Competitive adsorption at surface aluminum sites: An approach to determining feldspar dissolution rates in mixed proton/ligand systems

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Bacteria can affect the dissolution rates of aluminum-silicate minerals by a number of mechanisms. Principal among these are the production of protons and complexing ligands resulting in proton-promoted and ligand-promoted dissolution. However, dissolution inhibition has also been noted as a result of exopolysaccharide production and adsorption on mineral surfaces (Welch and Vandevivere, 1994). In a natural setting, all of these mechanisms may take place simultaneously and the net impact of bacteria and microbial processes on mineral stability may be difficult to predict. A series of laboratory dissolution experiments with bytownite feldspar (An_{75}) in solutions containing both protons and ligands and ligands and polysaccharide suggest that a competitive adsorption model based on the Langmuir isotherm may be useful in making such predictions. This model supposes that the mechanism limiting dissolution rate is the adsorption of the attacking proton or ligand to mineral surface sites and that dissolution is then directly related to the number of sites that have been attacked.

The models

The Langmuir isotherm model for a single adsorbate is described by the following equilibrium and equations:

$$A + X_s \rightleftharpoons AX_s \qquad K_A = \frac{(AX_s)}{(A)(X_s)}$$

or

$$(AX_s) = \frac{K_A(A)}{[1 + K_A(A)]} \qquad (1)$$

Where (A) is the concentration of adsorbate A in solution, (X_s) and (AX_s) are the fractions of available and complexed surface sites ($X_s + AX_s = 1$) and K_A is the equilibrium constant describing the adsorption. It is assumed that the total number of adsorption sites is limited (fixed for a particular mineral composition) and that, in the case of feldspars, the number of sites is related to the density of aluminum tetrahedra at the mineral surface (Welch and Ullman, 1993, 1996). If the rate of dissolution is linearly related to the concentration of the adsorbed species, the rate of dissolution associated with this adsorption is described by:

$$R_A = r_A(AX_s) = \frac{r_A K_A(A)}{[1 + K_A(A)]} \qquad (2)$$

where R_A is the overall dissolution rate and r_A is a rate constant.

This model (Equation 2) can be expanded can be expanded to the case of a number of adsorbates:

$$R_T = \sum R_i = \sum r_i(A_i X_s) = \frac{\sum r_i K_i(A_i)}{[1 + \sum K_i(A_i)]} \qquad (3)$$

where R_T is the overall dissolution rate, i is the index describing each adsorbate A_i, R_i and r_i are the dissolution rate and rate constant associated with each adsorbate A_i, K_i is the adsorption constant for each A_i, and $X_s + \sum A_i X_s = 1$.

The solution to this model (Eq. 3) can be illustrated for the case of competition between protons and a single ligand (Fig. 1). This model curve illustrates a number of features of feldspar dissolution curves that we have previously observed (Welch and Ullman, 1992, 1993, 1996): (A) a leveling out of dissolution rates at low pH; (B) an approximately linear region where ligands (gluconate and oxalate, in our experiments) appear to have limited impact on dissolution rates and the slope, $\delta\log R/\delta ph$ is close to 1; (C) an extension of the linear region to neutral pH in the case where no ligand is present; and (D) an increase in mineral dissolution
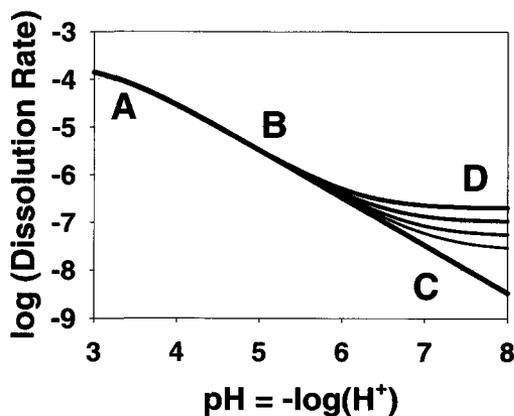
FIG. 1. Competitive adsorption model (Eq. 3) for proton/gluconate competition at 20°C. Gluconate concentrations were varied from 0 to 2000 :M. Dissolution rates are in moles/m²/day.

TABLE 1. Results of batch experiments as fitted to the competitive Langmuir adsorption model (Eq. 4). Chemical affinity ignored. Only pH > 4 data were used

Experiment	Proton ($r_H K_H$)	Ligand ($r_L K_L$)
Gluconate (5°C)	9.97×10^{-2}	0*
Gluconate (20°C)	2.54×10^{-1}	1.57×10^{-4}
Gluconate (20°C)[†]	3.29×10^{-1}	1.05×10^{-4}
Gluconate (35°C)	2.37×10^{-1}	1.60×10^{-4}
Oxalate (20°C)	4.80×10^{-1}	1.35×10^{-3}

* Indistinguishable from zero.
[†] Full pH range of data used and data fitted to Eq. 3.

rate in the neutral region with increasing ligand concentration. We have also observed evidence of competition between two ligands with differing impacts on dissolution (Welch and Vandevivere, 1994).

If it is assumed that the number of sites that are occupied by ligands or protons is only a small fraction of the total numbers of available sites, a condition that might be appropriate at higher pH, low total ligand concentration, and/or when ligands have only a weak affinity for the mineral surface, Equation 3 can be simplified to:

$$R_T = \Sigma R_i = \Sigma r_i(A_i X_s) = \Sigma r_i K_i(A_i) \qquad (4)$$

Model application

This model (Eq. 4) was applied to a series of unbuffered batch experiments with bytownite feldspar as the mineral substrate and with gluconate and oxalate ions as the reactive ligands. At each step of the batch experiment the incremental rate of dissolution and average pH were calculated and

used to determine the parameters of the model. Without independent estimates of adsorption coefficients, actual reaction coefficients can not be determined. However the products of the reaction coefficients and equilibrium constants describing adsorption ($r_i K_i$, see Eqs. 3 and 4) could be fitted to the experimental data. Only the results above pH = 4 where fitted and although the effects of chemical affinity were observed in a number experiments, particularly those with the weaker complexing ligand (gluconate) and at higher temperature (35°C), these effects have been ignored in this preliminary model. The calculated values of $r_i K_i$ for these experiments are given in Table 1. The results clearly indicate the effect of the stronger Al-oxalate complex on feldspar dissolution rates.

References

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