AN Fe-BERTHIERINE FROM A CRETACEOUS LATERITE: PART II. ESTIMATION OF Eh, pH AND pCO_2 CONDITIONS OF FORMATION

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Abstract—Transgression by the Western Interior Sea during the Late Cretaceous in southwestern Minnesota caused swampy conditions to be imposed upon a laterite consisting of gibbsite, goethite and kaolinite. Reducing conditions overprinted upon the laterite reduced ferric Fe in goethite for incorporation of ferrous Fe into Fe-berthierine. Attendant oxidation of organic matter provided CO_2 for siderite's formation. Thermodynamic calculations indicate that berthierine, gibbsite, goethite, kaolinite and siderite were in equilibrium with a solution whose pH was 5.2 and whose pCO_2 was on the order of 0.3 atm. Formation of Fe-berthierine is favored by solutions having: 1) low silica concentration; 2) low $[Mg^{2+}]/[Fe^{2+}]$ ratio; 3) high pCO_2; 4) extremely low sulfate content before reduction takes place; and 5) moderate reducing conditions (Eh around -0.05 V).

Key Words—Berthierine, Gibbsite, Goethite, Cretaceous, Kaolinite, pCO_2, pH, Siderite, Soil Zone, Weathering.

INTRODUCTION

It is difficult to obtain *in situ* measurements of pH, pCO_2 and Eh within weathering profiles. This is especially true for pH and Eh of solutions in the vadose zone. These parameters can be calculated using thermodynamic data for minerals in the profile that are in equilibrium with the ambient solution and soil gas. Obviously, the calculation option is the only recourse in reconstructing conditions under which a mineral assemblage formed within a weathering profile in the geologic past.

The previous paper described a Cretaceous-aged laterite in which the phases consisted of 4 common minerals (gibbsite, kaolinite, siderite, goethite) and Fe-berthierine. Fortunately, the Fe-berthierine had no Mg component. In that case, the solute chemistry in equilibrium with these 5 minerals in this 6-component system (H_2O, CO_2, FeO, Fe_2O_3, Al_2O_3, SiO_2) can be calculated by algebraic manipulation of 5 solubility-product expressions and the solution's charge balance. The result is an estimate of the pH and Eh of the solution responsible for this assemblage as well as an estimate of the partial pressure of CO_2 in contact with these minerals.

These calculations support the previous paper's assessment that the berthierine–gibbsite–goethite–kaolinite–goethite assemblage formed by the imprinting of reducing conditions upon a laterite originally composed of gibbsite, kaolinite and goethite. The onset of reducing conditions occurred by the change of base level caused by transgression of the Western Interior Sea. The result was establishment of bog-like conditions in which low-permeability muds were deposited on the laterite. Oxidation of organic matter to CO_2 reduces ferric Fe in the lateritic goethite. The result

would solubilize ferrous Fe, making it available for formation of Fe-berthierine and siderite.

We conclude with geochemically supported speculations on the conditions under which Fe-berthierine will (or won't) form. The conditions for Fe-berthierine formation are shown to be very restrictive.

ASSUMPTIONS, DATA SOURCES AND UNCERTAINTIES

The co-presence of berthierine, gibbsite, goethite, kaolinite and siderite in the same thin sections and X-ray diffractograms is the basis for our presumption that they constitute an equilibrium assemblage. This association enables us to elucidate the geochemical conditions responsible for the formation of these minerals. In the ensuing calculations, we assume that the average temperature was very close to 25 °C—a reasonable assumption given that the average surface temperature of sea water ranged between 20 and 25 °C during Cenomanian time (Kauffman 1977). Weathering of the soil in which the main minerals are composed of relatively insoluble hydrolysates yields solutions of low ionic strength. For this reason, we assume that all activity coefficients are unity; hence, molarities are used interchangeably in both equilibrium and charge-balance expressions. Lastly, we assume that Fe-berthierine has an idealized formula corresponding to $Fe_2Al_2SiO_5(OH)_4$. This idealized composition facilitates algebraic manipulation so that the reader can easily follow the computations with a hand calculator. Of course, a computer was used to calculate the chemical conclusions using the microprobe-derived chemistry of Fe-berthierine $[Fe_{2.08}Al_{1.79}Si_{1.12}O_5(OH)_4]$. These results are also presented.

580

Table 1. Values (and sources) of free energies used in the calculations.

Species	ΔG_f° in kJ mol^{-1}	Source
Berthierine (idealized)	−3489.	Tardy and Garrels (1974)
Berthierine (reported)	−3446.	Tardy and Garrels (1974)
Siderite	−674.2	Robie et al. (1979)
Kaolinite	−3798.	Stumm and Morgan (1981), Faure (1991)
Gibbsite	−1156.	Nordstrom et al. (1984)
Goethite	−490.	Woods and Garrels (1987)
Greenalite	−3014.	Tardy and Garrels (1974)
Amesite	−4213.	Woods and Garrels (1987)
Pyrite	−163.	Lindsay (1979)

The adopted −3798 kJ mol^{-1} value for kaolinite's ΔG_f° falls between −3796 (Faure 1991) and −3799 (Stumm and Morgan 1981). Free energies of formation for greenalite and the berthierines were calculated from the method of excess free energies (Tardy and Garrels 1974). Idealized berthierine refers to $Fe_2Al_2SiO_5(OH)_4$, while the "reported" value refers to the formula, $[Fe_{2.08}Al_{1.79}Si_{1.12}O_5(OH)_4]$, derived from microprobe analysis. Data from Woods and Garrels (1987), Tardy and Garrels (1974), Lindsay (1979) and Faure (1991) were converted to kJ mol^{-1} by multiplying the given value (in calories) by 0.004186. Significant figures of data vary from source to source.
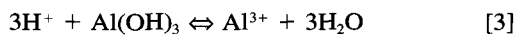
The main uncertainty in the calculations lies in the accepted ΔG_f° (Gibbs free energy of formation) values for the minerals (as opposed to the normally much better constrained ΔG_f° values for ions in aqueous solution). Table 1 lists free energy of formation for minerals (in units of kJ mol^{-1}) used in reactions. Because $\Delta G_r^\circ = -5.710 \log_{10} K_{eq}$, where ΔG_r° is the Gibbs free energy of reaction and K_{eq} is the constant, then a variation of ±1.00 kJ for ΔG_r° translates to about ±0.175 log units for an equilibrium constant. Uncertainty of the calculated pH is governed mainly by the uncertainty of the solubility-product constant for siderite which, in turn, is controlled by siderite's ΔG_f°. Published values for siderite's free energy of formation by Brookins (1988) and Wagman et al. (1982) vary less than 4.2 kJ mol^{-1} from the value used in Table 1. Increasing Fe-berthierine's ΔG_f° by 5 kJ mol^{-1} increases the calculated pH by 0.25 and decreases the $\log_{10}(pCO_2)$ by 0.36. Roughly the opposite effect occurs with a decrease of berthierine's ΔG_f° by 5 kJ mol^{-1}.

ESTIMATION OF pH, pCO$_2$ AND ION CONCENTRATIONS

Below are written the congruent dissolutions of berthierine (B), gibbsite (GB), kaolinite (K) and siderite (S) along with their solubility-product constants:
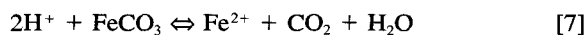
$$10H^+ + Fe_2Al_2SiO_5(OH)_4$$
$$\Leftrightarrow 2Fe^{2+} + 2Al^{3+} + H_4SiO_4 + 5H_2O \quad [1]$$
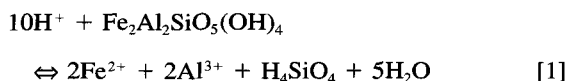
$$K_{sp(B)}$$
$$= \{[Fe^{2+}]^2[Al^{3+}]^2[H_4SiO_4]\}/[H^+]^{10} = 10^{25.55} \quad [2]$$

$$3H^+ + Al(OH)_3 \Leftrightarrow Al^{3+} + 3H_2O \quad [3]$$
$$K_{sp(GB)} = [Al^{3+}]/[H^+]^3 = 10^{8.27} \quad [4]$$

$$6H^+ + Al_2Si_2O_5(OH)_4 \Leftrightarrow 2Al^{3+} + 2H_4SiO_4 + H_2O \quad [5]$$
$$K_{sp(K)} = \{[Al^{3+}]^2[H_4SiO_4]^2\}/[H^+]^6$$
$$= 10^{6.94} \quad [6]$$

$$2H^+ + FeCO_3 \Leftrightarrow Fe^{2+} + CO_2 + H_2O \quad [7]$$
$$K_{sp(S)} = \{[Fe^{2+}][pCO_2]\}/[H^+]^2 = 10^{6.40} \quad [8]$$

The gibbsite/kaolinite equilibrium fixes the activity of H_4SiO_4:

$$[H_4SiO_4] = \sqrt{K_{sp(K)}/[K_{sp(GB)}]^2} = 10^{-4.80} \quad [9]$$

Since kaolinite is in equilibrium with berthierine, then the $[Al^{3+}]^2$ term in the $K_{sp(K)}$ expression is substituted into the $K_{sp(B)}$ equation:

$$K_{sp(B)} = \{[Fe^{2+}]^2 K_{sp(K)}\}/\{[H^+]^4[H_4SiO_4]\} \quad [10]$$

Because berthierine and kaolinite are also in equilibrium with siderite, then substituting the squared siderite expression for $[Fe^{2+}]^2$ in Equation [10] yields the equilibrium value for the partial pressure of CO_2:

$$pCO_2 = \sqrt{\{[K_{sp(S)}]^2 K_{sp(K)}/K_{sp(B)}[H_4SiO_4]\}}$$
$$= 10^{-0.51} \text{ atm} \quad [11]$$

Knowing the value of pCO$_2$ allows a means to calculate ferrous Fe via Equation [8]:

$$[Fe^{2+}] = \{K_{sp(S)}[H^+]^2\}/[pCO_2] = 10^{6.91}[H^+]^2 \quad [12]$$

The pH can be approximated from the charge balance. For dilute solutions in equilibrium with kaolinite and a carbonate mineral, the pH cannot be so low as to dissolve the carbonate-bearing siderite. Neither can the pH be very high due to the system's high partial pressure of CO_2 in contact with solution. Thus, the equivalents of hydronium and ferrous Fe in a mid-pH-range solution would be balanced by bicarbonate equivalents. In other words:

$$[H^+] + 2[Fe^{2+}] \approx [HCO_3^-] = K_oK_1pCO_2/[H^+]$$

$$= 10^{-8.33}/[H^+] \quad [13]$$

where K_o ($=10^{-1.47}$) is the Henry's Law constant for CO_2 dissolution in water and K_1 ($=10^{-6.35}$) is the 1st dissociation constant for carbonic acid.
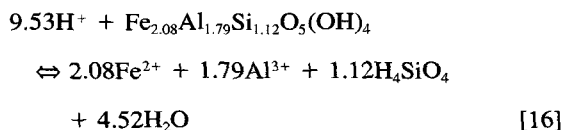
If Equation [12] is substituted into Equation [13], then:

$$\{[H^+]^2 + [10^{7.21}[H^+]^3]\} - 10^{-8.33} = 0 \quad [14]$$

or

$$pH \approx (7.21 + 8.33)/3 = \{\log_{10}[2K_{sp(S)}/K_oK_1pCO_2^2]\}/3$$

$$= 5.18 \quad [15]$$

This value is very close to a pH of 5.19 calculated by computer iteration of the charge balance and individual equilibria employing the complex ions and ion pairs for this CO_2-H_2O-FeO-Fe_2O_3-Al_2O_3-SiO_2 system. Molarities of total species are 3.54×10^{-4} (for Fe), 1.58×10^{-5} (for silica) and 3.56×10^{-7} (for Al). The ionic strength of this solution, 0.0002, is so low that our assumption of unit activity coefficients for the ionic species is effectively sustained. The calculated value for $[H^+]$ is now substituted into Equation [12] to solve for the concentration of $[Fe^{2+}]$ ($=10^{-3.46}$).

If the reported structural formula for berthierine is used in the calculations, then the congruent dissolution of this mineral takes the form of:

$$9.53H^+ + Fe_{2.08}Al_{1.79}Si_{1.12}O_5(OH)_4$$

$$\Leftrightarrow 2.08Fe^{2+} + 1.79Al^{3+} + 1.12H_4SiO_4$$

$$+ 4.52H_2O \quad [16]$$

$$K_{sp(B)}$$

$$= \{[Fe^{2+}]^{2.08}[Al^{3+}]^{1.79}[H_4SiO_4]^{1.12}\}/[H^+]^{9.53}$$

$$= 10^{23.83} \quad [17]$$

Although the general forms of Equations [2] and [17] are unchanged, substituting the above equilibrium into these equations yields quite bulky expressions. Nevertheless, the calculated pH (5.18), pCO_2 ($10^{-0.50}$ atm) and solute concentrations using the reported structural formula for berthierine are very close to those values calculated using the idealized formula. There is a large difference in ΔG_f° between the reported and idealized structural formulae (Table 1), and this difference generates different equilibrium constants for reactions involving the ideal berthierine and the berthierine having the composition as determined by microprobe. However, it appears that the different stoichiometries arising from using different structural formulae for berthierine are self-compensating in that very similar equilibrium concentrations occur irrespective of the formula chosen.

Quantifying the Redox Conditions

The redox potential under which these minerals formed can be gauged to the same precision as the pH. Since goethite is also in equilibrium with the kaolinite–gibbsite–berthierine–siderite assemblage, then goethite shares a redox equilibrium with both ferrous Fe and siderite/berthierine. In that case, a pH with which goethite is in equilibrium with both ferrous Fe and siderite (or berthierine) can be computed by equating 2 half-cell reactions. The closeness of the calculated pH involving goethite serves as an independent check of the 5.18 value calculated via Equation [15]. The constant $\mathcal{F}$ is the Faraday, having a value of 23,062 cal V^{-1} (Krauskopf 1967), or 96.54 kJ V^{-1}.

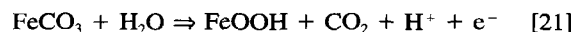The oxidation of ferrous Fe to yield goethite can be written as:

$$Fe^{2+} + 2H_2O \Rightarrow FeOOH + 3H^+ + e^- \quad [18]$$

where

$$E^\circ \text{ (standard potential)}$$

$$= \Delta G_r^\circ/\mathcal{F} = 63.70/96.54 = 0.660 \text{ V} \quad [19]$$

such that:

$$Eh = 0.660 - 0.177 \text{ pH} - 0.059 \log_{10}[Fe^{2+}]$$

$$= 0.864 - 0.177 \text{ pH} \quad [20]$$

Siderite reacting to form goethite can also be written in half-cell form according to:

$$FeCO_3 + H_2O \Rightarrow FeOOH + CO_2 + H^+ + e^- \quad [21]$$

where

$$E^\circ = \Delta G_r^\circ/\mathcal{F} = 27.18/96.54 = 0.282 \text{ V} \quad [22]$$

such that:

$$Eh = 0.282 - 0.059 \text{ pH} + 0.059 \log_{10}[pCO_2]$$

$$= 0.252 - 0.059 \text{ pH} \quad [23]$$

The intersection of these 2 lines on an Eh/pH diagram defines an Eh and a pH unique to the goethite-Fe^{2+}-siderite equilibrium association under the pCO_2 and ferrous-ion concentration in equilibrium with the kaolinite–berthierine–siderite assemblage. The pH is obtained by equating [20] and [23]:

$$pH = (0.864 - 0.252)/(0.177 - 0.059) = 5.19 \quad [24]$$

It is important to note that goethite was not used in the initial calculation of the pH in equilibrium with kaolinite, gibbsite, berthierine and siderite; hence, its use to arrive at the same pH through redox reactions constitutes an independent verification of the original pH calculation.

The system's Eh can now be computed by substituting this pH into either Equation [20] or [23]:

$$Eh = 0.864 - (0.177 \times 5.19)$$

$$= 0.252 - (0.059 \times 5.19) = -0.055 \text{ V} \quad [25]$$

Mechanism of Ferric Fe Reduction

Because berthierine is always associated with goethite or hematite, then reducing conditions have to be imposed to reduce ferric Fe to the 2+ state for incorporation into berthierine. Reduction of Fe^{3+} to Fe^{2+} can be accomplished by geologically relevant redox couples like CH_2O-to-CO_2, CH_4-to-CO_2, NH_4^+-to-NO_3^-, Mn^{2+}-to-Mn^{4+} or S^{2-}-to-SO_4^{2-}. The very high pCO_2 is a powerful argument for invoking oxidation of carbon to produce CO_2. But which valence of carbon served as the reducing agent: $4-$ (CH_4) or 0 (CH_2O)?

Isotopic data do not provide a clear answer. The $\delta^{13}C$ of hand-picked siderite from the Purgatory Creek profile was -6.4 per mill (‰) (Pee Dee Belemnites, PDB). According to Postma (1977), freshwater carbonates (mainly calcites) normally yield negative $\delta^{13}C$ values with an average of -4.12 ‰. Since the carbon in pedogenic calcite is largely derived from oxidation of organic matter without attendant methanogenesis, then the similarity of our -6.4 ‰ value with that of typical pedogenic calcites suggests that these Cretaceous siderites derived their carbon from simple oxidation of organic matter.

Modeling calculations suggest reduction of Fe occurred in the absence of methanogenesis. The main argument against CH_4 for acting as an electron donor is the low partial pressure of this gas that is calculated to have been in equilibrium with the mineral assemblage. If methane gas were also part of the equilibrium assemblage, then the half-cell reaction involving the oxidation of carbon in methane to CO_2 will yield a value for the partial pressure of methane:

$$CH_4 + 2H_2O \Rightarrow CO_2 + 8H^+ + 8e^- \quad [26]$$
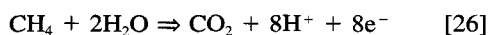
where

$$E^\circ = \Delta G_r^\circ/8\mathcal{F} = 130.8/(8 \times 96.54) = 0.169 \text{ V} \quad [27]$$

such that:

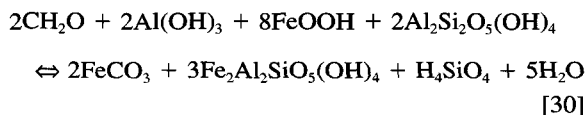$$Eh = E^\circ - 0.059 \text{ pH} + 0.007375 \log_{10}[pCO_2]$$

$$- 0.007375 \log_{10}[pCH_4] \quad [28]$$

Using the previously calculated values for pH (5.19), Eh (-0.055 V) and $\log_{10}[pCO_2](-0.51)$ yields:

$$[pCH_4] = 10^{-\{[-0.055 - 0.169 + 0.306 + 0.004]/0.007375\}}$$

$$= 10^{-11.6} \text{ atm} \quad [29]$$

This value is much less than today's atmospheric value of $10^{-5.7}$ atm (Weast and Astle 1981). If methanogenesis were a factor in the chemical reduction of ferric Fe, then the calculated partial pressure of meth-

ane in the Cretaceous soil profile would certainly be on the order of 0.01–0.1 atm: the present-day range of pCH_4 in Okefenokee Swamp sediments (Flebbe 1984).

The simple oxidation of organic matter (traditionally symbolized as CH_2O) fits well with the chemically described solution in contact with the 5 minerals:

$$2CH_2O + 2Al(OH)_3 + 8FeOOH + 2Al_2Si_2O_5(OH)_4$$

$$\Leftrightarrow 2FeCO_3 + 3Fe_2Al_2SiO_5(OH)_4 + H_4SiO_4 + 5H_2O \quad [30]$$

From this reaction we see that the gibbsite, kaolinite and goethite in the original (pre-transgressive) laterite are being consumed by the oxidation of organic matter. The attendant release of CO_2 upon the reduction of ferric Fe produces siderite. Due to the solution's low activity of silica, Fe-berthierine is produced from the more siliceous kaolinite. Kaolinite would be favored over Fe-berthierine if the dissolved silica produced by this reaction were not removed. This argues for a well-drained, highly permeable soil zone. The reaction continues to proceed as long as there are sufficient goethite and kaolinite to react as well as the maintenance of reducing conditions.

CONDITIONS UNDER WHICH Fe-BERTHIERINE WILL/WON'T FORM

Figure 1 is an Eh/pH diagram depicting conditions under which goethite, siderite and berthierine can coexist with a solution saturated with respect to kaolinite under various partial pressures of carbon dioxide. This plot shows that, for silica-deficient solutions having high concentrations of ferrous Fe, berthierine is stable under a considerably wide range of Eh and pH conditions. Yet, why is Fe-berthierine so uncommon? The answer is that very special conditions must be met in order for Fe-berthierine to form.

Qualitatively speaking, the solution from which Fe-berthierine precipitates must: 1) be reducing; 2) have extremely low sulfate concentrations; 3) not be in contact with quartz; and 4) have a low $[Mg^{2+}]/[Fe^{2+}]$ ratio.

The Effect of Sulfate

Formation of Fe-berthierine has zero tolerance for sulfate-bearing solutions. In order to precipitate Fe-berthierine, the solution's Fe has to be in a reduced form—necessitating that the solution maintain a negative Eh within a "normal" (4 to 10) pH range. But even under moderately reducing conditions similar to -0.055 V calculated via Equation [25], sulfate would be reduced to sulfide. The result is that pyrite, rather than Fe-berthierine, would be the sink for the Fe^{2+} ion. This can be demonstrated by writing a redox re-
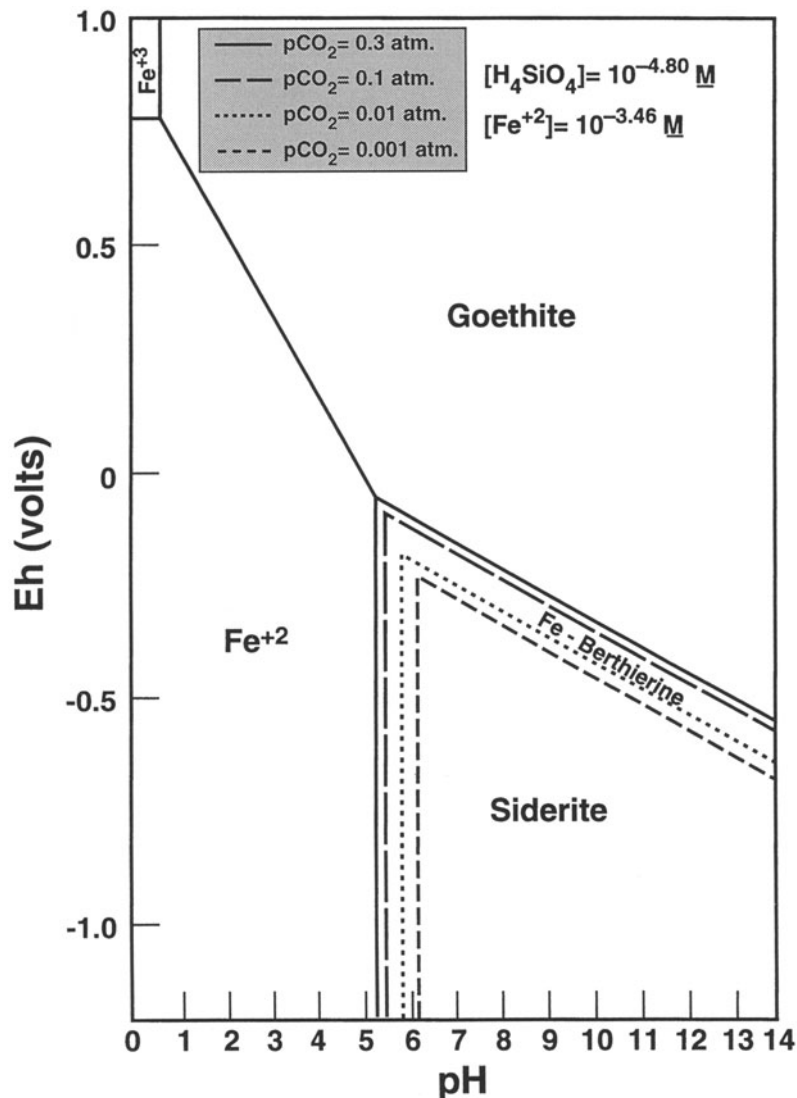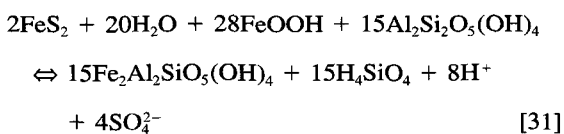
Figure 1.   Eh/pH diagram showing stability fields of goethite, siderite and Fe-berthierine as a function of various partial pressures of CO_2. Concentrations of Fe^{2+} and H_4SiO_4 are fixed at values calculated to be in equilibrium with the 5 minerals in the equilibrium assemblage. The stability field of Fe-berthierine shrinks as the pCO_2 increases until, at $pCO_2 = 0.3$ atm, the triple junction (for Fe^{2+}, goethite and siderite) defines the Eh and pH under which Fe-berthierine, gibbsite, goethite, kaolinite and siderite are all in equilibrium.

action involving pyrite, goethite, kaolinite and Fe-berthierine:

$$2FeS_2 + 20H_2O + 28FeOOH + 15Al_2Si_2O_5(OH)_4$$

$$\Leftrightarrow 15Fe_2Al_2SiO_5(OH)_4 + 15H_4SiO_4 + 8H^+$$

$$+ 4SO_4^{2-} \qquad [31]$$

$$K_{eq} = [H_4SiO_4]^{15}[H^+]^8[SO_4^{2-}]^4 = 10^{-139.9} \qquad [32]$$

(K_{eq} = equilibrium constant) such that:

$$\log_{10}[SO_4^{2-}]$$

$$= -35.0 - 3.75 \log_{10}[H_4SiO_4] + 2 \text{ pH} \qquad [33]$$

Figure 2 shows the concentration of sulfate in a solution that is in equilibrium with all 4 minerals as a function of pH and activity of dissolved silica. Even for low values of H_4SiO_4 and slightly acid conditions, it appears that the SO_4^{2-} ion would have concentrations so low as to be undetectable by standard wet-chemical methods.

The Effect of Dissolved Silica

Although Mg-bearing berthierine has been reported with siliceous sediments, Fe-berthierine is unlikely to be found with amorphous silica or quartz-rich sediments. Compared with other phyllosilicates in which
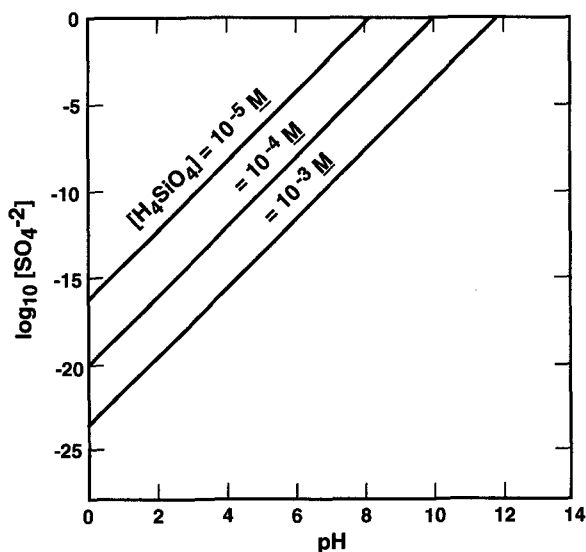
Figure 2.   Minimum sulfate concentrations (M) of a solution in contact with Fe-berthierine, pyrite, kaolinite and goethite as a function of silica activities. See Equation [33].

Figure 3.   Relationship of Equation [40] between Mg^{2+}, pH and pO_2 for a solution in equilibrium with Fe-berthierine, amesite and goethite. A 10^{-5} M solution of Mg^{2+} corresponds to 0.24 ppm.

Fe^{2+} is the dominant cation in octahedral coordination, Fe-berthierine has a relatively low silica content (17.6%). The percent SiO_2 for Fe-clinochlore $[Fe_5Al_2Si_3O_{10}(OH)_8]$ is 25.3, while greenalite $[Fe_3Si_2O_5(OH)_4]$ has a silica content of 32.3%. Thus if a soil solution has a very low activity of H_4SiO_4, then Fe-berthierine's formation should be favored over that of a more siliceous, ferroan phyllosilicate. This can be shown by writing a reaction between Fe-berthierine (B) and greenalite (Gr) in a solution that is also in equilibrium with kaolinite:
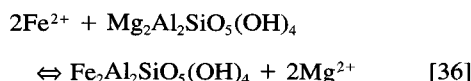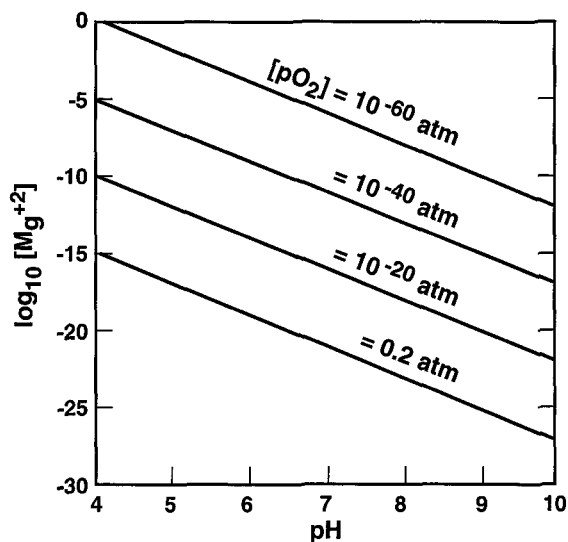
$$10H_2O + 2Fe_3Si_2O_5(OH)_4 + 3Al_2Si_2O_5(OH)_4$$

$$\Leftrightarrow 3Fe_2Al_2SiO_5(OH)_4 + 7H_4SiO_4 \qquad [34]$$
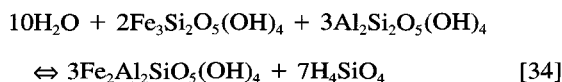
$$K_{B,Gr} = [H_4SiO_4]^7 = 10^{-28.63} \qquad [35]$$

In this case, berthierine is stable relative to greenalite only if the H_4SiO_4 activity is less than $10^{-4.09}$. When this value is compared with $10^{-2.82}$, the H_4SiO_4 activity of a solution in equilibrium with both kaolinite and amorphous silica, then it becomes clear that Fe-berthierine cannot coexist with quartzose sediments.

The Effect of the $[Mg^{2+}]/[Fe^{2+}]$ Ratio

The prevalence of Mg-bearing berthierines and septachlorites relative to Fe-berthierine testifies to the effect of even low concentrations of Mg to deter precipitation of Fe-berthierine. Consider the equilibrium between amesite (A) and Fe-berthierine (B):

$$2Fe^{2+} + Mg_2Al_2SiO_5(OH)_4$$

$$\Leftrightarrow Fe_2Al_2SiO_5(OH)_4 + 2Mg^{2+} \qquad [36]$$

$$K_{A,B} = [Mg^{2+}]^2/[Fe^{2+}]^2 = 10^{5.00} \qquad [37]$$

Here, amesite forms at the expense of Fe-berthierine only if the $[Mg^{2+}]/[Fe^{2+}] > 10^{2.50}$ (roughly 300). The Fe^{2+} concentration of the solution calculated to be in equilibrium with a berthierine–gibbsite–siderite–kaolinite–goethite assemblage was $10^{-3.46}$ M. Under these circumstances, concentration of Mg would have to exceed 0.347 M (or 8430 ppm) for amesite to precipitate. One would therefore presume that a solution's Mg content would have to be quite high for amesite to precipitate instead of Fe-berthierine. In fact, just the opposite is true, because the partial pressure of O_2 plays a key role in the formation of Fe-berthierine.

Ferrous Fe is very susceptible to oxidation in the presence of O_2 or dissolved oxygen. The prevalence of Fe^{2+} to form goethite (Gt) in the presence of oxygen is indicated by the large value of the equilibrium constant in Equation [39]:

$$Fe^{2+} + 0.25O_2 + 1.5H_2O \Leftrightarrow FeOOH + 2H^+ \qquad [38]$$
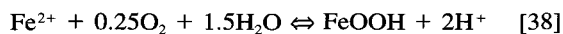
$$K_{Gt} = [H^+]^2/\{[Fe^{2+}][pO_2]^{0.25}\} = 10^{9.52} \qquad [39]$$

If amesite and Fe-berthierine are in equilibrium with goethite, then the relationship between $[Fe^{2+}]$, $[Mg^{2+}]$ and $[pO_2]$ is obtained by combining Equations [37] and [39]:

$$\log_{10}[Mg^{2+}] = -7.02 - 2\,pH - 0.25\,\log_{10}[pO_2] \qquad [40]$$

This relationship is displayed on Figure 3. Magnesium concentration of a solution in equilibrium with a berthierine–amesite–goethite assemblage would exceed 10^{-5} M (roughly the detection limit of this element by atomic absorption spectrophotometry) only under very low oxygen fugacities and low pHs. Even under mildly reducing conditions (such as $pO_2 = 10^{-20}$ atm), Fe-

berthierine would be replaced by amesite even if Mg were in the parts-per-billion range. Under atmospheric conditions (pO_2 = 0.2 atm), so little ferrous Fe would be available such that berthierine would be unstable under these circumstances.

SUMMARY

Fe-berthierine is formed under very restrictive conditions. First, there must be a suitable starting mineralogy consisting of kaolinite and goethite. Quartz must be absent; otherwise, a more siliceous ferroan phyllosilicate (like Fe-clinochlore or greenalite) will form at the expense of Fe-berthierine. Gibbsite's presence is not essential; however, a gibbsite–goethite–kaolinite starting assemblage ensures that solutions in contact with these minerals have 1 of the essential qualities to create Fe-berthierine: a low activity of dissolved silica. Put another way, Fe-berthierine is 1st created from a laterite.

Next, reducing conditions have to be superimposed upon the laterite. This is necessary to reduce the ferric Fe in goethite for release as ferrous Fe to be incorporated into siderite and Fe-berthierine. Reduction by the sulfate-to-sulfide couple will yield pyrite rather than Fe-berthierine. Reduction by manganic-to-manganous couple could yield Fe-berthierine without the accompaniment of siderite; and then it is likely that the berthierine would have a substantial Mn component. However, the most effective way to reduce the ferric Fe is by oxidation of carbon. Thus Fe-berthierine could be formed with or without methanogenesis. In either case, there would be a sideritic byproduct, since oxidation of either CH_4 or CH_2O produces CO_2.

Formation of Fe-berthierine is hindered by Mg. For that reason, Fe-berthierine is not likely to be found in marine sediments or in continental sediments influenced by marine waters. Rather, in these cases, an Mg-rich berthierine or septachlorite will form.

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