

## A CHEMICAL MODEL FOR THE ORIGIN OF GIBBSITE FROM KAOLINITE

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### ABSTRACT

Thermodynamic data have been employed to construct theoretical solubility diagrams for quartz, kaolinite, and gibbsite at room temperature and pressure. Analysis of these diagrams indicates that gibbsite should not precipitate as a result of the dissolution of kaolinite unless quartz is absent from the system, the pH of the infiltrating water attains a value of at least 4.2, and the initial concentration of total dissolved silica in the infiltrating water is less than  $10^{-4.6}$  moles per liter. These conclusions help explain why bauxites do not readily form on quartz rich rocks or in cooler regions where the pH of soil waters is commonly low because of the slow decay of organic matter.

### INTRODUCTION

Equilibrium diagrams provide guidelines for the elucidation and interpretation of natural processes and also commonly reveal limiting conditions for the formation of minerals. Sufficient thermodynamic data are now available to permit the construction of diagrams showing the solubility of a number of common silicate minerals at room temperature and pressure. Obviously such diagrams should direct us towards a clearer and fuller understanding of the conditions and processes involved in the formation of clay minerals from parent minerals in the zone of weathering.

The following discussion is devoted to the interpretation of solubility diagrams for quartz, gibbsite, and kaolinite which have been calculated on the basis of thermodynamic data available at present. As will be seen inspection of these diagrams indicates that gibbsite should not form as a result of the dissolution of kaolinite unless quartz is absent, the pH of the infiltrating water rises above a critical value of 4.2, and the initial concentration of dissolved silica is below a critical value of  $10^{-4.6}$  moles per liter. Furthermore, if the crystallization of gibbsite involves passage through a stage of amorphous  $\text{Al}(\text{OH})_3$ , then the critical pH of formation rises to 5.6 and the initial concentration of dissolved silica cannot exceed  $10^{-6.3}$  moles per liter. The bauxite deposits formed on kaolinitic sandstones at Weipa, Queensland (Loughnan and Bayliss, 1961) is a natural occurrence which can be interpreted in the context of the proposed model.

Similar diagrams have been developed by Garrels and Christ (1965, p 352-358) for the gibbsite-kaolinite system but the interpretation presented herein differs somewhat from theirs, particularly as regards the existence of a critical pH limit for gibbsite formation.

## CONSTRUCTION OF SOLUBILITY DIAGRAMS

*Data Employed.* Because published thermodynamic data are not entirely consistent and are subject to revision, the standard free energies of formation used in this study are listed in Table 1 along with sources. In the author's opinion these data are the most consistent and widely accepted data available at present. The data listed in Table 1 are compatible with

TABLE 1. STANDARD FREE ENERGIES OF FORMATION USED IN THIS STUDY

Species	Standard free energy of formation ( $\Delta F_r^\circ$ kcal)	Source of data, and remarks
H <sub>2</sub> O (1)	-56.7	Garrels and Christ (1965)
H <sup>+</sup>	0.0	Garrels and Christ (1965)
OH <sup>-</sup>	-37.6	Garrels and Christ (1965)
SiO <sub>2</sub> quartz	-204.8	Wise (1962)
Al(OH) <sub>3</sub> gibbsite	-274.2	Kittrick (1966a)
Al(OH) <sub>3</sub> amorphous	-271.9	Latimer (1952)
Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> kaolinite	-902.9	Kittrick (1966b)
H <sub>4</sub> SiO <sub>4</sub> (aq.)	-312.7	Calculated from solubility of quartz of 6 ppm as SiO <sub>2</sub> (Morey, <i>et al.</i> 1962)
H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup>	-299.5	Calculated from Helgeson, <i>et al.</i> (1969), Figure 1.
Al <sup>3+</sup>	-115.0	Garrels and Christ (1965)
Al(OH) <sup>2+</sup>	-164.8	Calculated from Helgeson, <i>et al.</i> (1969), Figure 1.
Al(OH) <sub>4</sub> <sup>-</sup>	-309.8	Calculated from Helgeson, <i>et al.</i> (1969), Figure 1.

diagrams published by Helgeson, Garrels, and Mackenzie (1969), with Kittrick's (1966a) gibbsite solubility measurements, and with kaolinite solubility measurements by Kittrick (1966b) and Polzer and Hem (1965).

*Methods of Calculation.* Equilibrium constants for reactions pertaining to the present study have been calculated by means of the well known relationship between the standard free-energy change of reaction,  $\Delta F_r^\circ$ , and the equilibrium constant,  $K$ , which for conditions of room temperature and pressure is given by (Garrels and Christ, 1965, p. 8):

$$\Delta F_r^\circ(\text{kcal}) = -1.364 \log K \quad (1)$$

The mass action equations derived by means of this formula are listed in Table 2 along with mass balance equations for total dissolved aluminum,

$\Sigma\text{Al}$ , and total dissolved silica,  $\Sigma\text{Si}$ . Procedures for obtaining solubility diagrams from mass action and mass balance equations are outlined by Roberson and Hem (1969, p. 7).

It should be noted that the brackets in the mass action and mass balance equations symbolize the activities of the particular substances enclosed. Thus the coordinates on the diagrams presented herein refer to total activity of dissolved Al or Si rather than total concentrations of dissolved Al or Si. Considering the uncertainty involved in some of the thermodynamic data, the discrepancy between activity and concentration is probably unimportant in solutions with ionic strengths less than 0.001, a value rarely attained in fresh rainwater. Because of the low

TABLE 2. EQUATIONS USED FOR SOLUBILITY CALCULATIONS  
AT 25°C 1 ATMOSPHERE TOTAL PRESSURE

Reactions	Mass Action Equations
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	$(\text{H}^+)(\text{OH}^-) = 10^{-14}$
$\text{Al}(\text{OH})_3(\text{gibbsite}) = \text{Al}^{3+} + 3\text{OH}^-$	$(\text{Al}^3+)(\text{OH}^-)^3 = 10^{-31.1}$
$\text{Al}(\text{OH})_3(\text{amorphous}) = \text{Al}^{3+} + 3\text{OH}^-$	$(\text{Al}^{3+})(\text{OH}^-)^3 = 10^{-32.4}$
$\text{Al}(\text{OH})^{2+} = \text{Al}^{3+} + \text{OH}^-$	$(\text{Al}(\text{OH})^{2+}) = 10^{9.0}(\text{Al}^{3+})(\text{OH}^-)$
$\text{Al}(\text{OH})_4^- = \text{Al}(\text{OH})^{2+} + 3\text{OH}^-$	$(\text{Al}(\text{OH})_4^-) = 10^{23.5}(\text{Al}(\text{OH})^{2+})(\text{OH}^-)^3$
$\text{SiO}_2(\text{quartz}) + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4(\text{aq})$	$(\text{H}_4\text{SiO}_4) = 10^{-4.0}$
$\text{H}_4\text{SiO}_4(\text{aq}) = \text{H}^+ + \text{H}_3\text{SiO}_4^-$	$(\text{H}_4\text{SiO}_4) = 10^{9.7}(\text{H}_3\text{SiO}_4^-)(\text{H}^+)$
$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 5\text{H}_2\text{O} =$ $2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4(\text{aq}) + 6\text{OH}^-$	$(\text{Al}^{3+})^2(\text{H}_4\text{SiO}_4)^2(\text{OH}^-)^6 = 10^{-77.3}$

Mass Balance Equations

$$\text{Al} = (\text{Al}^{3+} + (\text{Al}(\text{OH})^{2+}) + (\text{Al}(\text{OH})_4^-)$$

$$\text{Si} = (\text{H}_4\text{SiO}_4) + (\text{H}_3\text{SiO}_4^-)$$

solubility of quartz, gibbsite, and kaolinite in the normal range of pH (4 to 9) it is unlikely that their dissolution in rainwater would produce soil solutions with ionic strengths greater than 0.001.

The resulting theoretical solubility diagrams are shown in Figures 1 through 4. The solubility of kaolinite depends on three variables ( $\Sigma\text{Si}$ ,  $\Sigma\text{Al}$ , and pH) and therefore requires a three dimensional diagram for representation. Thus in Figures 3 and 4 the solubility of kaolinite has been contoured at various values of pH. Also shown on these two Figures are the diagrams for quartz and gibbsite at corresponding contours of pH.

#### INTERPRETATION AND DISCUSSION

*Congruent Dissolution of Pure Kaolinite.* To illustrate the use and significance of Figures 3 and 4, the dissolution of pure kaolinite in water buffered at pH 6 will be considered first. Buffering at pH 6 might ap-

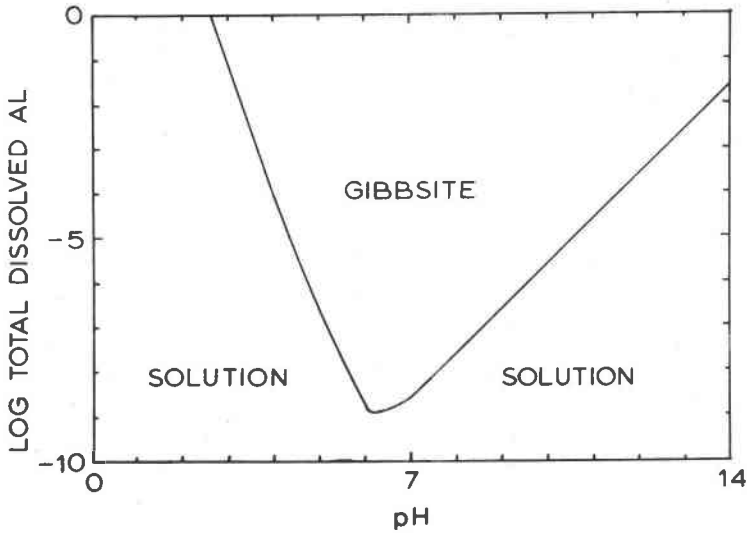


FIG. 1. Theoretical solubility of gibbsite.

proximate a natural system in which rainwater in equilibrium with  $\text{CO}_2$  of the atmosphere infiltrates into a deposit of kaolinite. In Figure 5 the solubilities of quartz, gibbsite, and kaolinite at pH 6 have been plotted

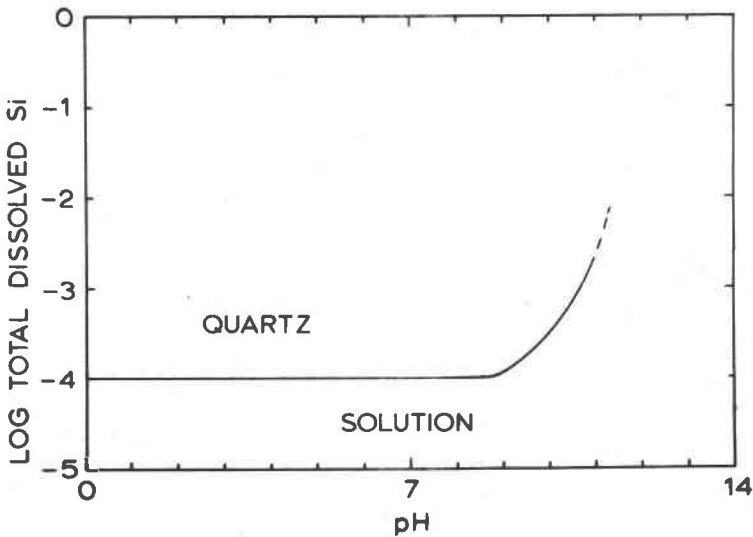


FIG. 2. Theoretical solubility of quartz.

as a function of total dissolved Si and total dissolved Al. The line ABC represents the congruent dissolution of kaolinite in pure water. If, for example, the rainwater entering the kaolinite has an initial composition of  $10^{-15}$  Si and  $10^{-15}$  Al (point A), the composition of the water will move along the congruent dissolution line toward point C where it will attain equilibrium with kaolinite at  $10^{-6.7}$  Si and  $10^{-6.7}$  Al. However, before reach-

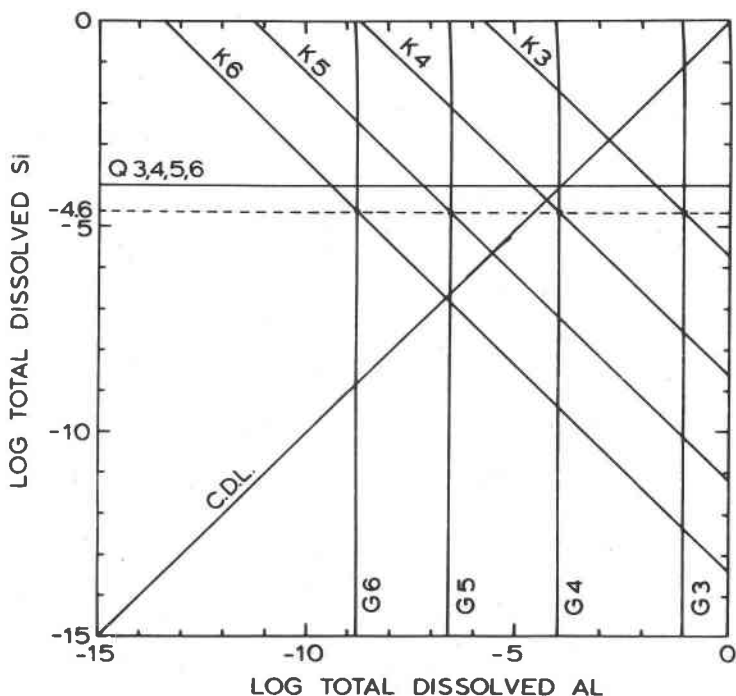


FIG. 3. Solubility of quartz, kaolinite, and gibbsite contoured at pH values from 3 to 6. K = kaolinite, Q = quartz, G = gibbsite. Associated numbers indicate pH contours. C.D.L. = congruent dissolution line of kaolinite.

ing point C the solution will encounter the gibbsite solubility line at point B and the gibbsite will begin to precipitate. The solution will then move along the gibbsite solubility line to point D where it will attain equilibrium with both gibbsite and kaolinite at  $10^{-4.6}$  Si and  $10^{-8.8}$  Al. The dashed lines shown approaching the congruent dissolution line of Figure 5 represent the paths followed by solutions with unequal initial concentrations of Si and Al. As can be seen from the diagram all solutions with initial Si concentrations less than  $10^{-4.6}$  moles per liter will intersect the gibbsite solubility line in the approach to equilibrium with kaolinite. However, solutions with an initial Si concentration greater than  $10^{-4.6}$

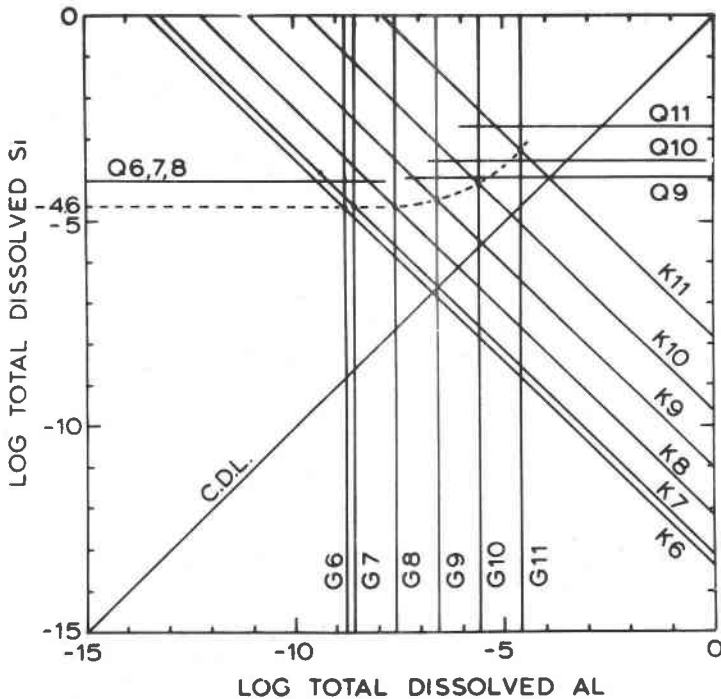


FIG. 4. Solubility of quartz, kaolinite, and gibbsite contoured at pH values from 6 to 11. K=kaolinite, Q=quartz, G=gibbsite. Associated numbers indicate pH contours. C.D.L. =congruent dissolution line of kaolinite.

moles per liter will intersect the kaolinite solubility line before encountering the gibbsite solubility line. Thus for solutions with initial Si concentrations less than  $10^{-4.6}$  moles per liter gibbsite will result from the dissolution of kaolinite whereas for solutions with initial Si concentrations greater than  $10^{-4.6}$  moles per liter kaolinite will dissolve leaving no residue.

Inspection of Figures 3 and 4 reveals that for all values of pH below 8 the gibbsite and kaolinite solubility lines intersect at a value of total dissolved Si of  $10^{-4.6}$  moles per liter. Thus, regardless of buffering conditions, for all values of pH below 8 gibbsite cannot form through the dissolution of kaolinite unless the initial concentration of Si in the infiltrating water is less than  $10^{-4.6}$  moles per liter. At higher pH the maximum permissible initial value of Si rises and at pH 11 reaches  $10^{-3.4}$  moles per liter.

Inspection of Figure 3 also reveals that at pH 4 the congruent dissolution line intersects the kaolinite solubility line before reaching the gibbsite line. This means that at pH 4 and below, kaolinite cannot dissolve

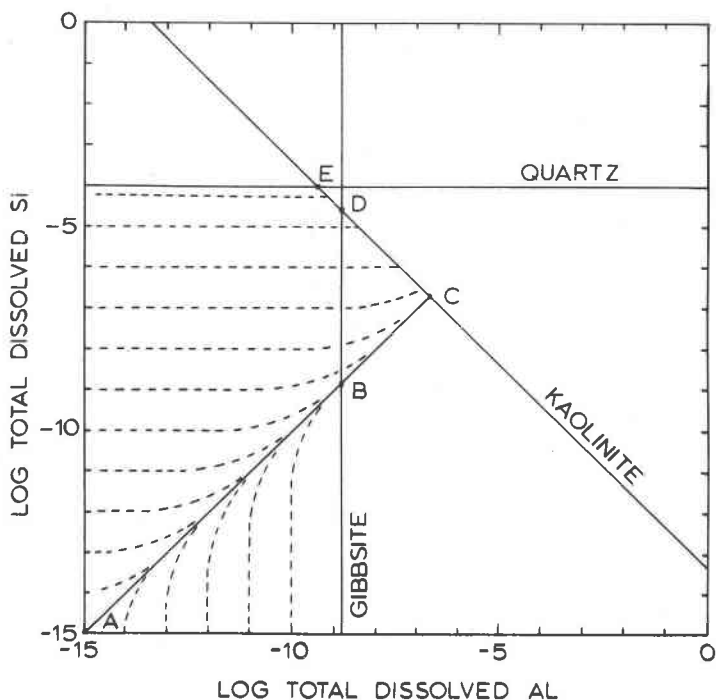


FIG. 5. Dissolution of kaolinite at pH 6. Dashed lines and letters are explained in text.

and leave a residue of gibbsite no matter what the initial value of Si may be. Actually the minimum pH at which gibbsite may form is 4.2. This is determined by locating the  $10^{-4.6}$  Si coordinate on the congruent dissolution line and interpolating between pH contours.

For unbuffered systems the minimum pH of gibbsite formation will be somewhat lower than 4.2 because the dissolution of kaolinite will cause a rise in pH which may bring the dissolution curve into the gibbsite stability field. From the work of Polzer and Hem (1965) it appears that the unbuffered dissolution of kaolinite in the pH range 3.7 to 4.0 results in a pH rise of about 0.3 pH units. Thus for unbuffered systems the minimum pH of gibbsite formation is probably about 3.9.

*Effect of Quartz.* If quartz and kaolinite are both present in the soil, infiltrating rainwater will attain equilibrium at the intersection of the quartz and kaolinite solubility lines which in Figure 5 is point E. In approaching this intersection the solution will never intersect the gibbsite solubility line, regardless of pH. Therefore, gibbsite will not form

from this system until quartz has been removed from reaction with the infiltrating water by either complete leaching or by coating with impermeable clay films. Once quartz has been removed gibbsite may or may not form from the remaining kaolinite depending on conditions previously discussed.

It is perhaps also worth noting that in the quartz-kaolinite system kaolinite should be the main contributor of Si to solution at pH below 3.8 because at this pH the congruent dissolution for kaolinite intersects the quartz solubility line. Thus in the dissolution of kaolinite below pH 3.8 saturation of Si with respect to quartz will occur before the solution attains equilibrium with respect to kaolinite. Therefore, kaolinite should be preferentially leached below pH 3.8, quartz above pH 3.8.

The retarding effect of quartz on the development of gibbsite is well illustrated by the bauxite deposits at Weipa, Queensland described by Loughnan and Bayliss (1961). The parent material for the bauxite is a kaolinitic sandstone consisting of nearly 90 percent quartz and 10 per-

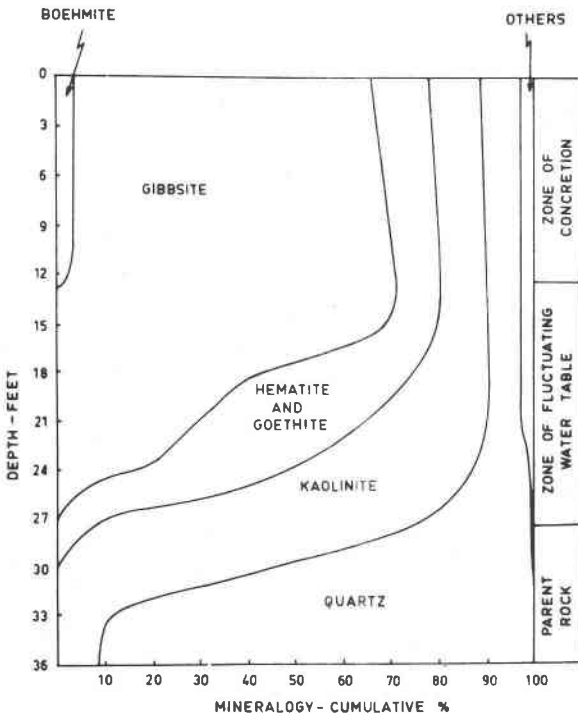


FIG. 6. Mineralogy in relation to depth in bauxite deposits at Weipa, Queensland (after Laughnan and Bayliss, 1961).



cent kaolinite. The mineralogy of the weathering profile on this sandstone is shown in Figure 6 where it can be seen that gibbsite does not appear in the profile until the quartz content drops below about 10 percent. Baker (1958) concluded from the etched and pitted nature of the residual quartz grains that they had been subjected to intense chemical attack. The persistence of small quantities of quartz throughout the intensively leached zones is attributed to the particularly coarse grain size of some of the quartz in the parent rock and to protective coatings of Al and Fe minerals. The pH of the soil water in the profile grades from about 5.5 near the surface to neutrality at the water table (Loughnan and Bayliss, 1961). Thus pH conditions here are suitable for the precipitation of gibbsite and the preferential leaching of quartz.

*Effect of Amorphous  $Al(OH)_3$ .* It is entirely possible, indeed quite probable, that the formation of gibbsite in the zone of weathering proceeds through an intermediate stage of amorphous  $Al(OH)_3$ ; that is, amorphous  $Al(OH)_3$  precipitates initially from solution and then crystallizes into gibbsite upon aging (see Hem and Roberson, 1967 and Hsu, 1966). Using Latimer's (1952) value for the free energy of formation of amorphous  $Al(OH)_3$ , it can be shown by means of the procedures outlined above that the initial concentration of Si must be less than  $10^{-6.3}$  moles per liter and that the minimum pH at which amorphous  $Al(OH)_3$  can precipitate as the result of the dissolution of kaolinite is about 5.6.

#### SUMMARY AND CONCLUSIONS

Thermodynamic data have been employed to construct theoretical solubility diagrams for quartz, gibbsite, and kaolinite at room temperature and pressure. Inspection of these diagrams reveals that gibbsite should not form as a result of the dissolution of kaolinite unless quartz is absent from the system, the pH of the infiltrating water is above 4.2, and the initial concentration of total dissolved Si is less than  $10^{-0.6}$  moles per liter. If gibbsite is required to pass through an intermediate stage of amorphous  $Al(OH)_3$  in its formation, the minimum pH of formation rises to about 5.6 while the maximum allowable initial concentration of total dissolved Si drops to  $10^{-6.3}$  moles per liter. These findings help explain why bauxites do not readily form on quartz bearing rocks nor in cool regions where the pH of infiltrating water is low due to the slow decay of organic matter and the production of organic acids.

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