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A MODEL OF FE³⁺-KAOLINITE, AL³⁺-GOETHITE, AL³⁺-HEMATITE EQUILIBRIA IN LATERITES

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ABSTRACT: The distribution of Fe^{3+} -kaolinite, Al-goethite and Al-hematite and their contents of Fe and Al in bauxites and ferricretes are controlled by water activity, dissolved silica activity, temperature and particle size. The proposed model, based on ideal solid-solution equilibria in the Fe_2O_3 -Al_2O_3-SiO_2-H_2O system, takes into account water and silica activities. By using the same considerations as those previously developed for the Fe_2O_3 -Al_2O_3-H_2O system, the model calculates the amounts of coexisting phases, Al or Fe substitution ratios in goethite, hematite or kaolinite, and the stability field distributions of the minerals under various conditions. Thermodynamic equilibrium conditions and element distributions within the mineral constituents are shown to be dependent on the parameters cited above. The model yields results compatible with natural observations on lateritic profiles.

Laterites include bauxites, ferricretes, mottle clays, lithomarges and saprolites, and are formed in humid tropical weathering conditions. In most lateritic profiles, kaolinite, goethites, hematites and quartz are the dominant minerals (McFarlane, 1976, 1983; Nahon, 1976; Leprun, 1979; Muller *et al.*, 1981) while gibbsite and boehmite are also present in bauxites, latosols, oxisols and several kinds of ferrallitic soils (Loughnan & Bayliss, 1961; Valeton, 1972; Sieffermann, 1973).

A considerable number of observations show that the amounts of aluminium (Al³⁺) substituting iron (Fe³⁺) in natural or synthetic goethites range between 0 and 33%. Aluminous goethites are formed under humid climates or in water-saturated environments. The Al/Fe ratio increases from wet to dry areas, *i.e.* from the bottom to the top of profiles, and from the lower to the higher parts of landscapes. The maximum substitution ratios are obtained when goethite is associated with gibbsite or boehmite (Schwertmann *et al.*, 1974; Kämpf & Schwertmann, 1983; Didier *et al.*, 1983; Cantinolle *et al.*, 1984; Tardy & Nahon, 1985; Muller & Bocquier, 1986).

In natural or synthetic hematites, the Al/Fe substitution ratio varies from 0 to 15%. Aluminous hematite can form in the driest parts of landscapes and its Al content increases from the bottom to the top of the weathering profiles (Bàrdossy, 1982; Kämpf & Schwertmann, 1983; Didier *et al.*, 1983; Tardy & Nahon, 1985).

Thermodynamic equilibria in the Fe_2O_3 - Al_2O_3 - H_2O system, involving minerals such as goethite, hematite, gibbsite and boehmite were previously examined in detail by Didier *et al.*

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(1983), Didier *et al.* (1985), Tardy & Nahon (1985), Trolard (1986) and Trolard & Tardy (1987). The variables which control the systems have been found to be essentially the grain size, temperature and the water activity which is dependent on the climatic conditions.

However, in most natural systems, aluminous goethite and hematite are associated with kaolinite which appears as the dominant mineral widely distributed in lateritic soils and weathering mantles. Furthermore, natural kaolinites have been found to include some Fe³⁺ ions in their structures (Meads & Malden, 1975; Herbillon *et al.*, 1976; Mestdagh *et al.*, 1980; Cases *et al.*, 1982; Bonnin *et al.*, 1982; Cantinolle *et al.*, 1984; Muller & Bocquier, 1986).

The purpose of this paper is to introduce kaolinite in the Fe_2O_3 -Al₂O₃-H₂O system treated previously by Trolard & Tardy (1987) and to show the importance of the silica activity on the degree of Al³⁺ substitution in goethite or hematite.

The thermodynamic mineral stability fields involving Fe^{3+} -kaolinite, Al^{3+} -goethite, Al^{3+} -hematite, gibbsite, boehmite and quartz are described in the Fe_2O_3 - Al_2O_3 - SiO_2 - H_2O system as functions of water and dissolved silica activities, at 25°C and 1 bar total pressure. In our model, aluminous goethite, aluminous hematite and ferruginous kaolinite are considered as ideal solid-solutions between the following end-members: FeOOH, goethite, and AlOOH, diaspore; $FeO_{1.5}$, hematite, and $AlO_{1.5}$, corundum; $AlSiO_{2.5}(OH)_2$, kaolinite and $FeSiO_{2.5}(OH)_2$, ferrikaolinite. The formulae of the minerals are written for one atom of Fe and one atom of Al, in order to respect the homogeneity among the solid-solution equations. The models based on the equilibria of these solid-solutions allow the calculation of the Fe and Al contents in the mineral associations and their distributions in goethite, hematite and kaolinite.

It will be shown that kaolinite may control the activity of Al ions in natural solutions and consequently the amount of Al in associated aluminous goethites and hematites, whereas goethite and hematite may control the activity of Fe in solution and consequently the amount of Fe in kaolinites.

SOLUBILITY PRODUCTS OF IRON AND ALUMINIUM OXIDES, HYDROXIDES, OXYHYDROXIDES AND KAOLINITE

The Gibbs free energies and the solubility products of Fe and Al oxides, hydroxides and oxyhydroxides have been taken from the literature (Robie & Walbaum, 1968; Naumov et al., 1971; Berner, 1969; Hem & Roberson, 1967; Hem et al., 1973; Hem & Lind, 1974; Parks, 1972; Ulbrich & Merino, 1974; Helgeson et al., 1978; Hemingway & Robie, 1977a,b; Hemingway et al., 1978; Robie et al., 1978; Tardy, 1982 or Tardy & Nahon, 1985). The most recent data are given in Table 1 (at 25°C and 1 bar total pressure).

In the following sections the terms in brackets designate the activity of the different species considered (Table 2). By definition, the solubility products (log K_{sp}) (Table 3) are deduced from the Gibbs free energies (Table 1) from the following classical relationship:

$RT \operatorname{Ln} K_{sp} = -\Delta G^{\circ}_{R}$

In laterites, goethite and hematite particles are very small, generally much smaller than $1 \mu m$, and are also much more soluble than the well crystallized corresponding mineral species (Berner, 1969; Langmuir, 1971; Trolard, 1986; Trolard & Tardy, 1987). The solubility products estimated by Tardy & Nahon (1985) and used later by Trolard (1986) and Trolard & Tardy (1987) correspond to minerals with very small particle size and differ considerably from those with large crystals listed in the literature. These solubility product values are in

Table

 $\begin{tabular}{|c|c|c|c|c|} \hline Fe^{3+} & Fe_2O_3 \\ FeOOI \\ Al^{3+} & Al_2O_3 \\ AlOOI \\ AloOI$

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MODELLING

The Fe_2O_3 -Al_2O_3thermodynamic eq dissolved silica an

Kaolinite equilibriu

In lateritic soils and aluminous her De Coninck (197: McHardy (1974), It is clear that, ir phase (Fritz & Ta *Gibbsite-kaolinite* and gibbsite, given 1988):

For kaolinite: AlSiO_{2.5}(OH)₂ + 3 $\log[Al^{3+}]/[H^+]^3 = 1$ 1986) and Trolard & Tardy d to be essentially the grain in the climatic conditions. tematite are associated with ibuted in lateritic soils and found to include some Fe³⁺ 1976; Mestdagh *et al.*, 1980; Muller & Bocquier, 1986). ₃-Al₂O₃-H₂O system treated to of the silica activity on the

olinite, $A1^{3+}$ -goethite, $A1^{3+}$ -O₃-Al₂O₃-SiO₂-H₂O system 1 bar total pressure. In our s kaolinite are considered as OH, goethite, and AlOOH, iO_{2.5}(OH)₂, kaolinite and written for one atom of Fe the solid-solution equations. the calculation of the Fe and s in goethite, hematite and

ons in natural solutions and tes and hematites, whereas nd consequently the amount

MINIUM OXIDES, KAOLINITE

Al oxides, hydroxides and baum, 1968; Naumov *et al.*, Hem & Lind, 1974; Parks, ingway & Robie, 1977a,b; & Nahon, 1985). The most sure).

tivity of the different species K_{sp} (Table 3) are deduced sical relationship:

enerally much smaller than rresponding mineral species ardy, 1987). The solubility rolard (1986) and Trolard & ize and differ considerably bility product values are in

Fe³⁺-kaolinite, Al-goethite, Al-hematite equilibria

	(1)	(2)	(3)	(4)
Fe ³⁺	-4.60	-4.60	-4.60	-4.60
Fe ₂ O ₃	- 745-40	-742.68	-728.07	-711.11
FeOOH		-488.55	-483.47	-474·31
Al ³⁺	- 489.36	- 489.40	- 489.90	- 489.90
Al ₂ O ₃	-1568-25	-1582-23	-1597-37	-1580-41
AlOOH(Dia)	-913.78	-922.00	-921.30	-912.70
AlOOH(Boe)	_	918-40		-916-15
Al(OH)3	-1155-48	-1154-89	-1153-98	-1154.14
Al₂Si₂O₅(OH)₄	- 3789-08	- 3799-36	- 3789.64	- 3789-37
H ₂ O	-237.19	-237.19	-237.19	-237.19

 TABLE 1. Gibbs free energies of formation of minerals and aqueous species used (kJ/mol). The data selected are those of reference (4).

(1) Helgeson et al. (1978)

(2) Hemingway & Robie (1977a,b)

Robie et al. (1978)

(3) Tardy (1982)

(4) Tardy & Nahon (1985)

Trolard & Tardy (1987)

fact sufficiently adequate to allow the different mineral stability fields to reproduce the succession of mineral associations commonly observed in nature.

MODELLING IN THE FE₂O₃-AL₂O₃-SIO₂-H₂O SYSTEM AT 25°C AND 1 BAR TOTAL PRESSURE

The Fe_2O_3 -Al_2O_3-SiO_2-H_2O models at 25°C and 1 bar total pressure are obtained from the thermodynamic equilibria between minerals as functions of the water activity, the activity of dissolved silica and the bulk composition of the system considered.

Kaolinite equilibrium reactions as functions of water and silica activities

In lateritic soils and ferricretes, kaolinite is frequently associated with aluminous goethite and aluminous hematite. The kaolinite distribution in soils has been studied by Eswaran & De Coninck (1971), Sieffermann (1973), Novikoff (1974), Wada *et al.* (1972), Parfitt & McHardy (1974), Tardy (1982), and Tardy & Novikoff (1988), among others.

It is clear that, in water-rock systems, the solubility of Al may be controlled by the kaolinite phase (Fritz & Tardy, 1974; Sarazin *et al.*, 1982).

Gibbsite-kaolinite equilibria as function of water activity. The solubility products of kaolinite and gibbsite, given in Table 2, are written as follows (Fritz & Tardy, 1974; Tardy & Novikoff, 1988):

For kaolinite:

 $AlSiO_{2.5}(OH)_2 + 3H^+ \rightleftharpoons Al^{3+} + SiO_{2(aq)} + 2.5H_2O$ with:

 $\log[A1^{3+}]/[H^{+}]^{3} = 1/2\log K_{sp}Kaol - \log[SiO_{2(aq)}] - 2.5\log[H_{2}O] + \log[A1SiO_{2.5}(OH)_{2}]$ (1)

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 TABLE 2. Solubility products of the pure minerals and end-members involved. The values used are given in the last column and are derived from the Gibbs free energies

 listed in Table 1, column (4).

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Species	Reaction	Solubility product definition						
Goethite	$FeO(OH) + 3H^+ \Rightarrow Fe^{3+} + 2H_2O$	$\log \frac{[Fe^{3+}]}{[H^+]^3} + 2 \log [H_2O] - \log [FeOOH] = \log K_{xp} \text{Goe}$	+0.819					
Diaspore	$AIO(OH) + 3H^+ \leftrightarrows Al^{3+} + 2H_2O$	$\log \frac{[A]^{3+}}{[H^{+}]^{3}} + 2 \log [H_2O] - \log [AlOOH] = \log K_{sp} Dia$	+8.949					
Hematite	$FeO_{1.5} + 3H^+ $ $\Rightarrow Fe^{3+} + 1.5H_2O$	$\log \frac{[\text{Fe}^{3+}]}{[\text{H}^{+}]^{3}} + 1.5 \log [\text{H}_2\text{O}] - \log [\text{FeO}_{1.5}] = \frac{1}{2} \log K_{sp} \text{Hem}$	+1.692					
Corundum	$AIO_{1\cdot 5} + 3H^+ \leftrightarrows Al^{3+} + 1\cdot 5H_2O$	$\log \frac{[A1^{3+}]}{[H^{+}]^{3}} + 1.5 \log [H_2O] - \log [A1O_{1.5}] = \frac{1}{2} \log K_{sp} \text{Cor}$	+19.266					
Boehmite	$AIOOH + 3H^+ \leftrightarrows Al^{3+} + 2H_2O$	$\log \frac{[Al^{3+}]}{[H^{+}]^{3}} + 2 \log [H_2O] - \log [AlOOH] = \log K_{sp} Boc$	+8.345					
Gibbsite	$AI(OH)_3 + 3H^+ \leftrightarrows AI^{3+} + 3H_2O$	$\log \frac{[Al^{3+}]}{[H^{+}]^{3}} + 3 \log [H_2O] - \log [Al(OH)_3] = \log K_{sp} \text{Gib}$	+8.205					
Kaolinite	$AlSiO_{2.5}(OH)_2 + 3H^+ \leftrightarrows Al^{3+} + SiO_2(aq) + 2.5H_2O$	$\log \frac{[A1^{3}+]}{[H^{+}]^{3}} + 2.5 \log [H_{2}O] + \log [SiO_{2}(aq)] - \log [AISiO_{2.5}(OH)_{2}] = \log K_{sp} Kaol$	+7.410					

$\log [Sit]$ Accordin $([H_2O] =$ In the aqueous : aqueous : If wate kaolinite by Sposii relationsl	At a gi When sili other har water act becomes By com 2), and e	where the considere the two r	goethite ar (2) (Al-goe For gibbs Al(OH) ₃	0.4 0.3 0.2 0.1 X_2 is the	0.9 0.7 0.5	[H ₂ 0]	[SiO2(aq)]	TABLE 3. (Al-goethit
D _{2(aq)}] = - g to Frit 1), log [S unsatural unsatural silica bec r activity r activity stability f stability f io (1981), io (1981),	ven water ica activit id, when ivity decr more stal ubining th ubining th	log e terms in d as pure ninerals, log	thite + boe thite : site: $+ 3H^+ \rightleftharpoons$	(3) (3) (3) (3) (3)	(1) (1) (1) (1) (-2109 - 0.2361 - 0.2361 - 0.2436 - 0.2436 - 0.2436 - 0.22 (2) (2) (2) (2) (2) (2) (2) (2) (2) (Y_2	10-4.5	Variations e + Fe ³⁺ -k

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Fe³⁺-kaolinite, Al-goethite, Al-hematite equilibria

TABLE 3. Variations of the substitution ratios in the associations (Al-hematite + Fe^{3+} -kaolinite) and (Al-goethite + Fe^{3+} -kaolinite) as functions of water and silica activities, at 25°C and 1 bar total pressure.

[SiO ₂ (aq)]	10-4-52		10-4-50			10-4.00				10-3.50		
[H ₂ O]	<i>Y</i> ₂	Z_2	X2	Y ₂	Z ₂	X 2	Z_2	Y_2	Z_2	X 2	Y ₂	Z_2
1.0	(1	.)		0.1801	0.9992			0.0568	0.9971		0.0178	0.9905
0.9	à	Ó		0.1899	0.9993			0.0599	0.9973		0.0188	0.9910
0.8	0.2109	0.9993		0.2014	0-9993			0.0636	0.9974	0.0046		0.9918
0.7	0.2361	0.9994	0.0533	0.2154	0.9994	0.0168	0.9978	0.0680	0.9976	0.0053		0.9928
0.6	0.2436	0.9995	0.0622	0.2326	0.9994	0.0196	0-9981	0.0734	0.9978	0.0062		0.9939
0.5	(2	2)	0.0746	0.2549	0.9995	0.0236	0.9934			0.0074		0.9949
0.4	(3)		0.2849	0.9996	0.0295	0.9987			0.0093		0.9959
0.3	(3)		(3)		0.0393	0.9991			0.0124		0.9969
0.2	Ċ	3)		(3)		0.0590	0.9994			0.0186		0.9980
0.1	(:	3)		(3)			(.	3)		0.0373		0.9990

 X_2 is the mole fraction of corundum in aluminous hematite, Y_2 the mole fraction of diaspore in aluminous goethite and Z_2 the mole fraction of kaolinite in ferruginous kaolinite. (1) (Al-goethite + gibbsite) stable; (2) (Al-goethite + boehmite) stable; (3) (Al-hematite + boehmite) stable.

For gibbsite:

 $Al(OH)_3 + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$ with:

$$\log [Al^{3+}]/[H^{+}]^{3} = \log K_{sp} \operatorname{Gib} - 3 \log [H_{2}O] + \log [Al(OH)_{3}]$$
(2)

where the terms in brackets designate activities of species. When kaolinite and gibbsite are considered as pure phases, their activities are equal to unity so that at equilibrium between the two minerals, the following relationship is obtained:

$$\log [SiO_{2(ao)}] = 1/2 \log [H_2O] + 1/2 \log K_{sp} Kaol - \log K_{sp} Gib$$
 (3)

At a given water activity, $\log [Al^{3+}]/[H^+]^3$ is a decreasing function of $\log [SiO_{2(aq)}]$ (Fig. 1). When silica activity decreases, the equilibrium activity ratio $[Al^{3+}]/[H^+]^3$ increases. On the other hand, when silica activity increases, the $[Al^{3+}]/[H^+]^3$ activity ratio decreases. When water activity decreases, these tendencies remain, but are shifted (Fig. 1) so that kaolinite becomes more stable.

By combining the numerical data of the solubility products of kaolinite and gibbsite (Table 2), and equation (3),

 $\log [SiO_{2(aq)}] = -4.5 + 1/2 \log [H_2O]$

According to Fritz & Tardy (1974), at saturation *i.e.* in the free and pure liquid water $([H_2O] = 1)$, $\log [SiO_{2(aq)}] = -4.5$.

In the unsaturated zone, *i.e.* when $[H_2O] < 1$ ($[H_2O] = 0.5$ for example), the activity of aqueous silica becomes lower: log $[SiO_{2(ac)}] = -4.65$.

If water activity decreases, the defined equilibrium activity of silica also decreases and the kaolinite stability field enlarges compared to that of gibbsite as has already been pointed out by Sposito (1981), Didier *et al.* (1983) and Tardy & Nahon (1985). Furthermore, these relationships may also explain why at the same level in a profile, kaolinite remains stable in





the finely porous materials while gibbsite is stabilized at the edges of large pores (Tardy, 1982; Tardy & Novikoff, 1988).

Boehmite-kaolinite equilibria as function of water activity. The solubility product equation of boehmite (Table 2) is written as follows:

AlOOH + $3H^+ \rightleftharpoons Al^{3+} + 2H_2O$ with

$$\log [Al^{3+}]/[H^{+}]^{3} = \log K_{sp} \text{Boe} - 2 \log [H_{2}O] + \log [AlOOH]$$
(4)

Boehmite is generally a pure phase, and so [AlOOH] = 1.

The limit of the gibbsite-boehmite formation is defined as follows:

$$\log [H_2O] = \log K_{sp} \text{Gib} - \log K_{sp} \text{Boe}$$
(5)

At 25°C and 1 bar total pressure, $\log [H_2O] = -0.14$ *i.e.* $[H_2O] \approx 0.724$. If water activity is >0.724, the kaolinite-gibbsite equilibrium can be reached. On the other hand, if water activity is <0.724, gibbsite is not stable and kaolinite-boehmite equilibrium has to be considered. In permanently humid zones with high water activity, gibbsite is more stable than boehmite, while in dry zones, at low water activity, boehmite is more stable than gibbsite (Tardy *et al.*, 1988).

FIG. 2. Stability

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At equilibrium be simultaneously, so t log [S: The expression (6) I log $[SiO_{2(aq)}] =$ At saturation ([H₂O log $[SiO_{2(aq)}] = -4.6$ increased. For exam

When water activ favours the stabiliza Stability fields in th the Al₂O₃-SiO₂-H₂O Fig. 2 illustrates th and dissolved silica a $< 10^{-4.57}$, kaolinite i kaolinite and boehm of silica activities [10 activities, the stabil increases.

Thermodynamic stabi

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Al³⁺]/[H⁺]³ ion activity in ent water activities.

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 $] \approx 0.724$. If water activity is n the other hand, if water nite equilibrium has to be ity, gibbsite is more stable ehmite is more stable than



^eq.(6)



FIG. 2. Stability field distribution of gibbsite, boehmite and kaolinite as functions of water and silica activities.

At equilibrium between boehmite and kaolinite, equations (1) and (4) must be verified simultaneously, so that

$$\log [SiO_{2(ao)}] = -1/2 \log [H_2O] + 1/2 \log K_{so} Kaol - \log K_{so} Boe$$
(6)

The expression (6) becomes numerically

 $\log [SiO_{2(aq)}] = -4.64 - 1/2 \log [H_2O]$

At saturation $([H_2O] = 1)$, the equilibrium between the two minerals is obtained when $\log [SiO_{2(aq)}] = -4.64$. In the unsaturated zone the activity of silica at the equilibrium is increased. For example, if $[H_2O] = 0.5$, $\log [SiO_{2(aq)}] = -4.49$.

When water activity decreases, the activity of silica defined at equilibrium increases, and favours the stabilization of boehmite at the expense of kaolinite.

Stability fields in the Al_2O_3 -SiO₂- H_2O system as functions of the water and silica activities. In the Al₂O₃-SiO₂-H₂O system, the minerals considered are kaolinite, gibbsite and boehmite.

Fig. 2 illustrates the stability field distribution of these three minerals as functions of water and dissolved silica activities. It can be seen that for all water activities, if silica activity is $<10^{-4.57}$, kaolinite is not stable. In the interval of silica activities $[10^{-4.57}; 10^{-4.5}]$ gibbsite, kaolinite and boehmite are successively stable at decreasing water activities. In the interval of silica activities [10^{-4.5}; 10^{-4.0}], only kaolinite or boehmite can be observed. For low water activities, the stability field of kaolinite diminishes while the boehmite stability field increases.

Thermodynamic stability range in the Fe₂O₃-Al₂O₃-SiO₂-H₂O system

From the simplified approach explained above, an analysis of the different possibilities of mineral associations in the Fe₂O₃-Al₂O₃-SiO₂-H₂O system can be attempted. First, the

Fe³⁺-kaolinite, Al-goethite, Al-hematite equilibria

Kaolinite

equilibrium conditions of Al-goethite and Al-hematite, both associated with kaolinite, are developed. In this section only pure kaolinite, free of Fe, is considered as controlling the amounts of Al substituting Fe in goethite and hematite. Then, for different activities of silica, stability diagrams are built up as functions of water activity and bulk composition of the system.

Equilibrium conditions and stability field of the Al-goethite + kaolinite association. The amounts of Al substituted in goethites is determined by the $[Al^{3+}]/[Fe^{3+}]$ activity ratio in aqueous solution. The $[Al^{3+}]$ aluminium ion activity is controlled by the equilibrium with kaolinite, as shown in equation (1).

The aluminous goethite $(Fe_{Y_1}Al_{Y_2})OOH$ is considered as an ideal solid-solution of pure goethite FeOOH, and diaspore AlOOH. Y_1 and $Y_2(Y_1 + Y_2 = 1)$ are the mole fractions of goethite and diaspore, respectively.

The equilibrium with the solution is reached if the partial equilibria of each of the two endmembers are satisfied together. For the aluminous end-member:

$$\log [Al^{3+}]/[H^{+}]^{3} = \log K_{sp} \text{Dia} - 2 \log [H_{2}O] + \log Y_{2}$$
(7)

and for the ferruginous end-member:

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$$\log [Fe^{3+}]/[H^+]^3 = \log K_{sp} \text{Goe} - 2 \log [H_2O] + \log Y_1$$
(8)

Consequently, by combining equations (1) and (7),

$$Y_{2} = \frac{(K_{sp} \text{Kaol})^{1/2}}{K_{sp} \text{Dia} [\text{H}_{2}\text{O}]^{1/2} [\text{SiO}_{2(aq)}]}$$
(9)

Because \mathcal{X}_2 is a mole fraction, the relationship (9) is valid only if $Y_2 \leq 1$ which is obtained when:

$$1/2 \log [H_2O] + \log [SiO_{2(aq)}] > 1/2 \log K_{sp} Kaol - \log K_{sp} Dia$$
 (10)

When the equation (10) is not valid, aluminous goethite is the only stable species and kaolinite cannot form. Moreover, the bulk-composition of the system controls the coexistence of the two minerals simultaneously. Al_t and Fe_t refer to the total amounts of Al and Fe respectively, in the system. In the following calculations, shown in the different figures, Fe_t = 2, which corresponds to 1 mole of Fe₂O₃. Furthermore, $b (\ge 0)$ and $e (\ge 0)$ refer to the number of aluminous goethite and kaolinite moles, respectively, and the mineral assemblage (see Trolard & Tardy, 1987) is written as:

b (Fe_{Y1} Al_{Y2})OOH + e AlSiO_{2.5}(OH)₂ Then Fe_t = 2 = bY_1 and Al_t = $bY_2 + e$ Because $Y_1 = 1 - Y_2$,

$$b = 2/(1 - Y_2)$$
 and $e = Al_1 - 2Y_2/(1 - Y_2)$ (11)

For Fe_t = 2 moles, the minimum amount of Al required for kaolinite to appear (e = 0) is given by:

$$Al_{t_{min}} = \frac{2Y_2}{1 - Y_2}$$
(12)

When the global Al content (Al_i) of the system considered is lower than the minimal value expressed in (12), only aluminous goethite is present and kaolinite cannot be formed. Inversely, in a system with a fixed number of Fe moles (Fe₁ = 2 moles, for example) and a

variable amount a expressions (11). Consequently, but the mole num composition, defi *Equilibrium con* amount of Al sul solution. The Al The aluminous moles of hematite previous equation together:

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for the ferrugino Hence:

The existence

lc A minimum A

Also, when one of aluminous hemat The numbers of system in which number of Al (A

In the coexisti each of these two but independent *Stability fields i* the dissolved silid stability field in does not exist. In detailed by Trola When associate aluminous goethi system but only activity decrease

ssociated with kaolinite, are onsidered as controlling the r different activities of silica, and bulk composition of the

+ kaolinite association. The Al³⁺]/[Fe³⁺] activity ratio in led by the equilibrium with

ideal solid-solution of pure 1) are the mole fractions of

libria of each of the two ender:

 $+\log Y_2$ (7)

 $+\log Y_1$

(9)

(8)

(10)

if $Y_2 \leq 1$ which is obtained

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er to the total amounts of Al ions, shown in the different hore, $b (\geq 0)$ and $e (\geq 0)$ refer spectively, and the mineral

 $-Y_{2}$

nite to appear (e = 0) is given

(12)

(11)

ower than the minimal value aolinite cannot be formed. 2 moles, for example) and a

Fe³⁺-kaolinite, Al-goethite, Al-hematite equilibria

variable amount of Al, the proportion of aluminous goethite and kaolinite are related by the expressions (11).

Consequently, if equation (10) is valid, the composition of each equilibrium phase is fixed, but the mole numbers of aluminous goethite and kaolinite change as a function of the bulk composition, defined by the parameters Fet and Alt.

Equilibrium conditions and stability field of the Al-hematite + kaolinite association. The amount of Al substituted in hematites is determined by the ratio [Al3+]/[Fe3+] in aqueous solution. The Al ion activity [Al³⁺] is controlled by the equilibrium with kaolinite.

The aluminous hematite (Fe_{x1} Al_{x2}) O_{1.5} is considered as an ideal solid solution of X_1 moles of hematite $\text{FeO}_{1.5}$ and X_2 moles of corundum $\text{AlO}_{1.5}$. Again $X_1 + X_2 = 1$. As for the previous equations for goethite, given above, the following relationships are satisfied together:

$$\log [Al^{3+}]/[H^+]^3 = 1/2 \log K_{sp} \text{Cor} - 3/2 \log [H_2O] + \log X_2$$
(13)

for the aluminous end-member and:

$$\log [Fe^{3+}]/[H^+]^3 = 1/2 \log K_{sp} Hem - 3/2 \log [H_2O] + \log X_1$$
(14)

for the ferruginous one. Hence:

$$K_{2} = \frac{(K_{sp} \text{Kaol})^{1/2}}{(K_{sp} \text{Cor})^{1/2} [\text{H}_{2}\text{O}][\text{SiO}_{2(aq)}]}$$
(15)

The existence validity of this result is constrained by the condition, $X_2 < 1$, *i.e.*

$$\log [H_2O] + \log [SiO_{2(aq)}] > 1/2 \log K_{sp} Kaol - 1/2 \log K_{sp} Cor$$
(16)

A minimum Al content is required to allow the association of Al-hematite and kaolinite.

$$Al_{t_{min}} = \frac{2X_2}{1 - X_2} \tag{17}$$

Q

Also, when one of the two conditions expressed in equations (16) or (17) is not valid, only aluminous hematite is stable and kaolinite should not appear in the system.

The numbers (a) and (e) of aluminous hematite and kaolinite moles, respectively, in a system in which there is a fixed mole number of Fe (Fe_t = 2 moles) and a variable mole number of Al (Al,) introduced, are the following:

$$a = 2/(1 - X_2)$$
 and $e = Al_t - 2X_2/(1 - X_2)$ (18)

In the coexisting limits of the (Al-hematite + kaolinite) association, the proportions of each of these two phases are functions of the water activity and of the dissolved silica activity, but independent of the Al content of the system.

Stability fields in the Fe_2O_3 - Al_2O_3 - SiO_2 - H_2O system, when silica activity is $< 10^{-4.57}$. When the dissolved silica activity is $< 10^{-4.57}$, kaolinite does not form and the distribution of the stability field in the Fe_2O_3 -Al_2O_3-SiO_2-H_2O system is the same as that in which kaolinite does not exist. In this peculiar case, the system is identical to the Fe₂O₃-Al₂O₃-H₂O system, detailed by Trolard & Tardy (1987). The major observations and results are recalled in Fig. 3.

When associated minerals are (Al-goethite + gibbsite) or (Al-goethite + Al-hematite), the aluminous goethite and hematite compositions do not depend on the bulk composition of the system but only on the water activity or temperature. The Al contents increase if water activity decreases.







When Al-goethite and boehmite are stable simultaneously, the Al-goethite composition does not depend on the composition of the system nor on the water activity. It is remarkable that, in this case, the Al content of Al-goethite is fixed (for example $(Al_{0.235}Fe_{0.755})OOH$, at 25°C). On the other hand, when only one mineral such as Al-goethite or Al-hematite is stable, the Al content depends neither on the water activity nor on the temperature. Al-goethite or Al-hematite composition depends only on the $(Al_2O_3/(Al_2O_3 + Fe_2O_3))$ ratio, *i.e.* on the bulk composition of the system. Similar results are obtained when kaolinite is present.

Stability of the Fe_2O_3 - Al_2O_3 - SiO_2 - H_2O system in the $[10^{-4.57}; 10^{-4.5}]$ range of dissolved silica. When the activity of dissolved silica varies between $10^{-4.57}$ and $10^{-4.57}$, the stability field distribution in the Fe_2O_3 - Al_2O_3 - SiO_2 - H_2O system is marked by a succession of possible equilibria of gibbsite, kaolinite and then boehmite as a function of the water activity.

Fig. 4, calculated for $[SiO_2] = 10^{-4.52}$ shows that only aluminous goethite can be associated with kaolinite in a small domain of water activity and Al content. Everywhere else, the

O.1 -FIG. 4. Stabilit tivity and Al co

0.9

0.883

0.8

0.7

0.5

0.3

H₂0] : Water activity

distribution of the $Fe_2O_3-Al_2O_3-H_2O$ The stability fiel activity in two cas gibbsite. At equili

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O₃

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FIG. 4. Stability field distribution in the Fe_2O_3 -Al₂O₃-SiO₂-H₂O system as functions of water activity and Al content, for silica activity = $10^{-4\cdot52}$. The tie lines have the same significance as in Fig. 3.

distribution of the stability fields is found to be identical to that obtained in the system $Fe_2O_3-Al_2O_3-H_2O$ (Trolard & Tardy, 1987).

The stability field of the mineral association (Al-goethite + kaolinite) is limited by a water activity in two cases. The first illustrates the stabilization of kaolinite at the expense of gibbsite. At equilibrium between gibbsite and Al-goethite,

$$Y_2 = \frac{K_{sp} \text{Gib}}{K_{sp} \text{Dia} [\text{H}_2 \text{O}]}$$
(19)

By combining equations (9) and (19), the water activity required for the equilibrium can be

calculated:

12

$$[H_2O]^{1/2} = \frac{K_{sp}Gib [SiO_{2(aq)}]}{(K_{sp}Kaol)^{1/2}}$$
(20)

In standard conditions of temperature and pressure (25°C, 1 bar) the numerical value of water activity obtained when the silica activity is equal to $10^{-4.52}$, is: $[H_2O]_{limit} = 0.832$.

The second constraint limiting the field of the association (Al-goethite + kaolinite) underlines the destabilization of kaolinite and the stabilization of boehmite. At equilibrium with boehmite (Trolard & Tardy, 1987), the mole fraction of diaspore in Al-goethite is defined by:

$$Y_2 = \frac{K_{sp} \text{Boe}}{K_{sp} \text{Dia}}$$
(21)

By combining equations (9) and (21), in which Y_2 defines the mole fraction of diaspore in Algoethite when aluminous goethite coexists with boehmite, the minimal water activity required for the coexistence of the aluminous goethite and kaolinite can be calculated:

$$[H_2O]^{1/2} = \frac{(K_{sp}Kaol)^{1/2}}{K_{sp}Boe [SiO_{2(aq)}]}$$
(22)

The corresponding numerical value is $[H_2O] = 0.631$ as a limit (Fig. 4).

A minimum Al content in the system gives the third limit of the expression of the mineral association (Al-goethite + kaolinite). For a given silica activity chosen in the interval considered, this last constraint is a function of water activity and is defined by equation (11). When the Al-content is smaller than this value (equation (11)), only aluminous goethite is stable.

Stability of the Fe_2O_3 - Al_2O_3 - SiO_2 - H_2O system in the $[10^{-4.5}; 10^{-3.0}]$ range of silica activity. Some examples are treated to describe the range of stability of minerals in the Fe_2O_3 - Al_2O_3 - SiO_2 - H_2O system when silica activity changes between $10^{-4.5}$ and $10^{-3.0}$ (Figs. 5, 6 and 7).

When the silica activity increases, from Fig. 5 to 7, the mineral (Al-hematite + kaolinite) and (Al-goethite + kaolinite) associations overlap progressively the (water activity - Alcontent) diagram. The convergence of these two stability fields occurs in a larger and larger range of water activities and in a narrower and narrower scale of minimum Al contents of the system. The field of (Al-hematite + boehmite) assemblage diminishes and disappears at about $[SiO_2] = 10^{-4\cdot45}$. The stability fields of the aluminous goethite, aluminous hematite and of their combination, are strongly reduced.

For a given water activity, the substitution ratios of Fe by Al in aluminous goethite and aluminous hematite, both associated with kaolinite, decrease if silica activity increases. For $[SiO_2] = 10^{-4.5}$ and in conditions in which the silica content is potentially sufficient, a progressive increase in the Al content in the system results in the following mineral evolution for a water activity ≈ 0.55 :



0.9 [H₂0] : Water activity 0,883 0.8 0.7 0.5 0.3 0.1 FIG. 5. Stabili Conclusion In the (water a gibbsite and then Consequently, sub drastically, and sta

favour the stabilizaluminous goethite activity, yielding $[H_2O] = 0.883$.

associations invad

numerical value of $[H_2O]_{limit} = 0.832.$ oethite + kaolinite) nite. At equilibrium re in Al-goethite is

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inous goethite and vity increases. For tially sufficient, a ; mineral evolution

oethite + plinite



FIG. 5. Stability field distribution in the Fe_2O_3 -Al₂O₃-SiO₂-H₂O system, for silica activity = $10^{-4.5}$. The tie lines have the same significance as in Fig. 3.

Conclusion

In the (water activity – Al content) diagram, when the silica activity increases, first gibbsite and then boehmite tend to disappear while kaolinite appears to be stable. Consequently, substitution ratios in aluminous goethite and aluminous hematite decrease drastically, and stability fields of the (Al-goethite + kaolinite) and (Al-hematite + kaolinite) associations invade the whole space progressively. An increase of the silica activity should favour the stabilization of the aluminous hematite and may reduce the fields in which aluminous goethite is present. The transition hematite–goethite is reached for higher water activity, yielding also a larger stabilization of hematite but still respecting the limit $[H_2O] = 0.883$.

Fe³⁺-kaolinite, Al-goethite, Al-hematite equilibria





FIG. 6. Stability field distribution in the Fe_2O_3 -Al₂O₃-SiO₂-H₂O system, for silica activity = $10^{-4\cdot0}$. The tie lines have the same significance as in Fig. 3.

STABILITY OF FE³⁺-KAOLINITE IN THE FE₂O₃-AL₂O₃-SIO₂-H₂O SYSTEM

Kaolinite, considered until now as a pure aluminous mineral, can, in fact, contain small amounts of Fe substituting for Al. This was illustrated by using electron spin resonance spectrometry (ESR) (Boesman & Schoemacker, 1961; Angel & Hall, 1973; Hall, 1980) and Mössbauer spectrometry (Malden & Meads, 1967; Janot *et al.*, 1973). By another method, Herbillon *et al.* (1976), and Mestdagh *et al.* (1980) have shown that an increase in the Fe content is accompanied by a reduction in the crystallinity and an increase in the disorder of kaolinite. Yvon *et al.* (1981) and Cases *et al.* (1982) have also shown that the disorder can be explained by the intercalation of iron oxides and hydroxides in the interlayer positions. In lateritic pro proportions alwa 1975; Herbillon Cantinolle *et al.*, in principle, a fur The degree of s associations are presentation of t *Equilibrium con* ideal solid-soluti



FIG. 7. Stability field distribution in the Fe_2O_3 -Al₂O₃-SiO₂-H₂O system, for silica activity = $10^{-3\cdot5}$. The tie lines have the same significance as in Fig. 3.

In lateritic profiles, there appears to be a slight substitution of Fe for Al in kaolinite, in proportions always < 3% mole fraction of ferrikaolinite (Janot *et al.*, 1973; Rengasamy *et al.*, 1975; Herbillon *et al.*, 1976; Fayolle, 1979; Mendelovici *et al.*, 1979; Didier *et al.*, 1983; Cantinolle *et al.*, 1984; Tardy & Nahon, 1985). Tardy (1982) has shown that Fe in kaolinite is, in principle, a function of its solubility and of the ratio [Fe³⁺]/[Al³⁺] in the aqueous solutions.

The degree of substitutions in goethite, hematite and kaolinite as well as the limits of their associations are calculated as functions of water and silica activities. Then, before presentation of the results, the solubility product of ferrikaolinite is estimated.

Equilibrium condition of the ideal solid solution. The ferruginous kaolinite is considered as an ideal solid-solution between the two end-members: kaolinite $(AlSiO_{2.5}(OH)_2)$ and

0.5

0.797

20 SYSTEM

ivity = 10^{-4.0}.

ct, contain small 1 spin resonance ; Hall, 1980) and another method, crease in the Fe n the disorder of e disorder can be ayer positions.

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Fe³⁺-kaolinite, Al-goethite, Al-hematite equilibria

ferrikaolinite (FeSiO_{2.5}(OH)₂). It is written as: (Fe_{Z1}Al_{Z2})SiO_{2.5}(OH)₂ where Z_1 and Z_2 designate the mole fractions of ferrikaolinite and kaolinite, respectively ($Z_1 + Z_2 = 1$).

When equilibrium is reached between the aqueous solution and the solid-solution, two partial equilibrium conditions must be respected, simultaneously:

 $\log [Fe^{3+}]/[H^+]^3 = 1/2 \log K_{sp} Fe-Kaol - \log [SiO_{2(aq)}] - 5/2 \log [H_2O] + \log Z_1$ (23)

 $\log [Al^{3+}]/[H^{+}]^{3} = 1/2 \log K_{sp} Kaol - \log [SiO_{2(aq)}] - 5/2 \log [H_{2}O] + \log Z_{2}$ (24)

These constraints modify the case developed in the preceding paragraphs.

Equilibrium conditions of the Al-goethite + Fe^{3+} -kaolinite association. In the Fe₂O₃-Al₂O₃-SiO₂-H₂O system, a given chemical composition allows the association of aluminous goethite and ferruginous kaolinite as follows:

 $b(\text{Fe}_{\gamma_1}\text{Al}_{\gamma_2})\text{OOH} + f(\text{Fe}_{Z_1}\text{Al}_{Z_2})\text{SiO}_{2\cdot 5}(\text{OH})_2$

The equilibrium conditions which fix the existence of these minerals are obtained by combination of the expressions (8) and (23) for the ferruginous end-member, and expressions (7) and (24) for the aluminous one. Since $Y_1 + Y_2 = Z_1 + Z_2 = 1$, the relationships between the mole fractions of the mineral association are obtained as follows:

$$Y_2 = Z_2 \frac{(K_{sp} \text{Kaol})^{1/2}}{K_{sp} \text{Dia} [\text{H}_2 \text{O}]^{1/2} [\text{SiO}_{2(\text{aq})}]}$$
(25)

$$Z_{2} = \frac{K_{sp} \text{Dia} \{ (K_{sp} \text{Fe-Kaol})^{1/2} - K_{sp} \text{Goe} [\text{SiO}_{2(aq)}] \cdot [\text{H}_{2}\text{O}]^{1/2} \}}{K_{sp} \text{Dia} (K_{sp} \text{Fe-Kaol})^{1/2} - K_{sp} \text{Goe} (K_{sp} \text{Kaol})^{1/2}}$$
(26)

At equilibrium, the coexistence of both minerals implies that the total contents of iron (Fe_t) , aluminium (AI_t) and silica (Si_t) verify the following equations:

$$\operatorname{Fe}_{t} = bY_{1} + \operatorname{Si}_{t}Z_{1} \tag{27}$$

$$Al_t = bY_2 + Si_1Z_2 \tag{28}$$

$Al_{t} > Si_{t}Z_{2} \tag{29}$

Thus the variables of the system are the water activity, the dissolved silica activity and the bulk silica content.

Equilibrium conditions of the Al-hematite + Fe^{3+} -kaolinite association. The association of aluminous hematite and ferruginous kaolinite in the $Fe_2O_3-Al_2O_3-SiO_2-H_2O$ system is expressed by the following formula:

 $a(\operatorname{Fe}_{\chi_1}\operatorname{Al}_{\chi_2})O_{1\cdot5} + f(\operatorname{Fe}_{Z_1}\operatorname{Al}_{Z_2})\operatorname{SiO}_{2\cdot5}(OH)_2$

with the condition

 X_1 and X_2 define the mole fractions of hematite and corundum, respectively, in the ideal solid-solution describing the aluminous hematite.

At equilibrium, two conditions must be satisfied simultaneously, and are obtained by the combination of the expressions (14) and (23) for the ferruginous end-member and (13) and (24) for the aluminous one. The solution of the system thus defined, leads to the following results:

$$X_{2} = Z_{2} \frac{(K_{sp} \text{Kaol})^{1/2}}{(K - \text{Cor})^{1/2} [\text{H}_{2}\text{O}] [\text{SiO}_{2(o)}]}$$
(30)

$$Z_{2} = \frac{(K_{sp}\text{Cor})^{1/2} \{ (K_{sp}\text{Fe-Kaol})^{1/2} - (K_{sp}\text{Hem})^{1/2} \cdot [\text{SiO}_{2(aq)}] \cdot [\text{H}_{2}\text{O}] \}}{(K_{sp}\text{Fe-Kaol})^{1/2} \cdot (K_{sp}\text{Cor})^{1/2} - (K_{sp}\text{Hem})^{1/2} \cdot (K_{sp}\text{Kaol})^{1/2}}$$
(31)

As in the preced $\cdot < 1$. When the alussilica contents are

in which Fe_1 is aga content.

This system, cor positive numbers, v contents is satisfied activity, the dissolv *Estimation of the* estimate the solubi temperature, the fo lithomarges, fine sa goethite contain ~ & Bocquier, 1986). laterite profiles, dis of the natural w corresponding silic The solubility pre as:

 $(K_{sp}$ Fe-Kaol)

where Z_2 designate kaolinite. The numerical re $Z_2 = 0.990000$ *i.e.*, a solubility prowhich is somewhat basis. In summary, ir

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Results. The num the theoretical expre the substitution rational as functions of wate fields described abore For a silica activities, the ferru

where Z_1 and Z_2 ($Z_1 + Z_2 = 1$). solid-solution, two

$$D] + \log Z_1 \quad (23)$$

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Fe³⁺-kaolinite, Al-goethite, Al-hematite equilibria

As in the preceding case, these relationships are only valid if X_2 and Z_2 are positive and <1. When the aluminous hematite coexists with the ferruginous kaolinite, the Fe, Al and silica contents are constrained by the equations:

$$Fe_t = aX_1 + Si_t Z_1 \tag{32}$$

$$Al_t = aX_2 + Si_tZ_2 \tag{33}$$

in which Fe_t is again the total Fe content, Al_t the total Al content and Si_t the total silica content.

This system, constituted by the expressions (32) and (33) is solvable, *i.e.* a and Si_t are positive numbers, when the condition defined by the equation (31) between the Al and silica contents is satisfied. The variables of the system which remain to be defined are the water activity, the dissolved silica activity and the silica content.

Estimation of the ferrikaolinite solubility product at 25°C and 1 bar total pressure. In order to estimate the solubility product of ferrikaolinite at the standard conditions of pressure and temperature, the following empirical procedure was used. First of all, it is assumed that in lithomarges, fine saprolites and water-saturated zones ($[H_2O] = 1$), kaolinites associated with goethite contain ~ 1 mole % Fe³⁺-kaolinite (Herbillon *et al.*, 1976; Didier *et al.*, 1985; Muller & Bocquier, 1986). Furthermore, in the conditions prevailing in water-saturated zones of laterite profiles, dissolved silica concentration is ~ 20 mg/kg H₂O, commonly found in most of the natural waters emerging from lateritic landscapes (Tardy, 1969, 1971). The corresponding silica activity is: $[SiO_2] = 10^{-3 \cdot 477}$

The solubility product of ferrikaolinite deduced from equations (25) and (26) is expressed as:

$$(K_{sp} \text{Fe-Kaol})^{1/2} = \frac{Z_2 \cdot K_{sp} \text{Goe} (K_{sp} \text{Kaol})^{1/2}}{K_{sp} \text{Dia} (Z_2 - 1)} - \frac{K_{sp} \text{Dia} K_{sp} \text{Goe} [\text{SiO}_{2(aq)}] \cdot [\text{H}_2 \text{O}]^{1/2}}{K_{sp} \text{Dia} (Z_2 - 1)}$$
(34)

where Z_2 designates the mole fraction of kaolinite in solid-solution describing the ferruginous kaolinite.

The numerical results obtained in our peculiar case are:

 $Z_2 = 0.990000$ and $1/2 \log K_{sp}$ Fe-Kaol = -0.6654,

i.e., a solubility product of the ferrikabilinite at 25°C and 1 bar total pressure equal to -1.331, which is somewhat higher than the -3.660 value estimated by Tardy (1982) on a different basis.

In summary, in the above cited condition (*i.e.* $[H_2O] = 1$, $[SiO_2] = 10^{-3 \cdot 477}$ and $1/2 \log K_{sp}$ Fe-Kaol = -0.6654) a Fe³⁺-kaolinite ideal solid-solution

(Fe_{0.01}Al_{0.99})SiO_{2.5}(OH)₂

can be in equilibrium with goethite as is generally observed in nature. Some numerical tests will now be developed.

Results. The numerical results computed at 25° C and 1 bar total pressure are obtained from the theoretical expressions developed in the preceding paragraphs. Table 3 lists the values of the substitution ratios in the aluminous goethite, aluminous hematite or ferruginous kaolinite as functions of water and silica activities compatible with the limits of the mineral stability fields described above.

For a silica activity $<10^{-4.57}$, the ferruginous kaolinite is not stable. For higher silica activities, the ferruginous kaolinite can be stable and coexist as a function of the water

activity with aluminous goethite or aluminous hematite. For a fixed water activity, the substitution ratios of Al by Fe in ferruginous kaolinite increase when the silica activity increases. They should be higher when ferruginous kaolinite is associated with aluminous goethite than with aluminous hematite. For a fixed silica activity, the ferruginous kaolinite substitution ratio decreases when the water activity decreases.

In the mineral associations, the substitution ratios in aluminous goethite and hematite are not significantly affected by the fact that kaolinite becomes ferruginous. Consequently, the diagrams proposed in the modelling of the Fe_2O_3 -Al_2O_3-SiO_2-H_2O system in the preceding section are still valid if Fe-kaolinite is considered instead of pure kaolinite.

CONCLUSIONS

Diagrams describing the conditions of formation of aluminous goethite, aluminous hematite, ferruginous kaolinite, gibbsite and boehmite, in laterites, bauxites and ferricretes, have been presented. They have been established by using a thermodynamic model based on equilibria among three ideal solid-solutions: $(Al_xFe_{1-x})O_{1.5}$ for aluminous hematite, $(Al_yFe_{1+y})OOH$ for aluminous goethite and $(Fe_zAl_{1+z})SiO_{2.5}(OH)_2$ for ferruginous kaolinite. From these diagrams and the data used to established them, several observations can be made.

The four major factors which directly control the system are water activity, dissolved silica activity, temperature and the chemical composition of the system. Another indirect variable is the particle size of goethite and hematite associated with kaolinite. The selected solubility data for goethite, hematite, diaspore and corundum are compatible with fine-grained, poorly-crystallized minerals.

Natural solid-solutions are most probably non-ideal. However, the type of solid-solution (ideal or regular, for example) chosen in the model does not drastically affect the mineral position in the stability field diagram. Therefore an ideal solution which is potentially extended continuously from one end-member to the other, can be affected by the emergence of other stability fields which partially overlap the equilibrium zones of the solid-solutions. This is the emergence of the stability of gibbsite and kaolinite which limits the Al content in goethite.

The composition limits of natural aluminous goethite (<30% mole fraction of diaspore), aluminous hematite (<15% mole fraction of corundum) and ferruginous kaolinite (<3%mole fraction of ferri-kaolinite), corresponding to those calculated, suggest that the solubility products (Table 2) used to construct the diagrams are appropriate to describe the stability field distributions of the different minerals in different ranges of water activities, dissolved silica activities and bulk compositions of the systems. This is the case for goethite which appears limited in composition at $\sim25\%$ of AlOOH when boehmite starts to form at $[H_2O] = 0.631$. Consequently the fact that in natural conditions, the Al-substitution ratios of goethite are limited to $\sim30\%$ does not prove that the solid-solution is not potentially continuous, and for this reason cannot be chosen as ideal or even regular.

The stability field of kaolinite in the presence of gibbsite or boehmite appears also to be dependent on (i) activity of water and (ii) activity of silica (Fig. 2). At 25°C and 1 bar total pressure, if the silica activity is lower than $10^{-4\cdot57}$, kaolinite is not stable whatever the water activity. In the dissolved silica activity interval $[10^{-4\cdot57}; 10^{-4\cdot50}]$ gibbsite, then kaolinite and finally boehmite can be stable, successively, when the water activity decreases. In the interval $[10^{-4\cdot5}; 10^{-4\cdot0}]$ only kaolinite and boehmite may exist. For decreasing water activity, the stability field of boehmite progressively overlaps that of kaolinite.

The presence of 1 should induce chang The Al-content of a activity or silica acti Al in lowland and profiles, or in soils structures are deple The Fe content of silica activity. An ir activity at a fixed we in the ferruginous k content in ferruginous decreases from the solubility and conse

We are deeply indebted careful review of the o

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d water activity, the en the silica activity iated with aluminous ferruginous kaolinite

hite and hematite are us. Consequently, the stem in the preceding colinite.

, aluminous hematite, ferricretes, have been el based on equilibria atite, (Al_yFe_{1+y})OOH aolinite. From these s can be made. tivity, dissolved silica ther indirect variable

he selected solubility fine-grained, poorlytype of solid-solution

ly affect the mineral which is potentially ed by the emergence of the solid-solutions. nits the Al content in

raction of diaspore), ous kaolinite (<3% est that the solubility lescribe the stability activities, dissolved e for goethite which te starts to form at substitution ratios of n is not potentially ular.

e appears also to be 25°C and 1 bar total whatever the water t, then kaolinite and eases. In the interval water activity, the The presence of kaolinite instead of gibbsite or boehmite in soils or weathering profiles should induce changes in the Al-contents of the associated aluminous goethite or hematite. The Al-content of aluminous goethite at equilibrium with kaolinite decreases when water activity or silica activity increases. This may explain why, in general, goethites are poorer in Al in lowland and hydromorphic soils than in ultisols or oxisols located at the top of the profiles, or in soils higher in the landscape where the aqueous solutions located in porous structures are depleted in silica.

The Fe content of kaolinite is shown to be dependent on the water activity and on dissolved silica activity. An increase of water activity at a fixed silica activity, or an increase of silica activity at a fixed water activity should induce an increase in the Al substitution ratio by Fe in the ferruginous kaolinite. However, the dominant factor which probably controls the Fe content in ferruginous kaolinite is its solubility related to its crystallinity which generally decreases from the bottom to the top of profiles: the lower the crystallinity, the higher the solubility and consequently the higher the Fe content in ferruginous kaolinite.

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