the total aluminum concentration to evaluate its biological and environmental effects. The chemical equilibrium calculation is a useful tool to achieve this aim. Previous studies have mainly focused on the gibbsite  $\text{Al}(\text{OH})_3$ <sup>3,4</sup>. However, the mineral phase the solution contacting with has a substantial influence on the extent of speciation. Although the aluminosilicate minerals are widespread, so far there has been little thorough investigation about it. In this paper, we inspect the aluminum speciation in natural water equilibria with kaolinite and discover some unique characteristics compared with the case of the equilibria with gibbsite, such as the dissolved silica has a remarkable influence on the speciation of Al, the concentrations of polymeric alumino-hydroxo species are insignificant and the total concentration of soluble Al is two units in magnitude lower.

### Theory

The general assumptions and procedures are the same as those in previous studies<sup>3,4</sup>. In case of kaolinite, two different assumptions are employed:

1. The concentration of  $\text{Al}^{3+}$  is in equilibrium with the mineral phase kaolinite<sup>1</sup>.  
 $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4^\circ + \text{H}_2\text{O}$   $\lg K_{\text{sp}} = 6.87$ ,  $[\text{Al}^{3+}] = K_{\text{sp}}^{1/2} / [\text{H}_4\text{SiO}_4^\circ][\text{H}^+]^3$

2. In natural waters and soil waters, the dissolved silica<sup>5</sup> can be represented by  $\text{H}_4\text{SiO}_4^\circ$ . There are three types of  $\text{SiO}_2$  that maybe control the concentration of dissolved silica:

$\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4^\circ$        $\lg K_{\text{sp}}$ : -2.74 (am  $\text{SiO}_2$ ), -3.10 (soil  $\text{SiO}_2$ ), -4.00 (quartz)

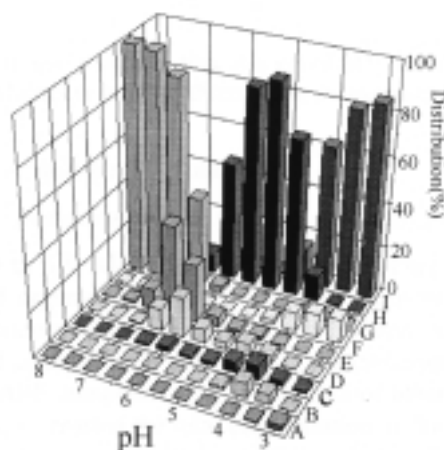
In consideration that the average concentration of dissolved silica in natural waters is  $300\mu\text{mol/L}$ <sup>5</sup>, we assume that quartz controls the concentration of the dissolved silica<sup>1</sup>.

The computer program is performed by using QBASIC at a Pentium II computer.

## Results and Discussion

### 1. Distribution of aluminum species in natural water equilibria with kaolinite.

**Figure 1** Speciation of aluminum as function of pH. ( $C_{\text{F}}^*=5$ ,  $C_{\text{SO}_4}^*=100$ ,  $\text{DOC}=100$ ,  $\mu\text{mol/L}$ ,  $t=25$  °C) A: Al-Poly, B: Al- $\text{SO}_4$ , C: Al(OH)<sup>2+</sup>, D: Al-Org, E: Al(OH)<sub>2</sub><sup>+</sup>, F: Al- $\text{PO}_4$ , G: Al(OH)<sub>4</sub><sup>-</sup>, H: Al-F, I: Al<sup>3+</sup>



The distribution of aluminum species is pH dependent. **Figure 1** illustrates that the speciation varies with the pH. In the pH range of 3 to 4, the dominant Al species is free Al<sup>3+</sup>, other forms of Al are insignificant. Compared with the case of gibbsite, the distribution of polymeric Al decreases markedly. The reason for this is that the solubility product of the kaolinite (let  $K_{\text{sp}}' = K_{\text{sp}}^{1/2}/[\text{H}_4\text{SiO}_4^\circ]$  and  $\lg K_{\text{sp}}' = 7.4$ ) is lower than that of the monocrystalline gibbsite ( $\lg K_{\text{sp}} = 9.35$ ), while the concentrations of the two kinds of polymeric Al species are proportional to the 2 and 3 squares of the solubility product respectively, the concentrations of polymeric Al species are therefore very low.

In the pH range of natural waters (4 to 7), the predominant Al species are the Al-F, Al-Org and Al-OH complexes. The free Al<sup>3+</sup>, Al- $\text{SO}_4$  and Al- $\text{PO}_4$  complexes are minor. Since pH is higher, the solubility of the kaolinite decreases and thus less concentration of Al is released into the solution. The concentrations of the ligands exceed that of the aluminum. After binding to ligands, the concentration of free Al<sup>3+</sup> is significantly low. The distribution of Al- $\text{SO}_4$  and Al- $\text{PO}_4$  are also low because the formation constants between  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$  and Al<sup>3+</sup> are so small that they are readily replaced by the F<sup>-</sup>, OH<sup>-</sup> and organic acids.

Beyond pH 7, the concentration of OH<sup>-</sup> is elevated, as it has approximately the same

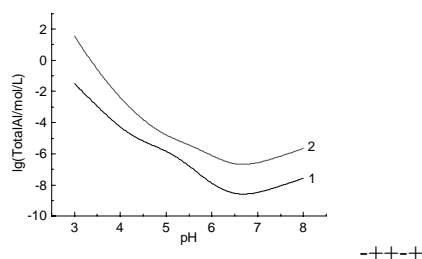
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radius as the one of the  $F^-$ , it competes strongly against  $F^-$  to bind to  $Al^{3+}$  and  $Al(OH)_4^-$  turns out to be the most abundant specie. It shows similar trends as the case of gibbsite.

**Figure 2** illustrates the total concentrations of soluble aluminum at different pH values in natural waters equilibria with mineral kaolinite and gibbsite respectively. It shows that the total concentration of Al is controlled by pH and the concentration of ligands such as  $OH^-$  binding to  $Al^{3+}$  to increase the solubility of the mineral. The total concentrations of soluble Al are lowest at about pH 6.5 under the influences of the two factors in both cases of kaolinite and gibbsite. It also indicates that at a given pH, the total concentration of soluble Al equilibria with kaolinite is two or three units in magnitude lower than the one with gibbsite.

**Figure 2**  $\lg(\text{TotalAl/mol/L})$  as function of pH (Parameters are the same as **Figure 1**)  
1. Kaolinite, 2. Gibbsite<sup>3</sup>



## 2. Factors influencing the speciation of aluminum

### 2.1 Concentrations of complexing ligands : $F^-$ , organic acids and $SO_4^{2-}$

In the pH range of 4.5 to 6.5, Al-F and Al-Org complexes are the main constituents in Al speciation. The  $F^-$  and organic acid compete against each other to bind to  $Al^{3+}$  and the extents of their distribution are largely associated with relative concentrations. At a fixed pH, increasing organic acid concentration will result in the increased distribution of Al-Org and apparent reduction of Al-F complexes, the distribution of other forms of Al changes little, see **Figure 3**. Similarly, increasing the total concentration of fluoride will lead to the increase of Al-F complexes and decrease of Al-Org, Al-OH and other forms of Al. Beyond pH 6.5, the concentration of  $OH^-$  is elevated and it competes strongly against  $F^-$  and organic acids to bind to  $Al^{3+}$ . The concentrations of  $F^-$  and organic acids therefore have somewhat smaller effects on the aluminum speciation.

The concentration of  $SO_4^{2-}$  in natural waters is relatively high (about  $400 \mu\text{mol/L}$ ), but according to the formation constants, it forms a weak complex with aluminum and its distribution is consequently insignificant.

### 2.2 Temperature

We employ the Van't Hoff equation to adjust the effect of temperature and the conclusions are similar to those in case of gibbsite.

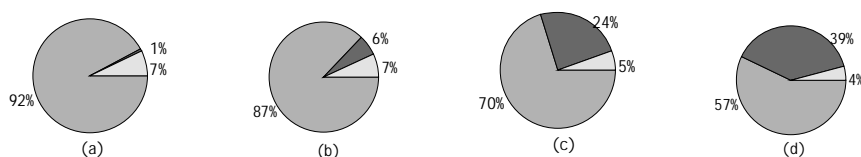
### 2.3 Concentration of dissolved silica

The equation mentioned above states a reciprocal solubility relationship between  $Al^{3+}$  and dissolved silica. When the  $H_4SiO_4^0$  activity is high, the activity of  $Al^{3+}$  is depressed due to the increased stability of the aluminosilicate. On the contrary, if the  $H_4SiO_4^0$  activity is lowered, that of  $Al^{3+}$  is increased. In this sense, the changes of the activity of the  $H_4SiO_4^0$  have the same effect as that caused by the changes of the solubility product  $K_{sp}$  of kaolinite. Since the changes of  $K_{sp}$  of gibbsite have a remarkable effect on the aluminum speciation<sup>3</sup>, it shows that dissolved silica is also an essential factor

influencing the concentration and distribution of aluminum species.

When the pH and the concentration of  $\text{H}_4\text{SiO}_4$  is low ( $10^{-6}\text{mol/L}$ ), the percentage distribution of free  $\text{Al}^{3+}$  is also low because of the large formation of polymeric aluminum. As the solubility product  $K_{\text{sp}}$  of kaolinite increases with the decrease of concentration of  $\text{H}_4\text{SiO}_4$ , it means that the distribution of polymeric aluminum increases with the increase of  $K_{\text{sp}}$ , this trend agrees with the case of gibbsite.

**Figure 3.** Influence of concentration of organic acid on the speciation of Al at pH 5.5. DOC( $\mu\text{mol/L}$ ): (a) 10, (2) 100, (3) 500, (4) 1000. Other parameters are the same as **Figure 1**: Al-F, Al-Org, All other Al species.



### 3. Analysis of the aluminum speciation in natural surface water

We apply our model to the practical analysis of surface water samples. Experimental work of some previous researchers is cited as the input data<sup>6-10</sup>. These systems are all in equilibrium with kaolinite. The calculated results are compared with those measured. The linear regression equations are the followings:

for concentration(mol/L) of inorganic Al:  $\text{Al}_{\text{cal}} = 3.56 \times 10^{-6} + 0.328 \text{Al}_{\text{meas}}$ , ( $r = 0.823$ ),

for total concentration(mol/L)of Al:  $\text{Al}_{\text{total,cal}} = -3.01 \times 10^{-7} + 0.804 \text{Al}_{\text{total,meas}}$ , ( $r=0.958$ ).

They are in near-perfect agreement with the experimental results.

Laboratory studies have shown that critical combined concentration of free  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_2^+$  to fish mortality is as low as  $7.5 \mu\text{mol/L}$ . Our model simulation suggests that in the acidified surface waters with  $\text{pH} < 4.5$ , the concentration of the toxic aluminum generally exceeds that critical level and may be potentially harmful to fish.

We employ Monte Carlo simulation to evaluate the discrepancies resulting from the selection of equilibrium constants from literature. The 98% confidence limits of the calculated distribution of aluminum are extremely broad, especially for  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_4^-$ . It's critical to select thermodynamic data to reduce the uncertainties in model calculation.

### Acknowledgments

This project is financed by the National Natural Science Foundation of China (Key Project No.49831005 & No.29777013).

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Received 28 September 1999